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ADVANCES IN COLLOID SCIENCE
VOLUME II

Advances in COLLOID SCIENCE

Inaugurated by the late ELMER O. KRAEMER
in collaboration with

FLOYD E. BARTELL
University of Michigan

and

S. S. KISTLER
Norton Company, Worcester

VOLUME II

ADVANCES IN COLLOID SCIENCE • VOLUME II

Scientific Progress in the Field of Rubber and Synthetic Elastomers

Initiated by the late ELMER O. KRAEMER

Edited by

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PREFACE

The plan for this second volume of *Advances in Colloid Science* was made by Dr. Elmer O. Kraemer, who felt that the quantity and importance of recent work in the field of natural and synthetic rubbers justified devoting an entire volume to it. After Dr. Kraemer's unfortunate and premature death, we carried out his intentions as closely as possible by continuing to work with authors selected by Dr. Kraemer for particular chapters and following suggestions found in his notes for specific authors and topics.

Although many of them were heavily engaged in various phases of war work, the authors of the various chapters kindly found time for the preparation of manuscripts. We want to express to them our appreciation and thanks and those of the publishers as well.

We hope that the various chapters will serve as an up-to-date presentation of fact and theory and as an inspiration to the further development of the scientific knowledge of elastic polymers. To serve both these aims was Dr. Kraemer's plan and intention; if they have been achieved, all credit goes to him and to the individual authors.

We want to express our sincere thanks also to Dr. A. Szegvari for a number of valuable suggestions, and to the publishers and their staff for indefatigable assistance in overcoming the many wartime difficulties involved in the production of the volume.

February, 1946

H. MARK
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CONTENTS

	PAGE
Preface.....	v
Elmer O. Kraemer—A Biography	xiii
Introduction. By G. STAFFORD WHITBY, Akron, Ohio.....	xxv
Second-Order Transition Effects in Rubber and Other High Polymers. By R. F. BOYER and R. S. SPENCER, Midland, Michigan.....	1
I. Introduction	2
II. Some Experimental Results on Second-Order Transitions in Rubber....	6
1. Volume-Temperature Curves.....	6
2. Heat Capacity Measurements.....	8
3. Crystallinity and Second-Order Transitions.....	12
4. Compressibility	13
5. Thermal Conductivity.....	13
6. Modulus of Elasticity.....	16
7. Refractive Index.....	16
8. Dielectric Properties.....	17
III. Factors Influencing Second-Order Transition Temperature as Determined by Thermal Expansion.....	21
1. Effect of Orientation.....	21
2. Time Effects.....	22
3. Molecular Weight.....	23
4. Vulcanization.....	24
5. External Forces.....	26
6. Copolymerization.....	26
7. Plasticizers.....	27
IV. The Brittle Point.....	31
1. Survey of Brittle Point Tests.....	31
2. Theory of the Brittle Point Tests.....	35
Effect of Molecular Weight on T_b	37
Effect of Vulcanization and Plasticizer.....	39
Effect of Fillers.....	40
3. Some Experimental Results Illustrating the Theory of the Brittle Point Test.....	40
Effect of Molecular Weight.....	41
Effect of Vulcanization.....	43
Effect of Plasticizers.....	44
Effect of Fillers.....	45
4. Young's Modulus of Unstretched Rubber.....	46

V. Summary	48
Bibliography	51
Crystallization Phenomena in Natural and Synthetic Rubbers. By LAWRENCE	
A. WOOD, National Bureau of Standards.....	57
I. Introduction.....	58
II. Methods of Study.....	59
1. Specific Volume.....	59
2. Thermal Measurements.....	60
3. X-Ray Diffraction.....	60
4. Optical Double Refraction.....	61
5. Light Transmission.....	61
6. Mechanical Properties.....	62
Modulus.....	62
Hardness.....	62
Flow and Creep.....	63
III. General Characteristics of Crystallization.....	63
1. Rate of Crystallization.....	63
2. Melting of Crystals.....	66
3. Change of Melting Range with Temperature of Crystallization...	68
4. Recrystallization.....	71
5. Effects of Crystallization on Mechanical Properties.....	71
6. Fraction of Material in the Crystalline State.....	73
7. Effects of Vulcanization on Crystallization.....	75
8. Size of Crystallites.....	77
IV. Materials Studied.....	78
1. Natural Rubber.....	78
2. Balata and Gutta-percha.....	78
3. Chloroprene Polymers (Neoprene).....	79
4. Organic Polysulfide Polymers (Thiokol).....	80
5. Isobutene Polymers and Copolymers (Vistanex and Butyl Rubber).....	80
6. Polyethylene (Polythene).....	81
7. Vinylidene Chloride Polymers and Copolymers (Saran).....	81
8. Butadiene Polymers and Copolymers.....	82
9. Noncrystallizable Polymers.....	82
10. Other Materials.....	83
V. Interpretation of Experimental Results.....	83
1. Kinetics of Crystallization.....	83
2. Range of Melting.....	85
3. Change of Melting Range with Temperature of Crystallization...	87
4. Nature of Crystals.....	87
Bibliography.....	88
The Study of Rubberlike Substances by X-Ray Diffraction Methods. By C. W. BUNN, Northwich, England.....	95
I. The Rubberlike State.....	95
II. The Crystal Structures of Rubberlike and Related Polymers.....	98

1. Methods and Limitations.....	98
2. The Polyisoprene Group—Gutta-percha, Rubber and Poly- chloroprene.....	105
Gutta-percha.....	106
Structure of β -Crystals.....	106
α -Gutta-percha.....	111
Rubber.....	111
Polychloroprene.....	116
3. Butadiene Polymers.....	117
4. Rubber Hydrochloride.....	118
5. Polyethylene.....	119
6. Polyvinyl Alcohol.....	121
7. Other Polyvinyl Compounds.....	123
8. Polyisobutene.....	125
9. Polyesters.....	128
10. Other Rubberlike Substances.....	131
III. Molecular Structure and Physical Properties.....	132
1. The Polyisoprene Group.....	134
2. Rubber Hydrochloride.....	136
3. Polyethylene.....	136
4. Polyisobutene.....	136
5. Polyesters.....	137
IV. Studies of Crystallization and Orientation.....	138
Bibliography.....	141
The Thermodynamic Study of Rubber Solutions and Gels. By GEOFFREY GEE, Welwyn Garden City, Herts., England.....	145
I. Introduction.....	145
II. Experimental Study of Thermodynamics of Rubber Solutions.....	147
1. Vapor Pressures of Rubber Solutions and Gels.....	147
2. Swelling Pressure.....	150
3. Osmotic Pressure.....	151
4. Cryoscopic Measurements.....	153
5. Free Energy of Dilution.....	154
6. Heat of Dilution.....	155
III. Statistical Calculations.....	156
1. Entropy of Mixing.....	156
2. Heat and Free Energy of Mixing.....	162
IV. Comparison of Theory and Experiment.....	165
V. Applications of Thermodynamics to Specific Problems.....	169
1. Molecular Weight of Rubbers from Osmotic Data.....	169
Micellar Theory of Rubber Structure.....	173
2. Solubility of Rubbers in Different Liquids.....	174
3. Limited Swelling of Rubbers in Liquids.....	179
4. Solubility of Solids in Rubbers.....	188
5. Fractionation of Rubber.....	190
6. General Conclusions.....	193
Bibliography.....	194

Significance of Viscosity Measurements on Dilute Solutions of High Polymers.

By R. H. EWART, Passaic, N. J.	197
I. Introduction.	197
II. General Characteristics of Viscous Flow.	199
III. Experimental Results of Viscosity Measurements.	207
IV. Determination of Molecular Weights of High Polymers.	216
1. End-Group Determinations.	218
2. Cryoscopic Determination.	218
3. Osmotic Pressure.	219
4. Ultracentrifugal Studies.	224
5. Light Scattering by High-Polymer Solutions.	226
V. Relation between Solution Viscosity and Molecular Weight.	228
1. Linear Relationships.	228
2. Nonlinear Relationships.	233
3. Discussion of Results.	239
VI. Theoretical Treatment of Viscosity.	239
1. Dependence of Intrinsic Viscosity on Particle Shape.	242
2. Dependence of Viscosity on Swelling.	244
Bibliography.	249

The Kinetic Theory of Rubber Elasticity. By E. GUTH, H. M. JAMES and H. MARK, University of Notre Dame, Purdue University and Polytechnic Institute of Brooklyn.

.....	253
I. Introduction.	253
Historical Excursion.	257
II. Structure of Rubbers.	259
1. Chemical Composition.	259
2. Average Molecular Weight.	261
3. Internal Flexibility of the Linear Macromolecules.	262
III. Configurational Statistics of an Isolated Chain Molecule.	263
IV. Model for Bulk Rubber and Its Statistical Treatment.	267
V. Stress-Strain Relation for Unilateral Stretch.	270
VI. General Deformations.	272
VII. Swelling.	273
VIII. Effect of Thermal Expansion, Thermoelastic Inversion.	274
IX. Statistical Treatment of Highly Extended Chains.	275
X. Molecular Significance of the Constants of the Theory.	278
XI. Influence of Crystallization.	279
XII. Comparison of Theory with Experiment.	285
1. Comparison of Theory with Total Stress-Strain Curves.	286
2. Comparison of Theory with Resolved Stress-Strain Curves.	290
A. Unaccelerated Hevea Gum.	290
B. Accelerated Hevea Gum.	290
C. Accelerated Hycar Gum.	292
3. Discussion.	293

XIII. Brief Discussion of Other Theoretical Work on the Elastic Behavior of Bulk Rubber.....	294
Bibliography.....	297
Vulcanization. By E. HAROLD FARMER, Welwyn Garden City, Herts., England.....	299
I. Introduction.....	299
II. Structural Transformations in Rubber.....	301
1. Structural Pattern.....	301
2. Thermal Decomposition and Cyclization.....	302
3. <i>Cis-trans</i> Isomerization.....	305
4. Polymerization.....	307
III. Reactivity in Relation to Constitution.....	308
1. Additive and Substitutive Tendencies.....	308
2. Vulcanizing Tendencies of Hydorrubber and Butyl Rubber.....	313
IV. Cross-Linking Processes.....	315
1. Action of Dibenzoyl Peroxides and Azo Compounds.....	315
2. Action of Nitro Compounds.....	317
3. Action of Light.....	319
4. Hydrogen Bonding.....	323
5. Insolubilization.....	323
V. Specific Reactivity of Vulcanizing Agents.....	324
1. Sulfur.....	324
2. Sulfur Monochloride.....	335
3. Grignard Reagents.....	336
VI. Constitution of Sulfur Vulcanizates.....	337
1. Proportion of Sulfur.....	337
2. Decrease in Unsaturation during Vulcanization.....	338
3. Dispersability and Molecular Integrity.....	340
4. Overcuring and Reversion.....	344
5. Accelerator Action.....	346
6. Effect of Zinc Oxide.....	355
VII. Conclusions.....	357
Bibliography.....	359
Rubber Photogels and Photovulcanizates. By HENRY P. STEVENS, Suffolk, England.....	363
I. Introduction.....	363
II. Formation of Photogels in Inactive Solvents.....	364
III. Role of Oxygen.....	365
IV. Peroxide Vulcanization.....	367
V. Carbonyl-Containing Activators.....	368
VI. Effect of Oxygen Inhibitors on Rate of Gelling.....	369
VII. Other Factors Influencing Rate of Gelling.....	369
VIII. Light Sources.....	371
IX. Properties of Photogels.....	372
X. Action of Light on Solid Rubber.....	373
XI. Properties of Dried Photogels and Irradiated Rubber.....	376

XII. Vulcanization—Thermal and Photochemical.....	378
XIII. Mechanism of Photovulcanization.....	381
XIV. Elastomers Other than Natural Rubber.....	384
XV. Photosynthesis of Rubber from Isoprene and Polymerization of Styrene.....	386
XVI. Summary.....	387
Bibliography.....	387
Reinforcing and Other Properties of Compounding Ingredients. By DONALD PARKINSON, Birmingham, England.....	389
I. Introduction.....	389
II. Physical Characteristics of Fillers.....	390
1. Particle Size.....	390
2. Particle Shape and Structure.....	392
III. Behavior of Fillers in Vulcanized Rubber.....	393
1. Reinforcement.....	393
2. Tensile Strength.....	394
3. Stiffness.....	396
4. Hardness.....	397
5. Tear Resistance.....	397
6. Abrasion Resistance.....	398
7. Work of Extension.....	399
8. Work of Retraction and Static Hysteresis.....	400
9. Dynamic Hysteresis and Rebound Resilience.....	401
10. Electrical Resistance.....	403
11. Mixtures of Fillers.....	404
IV. Fillers in Synthetic Rubber.....	404
V. Criteria of Reinforcement.....	406
VI. Dispersion and Flocculation.....	408
VII. Dispersing Agents for Carbon Black.....	413
VIII. Causes of Reinforcement.....	414
1. Particle Size and Specific Surface.....	414
2. Particle Shape and Structure.....	415
3. Flocculation of Particles.....	416
4. Particle Surface.....	416
IX. Mechanism of Reinforcement.....	417
X. Effect of Carbon Black on Hysteresis.....	426
XI. Conclusions.....	427
Bibliography.....	428
Appendix.....	431
Author Index.....	435
Subject Index.....	445



ELMER O. KRAEMER

1898-1943

Elmer O. Kraemer—*A Biography*

With the death of Elmer Otto Kraemer on September 7, 1943, the world lost one of the last pioneers with a comprehensive knowledge of the whole field of colloid chemistry. By his studies and published results he materially aided in the transformation of colloid chemistry from a qualitative to a quantitative science, and colloid science has lost a guiding hand through his passing.

When Dr. Kraemer began his scientific career in 1920, colloid chemistry was just emerging from its qualitative stage of describing colloid phenomena. The concept and possibilities of the ultracentrifuge were barely stirring in Svedberg's mind, x-ray diffraction of colloids, films, and fibers, was limited to one or two isolated examples, the molecular nature of proteins was still in question, and high polymers—such as cellulose and its derivatives, rubber, and gelatin—were considered to be colloids without any definite pattern or spatial arrangement. Moreover, polymerization phenomena were not put on a logical basis until Carothers' monumental efforts¹ in the 1930's. Before death terminated his career, Dr. Kraemer saw quantitative measurements being made in all colloid fields and had contributed not only to the development of methods for the making of such quantitative measurements but, more important, also to their interpretation.

Svedberg, writing in 1923, said²: "Research in colloid chemistry is at present working along two different lines: (1) the study of artificial systems of greatest possible simplicity with the object to find out general laws; (2) the study of natural systems which appear in the organisms or as technical products of high importance, with the object to learn their properties and the way to their synthesis." Professor Svedberg's words epitomize Dr. Kraemer's scientific career, starting as it did with work on systems of "greatest possible simplicity" (the study of manganese arsenate jellies and the study of the formation of colloidal solutions by means of the high-frequency alternating-current arc) and ending with highly complex

¹ *Collected Papers of Wallace Hume Carothers*. Vol. I of High Polymer Series, Interscience, New York, 1940.

² T. Svedberg, *Colloid Chemistry*. Am. Chem. Soc. Monograph, Chem. Catalog Co., New York, 1924, p. 12.

systems of natural or artificial origin (as instanced by his last published theoretical work on the colloidal behavior of organic macromolecules and the use of the ultracentrifuge in the study of such molecules). Between these, over a span of less than twenty-five years, came a steadily maintained flow of valuable original work, summaries, and critical evaluations in colloid science.

Contributions to Science

Dr. Kraemer's major research interests were: (1) gelatin and gelation; (2) the kinoultramicroscope for clarifying details of the structure of colloidal systems; (3) the viscous and ultracentrifugal behavior of natural and synthetic high polymers, especially cellulose, cellulose derivatives, rubber, neoprene, and nylon; (4) proteins and biochemical systems; and (5) molecular kinetic studies in general. In addition to these experimental approaches, however, his writings, teachings, and discussions covering the ever-widening field of colloid chemistry as it gradually expanded into the bio- and medicochemical fields and into high-polymer chemistry and physics, provided a leaven for colloid science, the working of which is continuing in all fields depending upon colloid phenomena for their development and clarification.

Gelatin. Very early in his career Dr. Kraemer initiated a comprehensive investigation of the colloid properties of gelatin solutions and gels, and to this problem applied, at various times, methods based on optical activity and light scattering, on the diffusion of small particles in the gels, and on the ultracentrifuge. Especially significant was his early study of the setting and melting of gelatin gels by observation with the kinoultramicroscope of the motion of colloidal mercury droplets suspended in the gels. With this latter apparatus he also demonstrated, very beautifully, the formation and coagulation of bismuth sols and the photocagulation of Carey Lea's silver sols.

Dr. Kraemer maintained an active interest in gelatin and gelation throughout his scientific career. One of his last published papers dealt with the state of dispersion of gelatin in concentrated potassium thiocyanate solutions.³ Of significant interest is his conclusion: "Considering the data as a whole, it may be tentatively concluded that gelatin disperses as single molecules in concentrated potassium thiocyanate solutions, as well as in dilute salt solutions above the gelation temperature. The dissolved molecules are folded and coiled up to approximately one-fifth

³ *J. Phys. Chem.*, **45**, 660 (1941).

the extended length, as they exist in the native collagen, and therefore resemble the molecular state in contracted collagen. . . . In spite of the high degree of coiling, the gelatin molecule is still a more extended, rod-like molecule than other proteins hitherto studied."

Ultracentrifuge Studies. His ultracentrifuge researches on the molecular size and distribution of high polymers won him world-wide recognition. Dr. Kraemer made consistent use of the ultracentrifuge in his researches on colloid problems from about 1928 onward and, because of his conviction of the value of the method in colloid science, devoted a considerable amount of attention to the interpretation of data obtainable from ultracentrifuge studies, becoming a recognized authority in this field. Under his direction the first well-defined linear macromolecule of known structure and molecular weight—a crystalline fractionated polymeric ω -hydroxydecanoic acid—was examined in the ultracentrifuge.⁴

Analysis of Mixtures of Macromolecules. One of Dr. Kraemer's most important contributions to the advancement of colloidal science was the development, in cooperation with the late Dr. W. D. Lansing, of the molecular weight analysis of colloidal mixtures by sedimentation equilibrium in the ultracentrifuge.⁵ It remains yet the best attack on this complicated problem.

A companion treatment of the analysis of polydisperse systems with negligible diffusion, undertaken with the cooperation of E. D. Bailey and J. B. Nichols, made it possible to deduce particle-size distribution from spectral transmission data.

This work, together with other phases of the problem with which Dr. Kraemer was intimately associated, is admirably summarized in one of his contributions⁶ to *The Ultracentrifuge* under the heading "Calculation and Recording of Results of Polydisperse Systems."

Correlation of Molecular Weight and Viscosity. By comparing ultracentrifugally determined weight average molecular weights of cellulose, cellulose derivatives, rubber, and neoprene with the intrinsic viscosities,⁷ Dr. Kraemer demonstrated the necessity of using an absolute method for the determination of molecular weights of macromolecules to insure a reliable calibration of the Staudinger expression correlating the molecular

⁴ E. O. Kraemer and W. D. Lansing, *J. Am. Chem. Soc.*, **55**, 4319 (1933).

⁵ *Ibid.*, **57**, 1369 (1935).

⁶ T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*. Oxford Univ. Press, London, 1940.

⁷ E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938). E. O. Kraemer and J. B. Nichols, in *The Ultracentrifuge*.

weights of high polymers to the specific viscosities of their solutions. The weight average molecular weights for these macromolecules obtained from ultracentrifuge studies were in general much higher than those predicted or extrapolated by Staudinger from the values for low molecular members of a homologous series.

He also gave much thought to the relative merits of the terms "molecular weight" and "particle weight" to designate the values determined for macromolecules in the ultracentrifuge. Although he was able, by considering the interrelationship between molecular weight and intrinsic viscosity, to adduce evidence that for very dilute solutions of cellulose and its derivatives in certain solvents, the cellulose material was most likely present as "single molecules, in which all bonds within the macromolecular skeleton are of the simple covalent type," he concluded⁸ that "the question concerning molecular dispersion and association must be raised for each and every type of polymeric material, and it can only be answered finally by a detailed ultracentrifugal and chemical investigation of each substance under a variety of conditions."

Solvation. Finally, he developed, with W. D. Lansing, a mathematical treatment of solvation in binary and ternary systems, and showed that it did not affect molecular weights obtained by the ultracentrifuge method in any way different from that for conventional methods.⁹ This work also showed that, while there is an effect to be considered in ternary and higher systems if the sedimenting component combines with one of the other components, or with two or more of the other components in proportions different from those in which they exist in the solution, the error in molecular weight by the sedimentation equilibrium method may be quantitatively evaluated.

Dr. Kraemer continued, up to the time of his death, to apply his knowledge and skill to the problem of molecular weight determination by the ultracentrifuge, being particularly concerned with the factors, such as the partial specific volume, which must be taken into account when considering the reliability of molecular weights determined in the ultracentrifuge. In addition to his section on "The Partial Specific Volume Factor" for *The Ultracentrifuge*, he published an important series of mathematical papers during 1940 in *The Journal of the Franklin Institute* dealing with (a) the specific volume factor in ultracentrifuge analysis, (b) the effect of solvation upon molecular weight determinations by means of the ultracentrifuge, and (c) the effect of solvation on friction constants and frictional ratios as deter-

⁸ *The Ultracentrifuge*, p. 422.

⁹ W. D. Lansing and E. O. Kraemer, *J. Am. Chem. Soc.*, **58**, 1471 (1936).

mined with the ultracentrifuge and by diffusion. He published a valuable summarizing paper¹⁰ in 1941 entitled "The Determination of Average Molecular Weights or Particle Sizes for Polydispersed Systems" in which he discussed the interrelations between several types of average values of significance in the determination of both molecular weights and particle sizes by various indirect methods, and critically examined the conditions under which different averages may be calculated from each other.

Biographical Sketch

Born at Liberty, Wisconsin, on February 27, 1898, Elmer O. Kraemer received his early education in the schools of that community. After obtaining his B.S. degree from the University of Wisconsin in 1918, he remained at Wisconsin as an instructor, doing graduate work in the department of chemistry. Exposure to Louis Kahlenberg's non-ionic philosophy and Victor Lenher's inorganic chemistry developed in him that perspective which was later to become so characteristic of his approach to a problem. Having decided to specialize in physical chemistry, and the colloid branch in particular, he spent 1921-1922 as a Fellow of the American Scandinavian Foundation in the laboratory of The Svedberg at the University of Uppsala in Sweden. He spent the next year doing colloid chemistry research with Herbert Freundlich at the Kaiser Wilhelm Institute for Physical Chemistry and Electrochemistry in Berlin-Dahlem, gaining practical experience in applying quantitative methods to the young science.

Dr. Kraemer returned to the University of Wisconsin shortly after Svedberg had arrived from Sweden, at the invitation of the University, to give lectures and to organize research in colloid chemistry, and was assistant to him while Professor Svedberg remained at Madison. The Department of Chemistry at Wisconsin took advantage of Professor Svedberg's residence there to organize and hold the first national symposium on colloid chemistry. Dr. Kraemer not only gave his first paper, "The Formation of Manganese Arsenate Jellies," at this symposium but also assisted in preparing the papers presented for publication in the first *Colloid Symposium Monograph*. During this time (1923-1924), Dr. Kraemer was working on the kinoultramicroscope and, in 1924, was granted his Ph.D. by the University. He remained there as National Research Council Fellow to carry out research on the optical properties of gelatin sols. In 1925 he was appointed Assistant Professor of Colloid Chemistry at Wisconsin; and, for the next two years, he and his research students continued to study the

¹⁰ *J. Franklin Inst.*, **231**, 1 (1941).

properties of gelatin. About this time, he married Huldah Florence Cook of Cleveland, Ohio, whom he had first met when she was a graduate student at the University of Uppsala in 1921.

His university connections were severed in 1927 when he joined the staff of the Chemical Department of E. I. du Pont de Nemours and Company at the Experimental Station in Wilmington, Delaware, as the leader of a group of research workers studying both fundamental and industrial colloid problems. For eleven years, until May, 1938, he remained with the du Pont Company, during which time he became well known for his profound knowledge of colloid chemistry, both fundamental and applied, and for the outstanding contributions on inorganic colloids and high molecular weight polymers published by him and his collaborators. It was during this time that he was instrumental in introducing into the du Pont Company's research laboratories an oil-turbine high-speed ultracentrifuge which had been constructed in Professor Svedberg's institute in Uppsala, Sweden. It was the first ever installed and operated outside the Uppsala laboratory, and for many years Dr. Kraemer was responsible for research carried on by means of this highly specialized tool of the colloid chemist.

In 1938, Dr. Kraemer was awarded a Lalor Foundation Fellowship to continue his ultracentrifuge studies on gelatin and synthetic high molecular weight polymers with Professor Svedberg in the Institute of Physical Chemistry at the University of Uppsala. He resigned from his position with the du Pont Company before leaving for Europe and, after visiting a number of the more important European research laboratories on behalf of the Biochemical Research Foundation of the Franklin Institute, took up residence in Uppsala with his wife and two sons, Herbert and Paul. During the year spent in Uppsala (1939), he collaborated with Svedberg, Pedersen, and others in the writing of *The Ultracentrifuge*, the compendium of information on ultracentrifuges and their employment in colloid science, which appeared in the German edition in 1939 and in the English edition in 1940.

He was forced to return with his family to the United States in the Fall of 1939 because of the outbreak of World War II. Shortly after his return, Dr. Kraemer took up full-time duties with the Biochemical Research Foundation at Newark, Delaware, to supervise the physicochemical research on biochemical colloidal systems being carried on there. Up to the time of his becoming a full-time member of its staff, he had been associated with the Foundation as visiting consultant in colloid chemistry from its inception, in 1927, as the Cancer Research Fund of the Graduate School of Medicine, University of Pennsylvania.

Dr. Kraemer had been actively interested for many years in the University of Delaware and, in 1940, was appointed to the Faculty of that university as special lecturer in colloid chemistry, which gave him the opportunity of presenting a course in colloid science which attracted many, both students and graduate chemists in industry. He was, at the time of his death, preparing for publication a thoroughly modern and comprehensive textbook on colloid science based on his lectures at the University of Delaware.

Publications and Activities

Because of his love of science and his sustained energy, Dr. Kraemer found much of his relaxation from research problems in editorial work and in writing as well as in teaching. As would be expected from so active a research worker and from so clear and facile a writer, many publications stand to Dr. Kraemer's credit in the literature of science. In addition to publishing some forty-four research papers (alone or with collaborators) in scientific journals, he was also the author of many summaries of colloid science and of special sections in advanced scientific treatises, such as the section on "Colloids" which he wrote for the 1931 and 1932 *Annual Survey of American Chemistry*. His chapter on "Colloids" in Taylor's *Treatise on Physical Chemistry* is well known, and he was actively engaged in a thorough revision of this section for the forthcoming enlarged edition of the treatise (Glasstone and Taylor) at the time of his death. He was the author of two chapters on the chemistry of large molecules in the monograph published in 1943 by Interscience Publishers for Western Reserve University, having been chosen the authority to deal with the colloidal behavior of organic macromolecules, and with the ultracentrifuge and its application to the study of such macromolecules, in the series of lectures entitled "Frontiers in Chemistry" held at Western Reserve in 1942. His authorship or co-authorship of several important chapters on the analysis of polydisperse colloidal systems, and on linear polymers, in *The Ultracentrifuge* has already been mentioned.

Dr. Kraemer was one of the founders of the Society of Rheology, and was an assistant editor of the *Journal of Rheology* and, later, of *The Journal of Chemical Physics*. He was on the editorial board of the Interscience series of monographs on high polymers, was the editor of Volume I of *Recent Advances in Colloid Science*, and also one of the editors of *Archives of Biochemistry*.

He enjoyed membership in many scientific societies and was frequently an active participant in important meetings, taking particular delight in contributing to the specialized symposia on colloids and methods in colloid

science held at the New York Academy of Sciences, and in attending and contributing to the Gibson Island Conferences. He was, at the time of his death, serving as consultant for a number of special Government committees concerned with the prosecution of World War II.

For his contributions to the world's scientific knowledge he was honored in 1938 by being listed among the 250 outstanding United States scientists by *American Men of Science*.

Throughout his career, Dr. Kraemer found the writings of early chemists and colloid chemists a source of increasing interest and inspiration. Over a period of years he assembled a noteworthy collection of the books and scientific writings of Michael Faraday, in whom he was particularly interested, and of rare chemistry books from previous centuries. Other hobbies he took up with typical thoroughness were photography and music.

Personality

His early training apparently gave Dr. Kraemer the unusual combination of hand and head skills which was one of his outstanding characteristics. He was an outstanding experimentalist as well as a clear and logical thinker. He had a striking ability to assimilate ideas, to probe to the fundamentals of a problem, to develop modes of attack on complex phenomena, and to describe such phenomena in relatively simple terms.

The same thoroughness appeared in all his efforts, whether it was the selection of a piece of scientific equipment, organizing material for a lecture or for publication, or some more mundane matter, as choosing a car or a radio. He inspired similar thoroughness in work and thought in those who were associated with him.

His willingness to place his wealth of knowledge on scientific matters unreservedly at the service of his co-workers, his pronounced critical faculty and well-thought-out opinions, the simplicity of his manner, his even-tempered, unruffled disposition, and his pleasure in other people's successes won for him the respect, admiration, and friendship of all who were privileged to know him and work with him.

His many friends and associates throughout the world of science can but wish that his career, which was still in the ascendancy, had not been terminated so early by his untimely death.

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INTRODUCTION

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General

The advent on a large scale of synthetic rubbers, especially of tire and general-purpose rubbers such as GR-S, has markedly increased the complexity and difficulty of rubber as a field of research. Manifold and difficult as are the scientific problems presented by the high molecular, elastic colloid, natural caoutchouc, they are now seen to be less numerous and relatively simpler than those presented by synthetic rubbers. And there would seem to be ample justification for the publication of the present book, not only because it covers recent work which has not previously been brought under review in a single volume, but also because, though the volume is concerned largely (but by no means wholly) with natural rubber, it deals with fundamental aspects of the subject of equal if not greater importance in the study of synthetic elastomers as in the study of natural rubber. Hence it may be hoped that the volume will be useful in assisting in the further study of synthetic rubbers and of elastomers generally, as well as of natural rubber.

Nomenclature

As a general descriptive term for rubberlike polymeric materials, the now widely used term "elastomer," introduced by H. L. Fisher (10), has been employed in this volume. But it is to be pointed out that the term should be regarded as merely an abbreviation for "elastopolymer" or "elastic polymer." The Greek "mer" means "part" or "unit." A "mer" itself is never elastic, and hence there can, strictly speaking, hardly be such a thing as an elasto-mer. Only by producing a poly-mer from a suitable monomer or monomers, is an elastic material obtained. Considerations of convenience, however, lead to approval of the term "elastomer" as an abbreviation.

Further: some years ago there was considerable discussion as to the propriety of applying the description "synthetic rubber" to synthetic

rubberlike materials differing chemically from natural rubber in being composed of units other than isoprene. In the field of high polymers, however, as distinct from that of classical organic chemistry, products are assessed and prized chiefly from the point of view of their mechanical and physical properties, rather than from the point of view of their chemical constitution and chemical reactivity: they are valued as *materials* (mostly materials of construction or fabrication) rather than as *chemicals*. Hence we are disposed to take the view that, stated epigrammatically, "rubber is as rubber does," and we are ready to designate as "synthetic rubbers" many materials which, while chemically different from natural rubber, have mechanical and physical properties broadly similar to those of the latter. In borderline cases, of course, there may be room for argument as to whether some particular material is sufficiently rubberlike to justify its being called a synthetic rubber.

The Rubber State

It is now well known that the rubber state is not confined to polyisoprene such as constitutes the hydrocarbon of *Hevea brasiliensis* and other rubber-producing trees. It is true that the hydrocarbon of several rubber-containing plants which have been examined closely for the first time during the war, such as *Cryptostegia grandiflora* (22) and *Asclepias syriaca* (the common milkweed) (19), have been found to be polyisoprenes very similar to *Hevea* rubber, giving the same x-ray pattern on stretching and, if free from contamination, showing when vulcanized mechanical properties almost as good as those of *Hevea* rubber. But it has been found by Kemp and Peters (16) that the rubber which occurs on the seeds of *Smilax rotundifolia* is not a hydrocarbon at all, but a polyester. The present writer has made a similar finding with regard to the elastic skin on the seeds of *S. bona-nox* and *S. hispida*, and has found the "rubber" to have, without fillers, a tensile strength of about 2400 p.s.i. and an elongation of about 650%. It will be interesting to see whether other nonhydrocarbon rubbers can be found in nature.

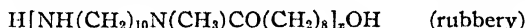
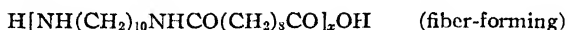
It is in the field of synthetic elastomers that the fact that the rubber state is not limited to a single or even to a small number of chemical compositions is most amply illustrated. Rubbers have been or are being made commercially—to mention only some examples—by the polymerization of (a) butadiene, (b) 2,3-dimethylbutadiene and (c) 2-chlorobutadiene, and by the copolymerization of (d) butadiene and styrene in various ratios, (e) butadiene and acrylonitrile in various ratios and (f) isobutylene and isoprene. Many others have been made on a pilot-plant scale, for example,

in Germany, copolymers of butadiene and methyl methacrylate and copolymers of butadiene and methyl vinyl ketone (8). And many more have been made in the laboratory, for example, copolymers of butadiene with dichlorostyrenes (17), with vinylidene chloride (15), with α -vinylpyridine (7), with β -ethoxyethyl methacrylate (12), with vinyl ethinylcarbinol (20) and with derivatives of unsaturated acids such as maleic and fumaric (11). These represent only a very limited number of the examples which might be quoted to illustrate the fact that many different polymerizable systems consisting of or containing conjugated dienes are capable of yielding rubber-like polymers. And undoubtedly many more such will be developed in the future.

Then, again, rubberlike materials can be synthesized by condensation polymerization, as distinguished from addition polymerization exemplified by the foregoing instances. Elastic mixed polyester-polyamides have been described in the patent literature (9), and some polyesters capable of undergoing vulcanization with the formation of elastic products have been introduced commercially under the name "Paracons" (5). The latter can be prepared by the condensation of dibasic acids with suitable glycols. By suitable choice of the reactants subjected to condensation polymerization, the properties of the products can be varied. If the products contain a sufficient amount of unsaturation (introduced by using 15-25% of unsaturated acid in their preparation), they are susceptible to vulcanization by sulfur. If they are completely saturated, they can be vulcanized by 4-5% of benzoyl peroxide, the free radicals from which are presumed to unite the chains through the carbon atoms adjacent to the carbonyl groups of the ester linkages of the polyester molecules. The length of the carbon chain in the dibasic acid components chosen for the preparation of the polyester influences the brittle point (which is lower the longer the carbon chains between the ester linkages) and the oil resistance (which is greater the shorter the carbon chains and hence the higher the concentration of polar, amido groups).

The structure of condensation polymers can be more definitely controlled than, at present, that of typical diene polymers and copolymers. Their molecules must perforce be linear, provided the reactants undergoing condensation are linear and bifunctional. Hence their further study may be expected to be of value in throwing light on the conditions necessary to the rubber state. In this connection an observation of Baker and Fuller (4) may be noted. These authors found that the polyamide from sebacic acid and decamethylenediamine had fiber-forming properties similar to nylon and gave similar x-ray diagrams, while the polyamide from sebacic

acid and decamethylenemonomethylidiamine was rubbery. In the former product, the molecules readily entered into a crystallite lattice when the material was drawn and yielded fibers. In the latter product, the presence



of a methyl substituent in every alternate amido group had reduced the intermolecular forces between the chains and allowed them to slip over one another.

Further Research on Synthetic Rubbers

The rapid establishment during the war of the production on a vast scale of serviceable synthetic rubber for general purposes is a truly remarkable feat of chemical manufacturing. But much research remains to be done before a sufficient degree of control has been secured over the polymerization of conjugated diene hydrocarbons to permit the manufacture of completely satisfactory products. In the polymerization procedures now known, dienes such as butadiene, either alone or in admixture with comonomers such as styrene and acrylonitrile, fail to give polymers which, like natural rubber, are strictly linear and regular in structure and have as high a molecular weight and as narrow a distribution of molecular weights as the latter. In contrast to natural rubber, synthetic rubbers such as GR-S fail to form crystallites when stretched, as the absence of an x-ray diffraction pattern shows; when vulcanized alone (without fillers) have very low tensile strength and poor extensibility; at elevated temperatures suffer a serious loss in strength and (directly contrary to the behavior of natural rubber) in extensibility; show lower resilience, both static and dynamic, and hence heat up more in service; have inferior resistance to tearing; permit cuts, once started, to grow under flexing conditions more rapidly than is the case with natural rubber; in aging tests, readily become stiff (high modulus) and short (low elongation); on milling, fail to break down and become plastic and to develop tackiness in the way that natural rubber does; may contain initially or develop during processing insoluble polymer ("gel"), representing in effect a prematurely vulcanized fraction. GR-S has been described by Braendle and Wiegand (6) as "an elastically inverted polymer," because, as compared with *Hevea* rubber, it shows high hysteresis at low deformations and low hysteresis at elongations near rupture, with the result that, in tires, it builds up more heat on the one hand, and on the other (because of its failure to relax and lengthen at high elongations) suffers the growth of cuts.

To secure an adequate understanding of the peculiarities of behavior such as those enumerated and to develop basically improved general-purpose synthetic rubbers clearly calls for continued and persistent research.

A German writer (18) some years ago, after claiming that a satisfactory synthetic rubber was being produced in Germany, added "I may, however, especially emphasize that the road to it was very stony and full of thorns." The claim may be considered to have been premature, and, despite the progress which has been made in the synthetic rubber field, the road ahead to a fully satisfactory synthetic rubber still remains "sehr steinig und dornenreich."

Compounding

In contrast to natural rubber, synthetic rubbers such as GR-S are entirely dependent on the incorporation of particulate fillers for the possession of any reasonable degree of mechanical strength. Natural rubber has a high tensile strength, for example, 4000 p.s.i. in gum stocks, that is, when vulcanized in a mixture or "compound" free from fillers and containing only the ingredients (sulfur, accelerator and a minor amount of zinc oxide) necessary to vulcanize it fully to the soft rubber stage. Synthetic rubbers such as GR-S, Buna S, Buna N and sodium-polymerized butadiene, however, when fully vulcanized have a low tensile strength in gum stocks—of the order of 300–400 p.s.i. The strengths just mentioned are calculated on the unstrained cross section. If the ultimate tensile strengths are calculated on the cross section at rupture, the contrast between gum stocks of natural rubber and of typical synthetic rubbers is much greater, because the elongation at break is higher and hence the cross section at break smaller with natural rubber than with the synthetics.

When loaded with suitable particulate fillers, especially with carbon black, polymers such as GR-S and Buna N show a vast increase in tensile strength. Natural rubber also shows some increase, but the increase in the case of the synthetics is, in relative terms, vastly greater. At an optimum loading, carbon black raises the ultimate tensile strength of natural rubber by perhaps 20%—from, say, 4000 to, say, 4800 p.s.i. At the optimum loading, carbon black raises the tensile strength of GR-S by perhaps 1000%—from, say, 300 to, say, 3000 p.s.i.

Further, whereas the presence of particulate fillers reduces the extensibility of natural rubber, their presence increases the extensibility of GR-S; that is to say, it appears that, in GR-S and similar polymers, when the elastomer is able to anchor itself to filler particles it can be stretched much farther without rupture than when no filler is present. This is a significant

aspect of the behavior of typical synthetic rubbers which has not received as much emphasis as it deserves. By loading it with carbon black, the elongation at break of natural rubber is in typical stocks reduced from, say, 775% to, say, 650%; that of GR-S is raised from, say, 400% to, say, 550%.

These broad considerations serve to underline the fact that the surface relationships between filler and polymer are of surpassing importance in the case of GR-S and similar elastomers, and call for fundamental study. Among the factors which would seem to deserve study in this connection are: (a) the influence of dispersing and wetting agents on the filler-polymer relationships in the case of various fillers and various polymers; (b) the influence on the filler-polymer relationships, especially with non-carbon fillers, of the presence in certain copolymeric elastomers of non-hydrocarbon groups, especially polar groups, such as $-\text{CN}$, $-\text{CONH}_2$, $-\text{Cl}$.

Structure of Diene Polymers and Copolymers

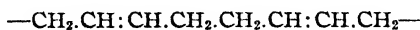
The difficulty of making satisfactory rubbers by the polymerization or copolymerization of butadiene and its homologues undoubtedly stems from the fact that these dienes are capable of undergoing, and by our present-known methods of polymerization do in fact undergo, union, not only in the 1,4- sense (as the isoprene elements are united in natural rubber), but also in the 1,2- and 3,4- sense. A further difficulty may quite possibly be (there is at present no evidence on the point) that the union of the diene elements takes place in different sterical senses and produces polymeric chains in which there occur both *cis*- and *trans*-arrangements about the double bonds. In natural rubber, a *cis*-configuration is considered to prevail throughout the whole molecule.

It is very desirable that solid ground be secured regarding the exact chemical structure of the synthetic diene polymers and copolymers. In spite of the difficulties involved when vast, irregularly constructed molecules are concerned, a more determined effort should be made to attain it. Physical methods, such as spectroscopy in the infrared and ultraviolet, are capable of contributing something, especially with regard to the occurrence of vinyl side groups (21). But, for direct chemical information on the structure of the complex polymer molecules, scission into fragments seems at present to be the best line of approach. And about the only method of producing the scission of complex unsaturated molecules in a definite manner seems to be ozonolysis, which splits the molecules at the double bonds, with the formation of oxygenated products. The

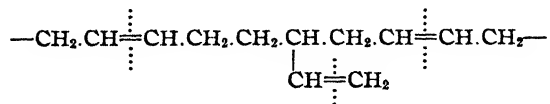
method has been successful with natural rubber to the extent of yielding 90% of the molecules in the form of levulinic acid and aldehyde—the products to be expected from the regular, linear, 1,4- union of isoprene units. In the more complex cases of synthetic diene polymers and copolymers, it has given a less complete story of the molecular structure of the materials. It has, however, as the following review will indicate, already yielded some measure of insight into molecular structure—enough to justify the assertion that the method is well worth further study, despite the difficulties introduced by the complexity of the fragments likely to result from chain irregularities and chain branching and by complications such as the effects of overozonization and the occurrence during scission of the ozonides, as effected by methods hitherto practiced, of secondary transformations of the primary scission products.

Polybutadiene.—Hill, Lewis and Simonsen (13) subjected to ozonolysis a sample of polybutadiene made in an acid emulsion with a cationic emulsifier according to the following recipe: butadiene, 100; carbon tetrachloride, 34.8; cetyltriethylammonium bromide, 3.2; *N* acetic acid, 9.6; water, 174. The emulsion was heated for 118 hours at 60° C. and gave an 80% yield of polymer. It will be noted that no catalyst was used and that the rate of polymerization was, by present standards, slow. The “regulator” or “modifier,” carbon tetrachloride, is one mentioned in the earlier patent literature and not an up-to-date one. The polymer was substantially insoluble in benzene. On ozonolysis, the following products were obtained:

(1) Succinic acid and succindialdehyde in amount which showed that at least 21.7% of the butadiene in the polymer represented pieces of chain produced by the 1,4- addition of at least two butadiene units in succession. Thus:

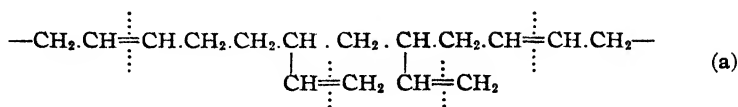


(2) Butane-1,2,4-tricarboxylic acid, $\text{COOH.CH}_2\text{.CH(COOH).CH}_2\text{.CH}_2\text{.COOH}$, in amount indicating that at least 10.6% of the butadiene was present in chain portions formed by alternate 1,4- 1,2- addition. Thus:

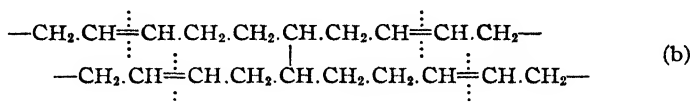


(3) Acidic material the methyl ester or esters of which boiled above the trimethyl ester of the acid just mentioned and failed to distil at 190° (20 mm). The authors suppose this fraction to be derived from sections

of chain in which 1,2- addition has predominated, for example (to give the simplest arrangement):



or from sections of chain where branching has occurred, as for example (to give the simplest arrangement):



The methyl ester or esters from this fraction amounted to 18.4 grams from 100 grams of polybutadiene. The constitution of the fraction was not determined. If the fraction were derived from chain sections such as (a), it would represent 9.4% of the butadiene in the polymer; if derived from branched sections such as (b), 12.5%. If derived from more complex chain sections, it would correspond to a higher percentage of butadiene.

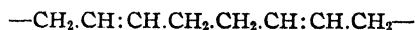
(4) Resinous acidic material which failed to undergo esterification when treated with methanolic hydrochloric acid. This fraction amounted to 21.2 grams from 100 grams of polymer. The authors assume that it must have been derived from sections of the polymer molecule still more complex than those hitherto illustrated and formed predominantly by 1,2- addition and chain branching.

(5) In addition, from 100 grams of polymer there were obtained carbon dioxide and formic acid equivalent to 3.66 grams of =CH_2 groups. If it is assumed that, in fact, these products are derived from the terminal methylene groups of pendant vinyl side groups, it may be calculated that 14.1% of the butadiene has entered in the 1,2- position without leading to branching. The figure of 14.1% does not seem to be too high to correspond to the products mentioned under (2), (3) and (4). Hill, Lewis and Simonsen, however, refrain from calculating the content of vinyl groups from the amounts of carbon dioxide and formic acid found, "since the solvent (chloroform) undergoes some decomposition under the conditions of ozonolysis with formation of phosgene, and secondary reactions may ensue with formation of some formic acid and possibly carbon dioxide."

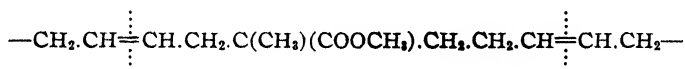
Butadiene-Methyl Methacrylate Copolymer.—Hill, Lewis and Simonsen (14) have also reported on the ozonolysis of an emulsion copolymer of butadiene and methyl methacrylate. The monomers were used in an

equimolar ratio, *viz.*, 35 butadiene/65 methyl methacrylate by weight. This is a higher proportion of the ester than will give a satisfactory rubber. The high proportion of ester will presumably be quite favorable to the exercise by it of a 1,4- directive influence in the copolymerization of the diene. (In the regular GR-S mixture of monomers there is only about one mole of styrene to six moles of butadiene.) Polymerization was effected in an acid emulsion without catalyst or modifier. Conversion was carried to 97%, and the product was soluble in benzene. On ozonolysis, the following products were obtained:

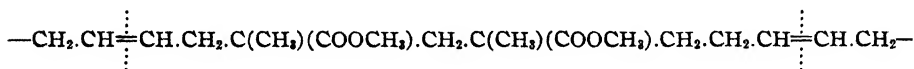
(1) Succinic acid and succinaldehyde in amount indicating that at least 3.7% of the polymer or 10.5% of the contained butadiene is represented by chain sections derived from the 1,4- addition of at least two butadiene units in succession, thus:



(2) 2-Methylbutane-1,2,4-tricarboxylic acid, $\text{COOH}.\text{CH}_2.\text{C}(\text{CH}_3)-(\text{COOH}).\text{CH}_2.\text{CH}_2.\text{COOH}$, in amount showing that at least 49.3% of the polymer molecules consisted of sections of chain in which butadiene (in the 1,4- sense) and methyl methacrylate have united in a regular, alternate manner, thus:



(3) A tetracarboxylic acid, $\text{C}_8\text{H}_{14}(\text{COOH})_4$, in amount indicating that at least 6.59% of the polymer molecules consisted of sections of chain in which two ester units have entered in succession, thus, for example:



(4) Higher acids the methyl ester or esters of which failed to distil at 180° (3 mm.). This fraction amounted to 29.23 grams of methyl esters from 100 grams of polymer. The fraction may arise from sections of chain in which three ester units occur in succession (in which case it can be calculated to represent 23.2% of the polymer) or it may arise from similar sections in which more than three ester units occur in succession or from sections in which butadiene has entered in the 1,2- manner or from branched sections.

(5) Carbon dioxide and formic acid in amount equivalent to 4.64% of $=\text{CH}_2$ groups in the polymer. For the reasons stated in connection with their study of the ozonolysis of polybutadiene, Hill, Lewis and

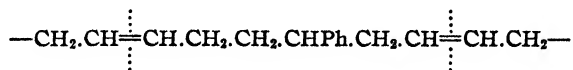
Simonsen refrain from calculating this back to butadiene in 1,2- combination. And it may be pointed out, as justifying this caution, that on such a calculation the carbon dioxide and formic acid correspond to 17.9 parts of butadiene in 1,2- union per 100 parts of polymer, which is more than can possibly be present in view of the amount of butadiene already accounted for in fractions (1) to (3). This state of affairs throws doubt on the reliability in other cases of basing conclusions as to the content of vinyl side groups in diene polymers on the yield of C₁ compounds (see below).

Butadiene-Styrene Copolymer.—Aleksieva and Belitzkaya (3) subjected to ozonolysis a polymer made from an equiweight mixture of butadiene and styrene (two moles butadiene to one mole styrene) by bulk polymerization at 60° C. with 3% of benzoyl peroxide as a catalyst. The polymer was apparently not soluble or not completely soluble in chloroform. The ozonide was decomposed by heating with a 3% hydrogen peroxide solution, which had the effect of converting any aldehydic scission products into acids. The ozonolysis products were as follows:

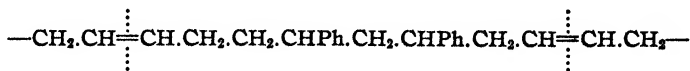
(1) Succinic acid in amount indicating that at least 39.5% of the butadiene had formed sections of chain by 1,4- addition, without any styrene, thus:



(2) Phenyladipic acid, $\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CHPh}.\text{CH}_2.\text{COOH}$, in amount indicating that at least 15.7% of the butadiene and 31.2% of the styrene occurred in sections of chain formed by the regular, alternate union of butadiene (in the 1,4- sense) and styrene, thus:



(3) Diphenylsuberic acid, $\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CHPh}.\text{CH}_2.\text{CHPh}.\text{CH}_2.-\text{COOH}$, or possibly $\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CHPh}.\text{CHPh}.\text{CH}_2.\text{CH}_2.\text{COOH}$, in amount indicating that 10% of the butadiene and 40% of the styrene formed sections of chain in which two styrene residues adjoined each other, for example:

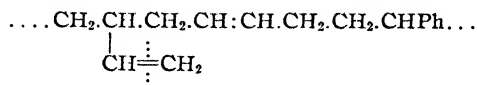


(4) Higher water-soluble acid or acids the methyl esters from which (7.0 g. from 100 g. polymer) were undistillable under 0.05-mm. pressure.

(5) More complex, water-insoluble acids, the methyl esters of which were undistillable under a high vacuum. These were much richer in

carbon than the preceding acids and presumably came from larger and more complex chain sections. They amounted to 59.4 grams per 100 grams of polymer.

(6) Formic acid in amount corresponding to 23.3% of butadiene having entered into the polymer in the 1,2- position without having caused branching, for example:

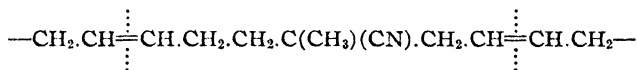


This figure may well be too high, having regard to the quantities of other products isolated and the improbability that they were isolated quantitatively.

Butadiene–Methacrylonitrile Copolymer.—Alekseeva has also reported on the ozonolysis of copolymers of butadiene with (*a*) acrylonitrile (1) and (*b*) methacrylonitrile (2). The results found in the latter case were as follows. The polymer was made by the bulk polymerization of an equimolar mixture of the monomers. After ozonolysis, the following were isolated:

(1) Succinic acid in quantity indicating that about 21% of the butadiene was present in sections of chain formed by the successive 1,4- addition of butadiene units.

(2) 2-Methylbutane-1,2,4-tricarboxylic acid in quantity indicating that at least 62.2% of the polymer molecules were composed of sections in which the two monomers had entered in a regular, alternate way, thus:



The ozonolysis of a copolymer made by the bulk polymerization of an equimolecular mixture of butadiene and acrylonitrile indicated that about one-half of the polymer chains consisted of sections in which the two monomer units were united in regular, alternate fashion, and about one-third consisted of sections in which two or three nitrile units were in juxtaposition (1).

From an examination of the infrared absorption spectrum of an emulsion copolymer of butadiene and acrylonitrile, it was concluded by Thompson and Torkington (21) that vinyl side groups may be present.

Sodium Polybutadiene.—There are indications that 1,2- union of butadiene units is particularly prone to occur and lead to the presence of vinyl side groups when polymerization of the diene is brought about

by metallic sodium. Yakubchik, Vasil'ev and Zhabina (24) estimated the content of vinyl groups by ozonizing various polymers, then decomposing the ozonides by heating to boiling with water and analyzing for formic acid and formaldehyde. Their data indicated that, in samples of polybutadiene made with sodium at 60° C., about 43% of the diene had entered the chains in the 1,2- sense and had left pendant vinyl groups. For a sample of polybutadiene made with sodium at 22°, the corresponding figure was 59.4%. (In passing, it may be noted that their procedure showed, in samples of butadiene-styrene rubbers prepared either by emulsion or bulk polymerization, vinyl groups corresponding to 31.5 to 34.5% of 1,2- polymerization.)

Ziegler and coworkers (25) had earlier arrived at the conclusions that the polymerization of butadiene by alkali metals and by alkali metal alkyl and alkali metal aralkyl compounds leads to the occurrence of a high proportion of 1,2- addition, and that the lower the temperature at which polymerization by such catalysts is effected the greater is the amount of 1,2- addition. In most of their experiments, the catalysts were employed in large proportion, and low molecular polymers were isolated containing vinyl side groups, such as 5-vinyl-2-decene, which was reduced to 5-ethyldecane and oxidized to α -amylsuccinic acid. When the polymer obtained by treating seven moles of butadiene with one mole of lithiumbutyl at 150° C. was ozonized and the ozonide subjected to oxidative scission, succinic acid was obtained in amount corresponding to about 60% of the polymer, whereas the yield of succinic acid was only 10% when polymerization was effected at room temperature.

Comments.—The identification of butane-1,2,4-tricarboxylic acid in the ozonolysis products of polybutadiene made in emulsion is conclusive proof of the presence of vinyl side groups in the polymer; and there is reasonably good, although less clear-cut, evidence that such groups occur in polybutadiene made by sodium and in typical butadiene copolymers. The results do not, however, afford any clear-cut evidence on the important question as to whether chain branching occurs in the polymers and, if so, to what extent. And the question remains as to how far the characteristic behavior of synthetic diene polymers is conditioned by the presence of vinyl side groups (absent or substantially absent from natural rubber) and how far it is conditioned by the presence, which has been generally assumed but not definitely proved, of chain branching.

With regard to the behavior of vinyl side groups, little unfortunately can be said at present, but it may be hoped that if the synthesis and study of simpler molecules in which vinyl groups are pendant to a long, main hydro-

carbon chain are undertaken, something may be learned by analogy. With regard to the part played by chain branching, it may be pointed out that, if the general apprehension that branching occurs in the molecules of diene polymers is correct, it is not unlikely that cross linking under the influence of oxygen, vulcanizing agents, etc. may produce, not only intermolecular, but also intramolecular, bonding. (Intramolecular bonding is not possible in natural rubber, except for the special case of the formation of six-membered rings by cyclization.) If branches are, in fact, present in the molecules of diene polymers, the number of branches in any one molecule may be relatively few. For if the branches were as numerous and as complicated as some of the hypothetical, highly ramified representations of diene polymers have shown, then it might be expected that cross linking would develop a network so tightly bound that the products would approach thermoset resins in their rigidity rather than rubbers in their extensibility.

Attainment of a clear picture of the chemical structure of diene polymers is of such great importance, both theoretical and practical, that it is to be hoped the subject will attract the attention of more organic chemists than have hitherto addressed themselves to it. Admittedly, the subject is one of considerable difficulty and will call for the efforts of many workers, from both the analytic and synthetic points of view, but it is of basic importance to that section of the field of polymerization which concerns conjugated dienes.

Natural Origin of Rubber

Considering the difficulties which, with our present stock of knowledge, are presented by the production from conjugated dienes of regular, 1,4-polymers, we may perhaps expect that in the future serious consideration will be given to the question (hitherto considered only casually if at all) of the way in which the rubber tree produces caoutchouc. Butadiene, the basis of most of today's synthetic rubbers, is a building stone of which nature is unaware. Isoprene, the β -methyl homologue of butadiene, is, on the other hand, a unit with which nature builds not only rubber but also an amazing number and variety of other products. It is traceable in the terpenic essential oils and resins of plants; in the coloring matters of tomatoes, carrots and other plants; in vitamins A, D, E and K; in the photocatalyst, chlorophyll, upon which life on this globe depends; in the sex hormones, the cardiac poisons, the foam-producing components (saponins) of plants, etc.; even in a hydrocarbon, squalene, which occurs in the liver oil of certain sharks. A review of the chemical relationships of the many

and various naturally occurring isoprenoid substances makes it not implausible to conjecture that, starting with the primary products of photosynthesis, the sugars, these substances are built up in an essentially step-wise manner (together with processes of isomerization, cyclization, hydrogenation and dehydrogenation). But between all these substances, which so far as now known contain at most eight isoprenoid units, and rubber, which contains 5000 or so, there is a gap so vast that it is difficult to resist the conclusion that the mode of formation of rubber in nature is not step-wise but, rather, differs fundamentally from that of all other natural isoprenoid materials. It is difficult to resist the conclusion that rubber is formed by a veritable high-molecular polymerization process. The regularity which characterizes the mode of union of the isoprene units in rubber may possibly be secured by a process of condensation, but it is perhaps more likely that it arises from the generation in the plant of isoprene in a nascent or free radical condition adapted to undergo polymerization in the 1,4- sense.

At present there is no solid ground from which the contemplation of such a process can be approached. The following is mentioned only as an example of a purely speculative approach. Sorbic acid, $\text{CH}_3\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, which occurs in certain plants, has been found to give, when decarboxylated by vigorous chemical treatment (barium hydroxide at a high temperature), not the monomeric hydrocarbon, piperylene, $\text{CH}_3\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}_2$, isomeric with isoprene, but dimers and trimers of this hydrocarbon. *If* a plant were to elaborate an isomer of sorbic acid, *viz.*, $\text{CH}_2:\text{C}(\text{CH}_3)\cdot\text{CH}:\text{CH}\cdot\text{COOH}$ or $\text{CH}_2:\text{CH}\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{COOH}$, and *if* this were susceptible to decarboxylation at ordinary summer or tropical temperatures under the influence of an appropriate enzyme, then it is not inconceivable that there might arise isoprene in a nascent condition adapted to undergoing polymerization to caoutchouc.

In Conclusion

Some years ago (23), in a lecture entitled "Some Fundamental Rubber Problems", the author spoke as follows. "In a famous phrase Mr. Kipling once declared: 'And what should they know of England who only England know!' If I may take the liberty of paraphrasing this, I would ask: What do they know of rubber who only rubber know? I believe it is a mistake, particularly in regard to the more fundamental problems presented by rubber, to direct attention too exclusively to rubber itself, and that it is highly desirable and indeed almost essential to consider other materials which display in some degree the behavior and properties of

rubber. By drawing analogies from the study of simpler and more tractable systems, we may hope to obtain an insight into the more complicated and difficult case of natural rubber itself." These remarks, still pertinent, apply not only to the scientific problems presented by natural rubber but also to those raised by synthetic rubbers. Now, with the incoming on a large scale of synthetic rubbers of various types—all manufactured by polymerization processes—it is even clearer than before that the study of rubber forms part of the broad field of high polymers and cannot profitably be divorced from the study of that broad field; that work in other parts of the field will increasingly throw light on rubber problems, and, conversely, that the further study of rubber problems will contribute toward an understanding of other parts of the subject of high polymers. The present volume, the contributors to which clearly recognize this fact, will help to orientate the problems of rubber among those of high polymers generally.

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SECOND-ORDER TRANSITION EFFECTS IN RUBBER AND OTHER HIGH POLYMERS

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	PAGE
I. Introduction.....	2
II. Some Experimental Results on Second-Order Transitions in Rubber.....	6
1. Volume-Temperature Curves.....	6
2. Heat Capacity Measurements.....	8
3. Crystallinity and Second-Order Transitions.....	12
4. Compressibility.....	13
5. Thermal Conductivity.....	13
6. Modulus of Elasticity.....	16
7. Refractive Index.....	16
8. Dielectric Properties.....	17
III. Factors Influencing Second-Order Transition Temperature as Determined by Thermal Expansion.....	21
1. Effect of Orientation.....	21
2. Time Effects.....	22
3. Molecular Weight.....	23
4. Vulcanization.....	24
5. External Forces.....	26
6. Copolymerization.....	26
7. Plasticizers.....	27
IV. The Brittle Point.....	31
1. Survey of Brittle Point Tests.....	31
2. Theory of the Brittle Point Tests.....	35
Effect of Molecular Weight on T_b	37
Effect of Vulcanization and Plasticizer.....	39
Effect of Fillers.....	40
3. Some Experimental Results Illustrating the Theory of the Brittle Point Test.....	40
Effect of Molecular Weight.....	41
Effect of Vulcanization.....	43
Effect of Plasticizers.....	44
Effect of Fillers.....	45
4. Young's Modulus of Unstretched Rubber.....	46
V. Summary.....	48
Bibliography.....	51

I. Introduction

A second-order phase transition is manifested as a change in slope when any of the primary thermodynamic properties of a material, such as volume or heat content, are plotted against temperature; and hence as a discontinuity in the first derivative of these properties. Such transitions were originally treated by Ehrenfest (28) and later classified as to type by Mayer and Streeter (73). This transition occurs at -73° C. in the case of natural,

TABLE I
SECOND-ORDER TRANSITION TEMPERATURES FOR VARIOUS HIGH POLYMERS

Material	T_m , ° C.	Method ^a	Ref. No.
Polyisobutylene	-74	T, H	(31)
Natural rubber	-73	T, H	(9, 10)
GR-S rubber	-61	H	(92)
Hycar OR rubber	-23	H	(11)
Cellulose nitrate, F-2	52.6	T	(20)
Cellulose acetate, B-96	68.6	T	(20)
Cellulose acetobutyrate, AA-5	49.9	T	(20)
Cellulose acetopropionate, CP-1	38.8	T	(20)
Ethyl cellulose	43	T	(122)
Polyvinyl acetate	28	T	(49)
Polyvinyl alcohol	85	T	(49)
Polyvinyl partial butyral	50.1	T	(20)
Polyvinyl chloride	75	T	(20)
Polyvinylidene chloride	-17	T	(13)
Polyacrylic acid	80-95	T	(50)
Polymethyl acrylate	3	T	(48)
Polymethyl methacrylate	57-68	T	(122)
Polyvinyl ethyl ether	< -10	T	(49)
Polyvinyl isobutyl ether	< -10	T	(49)
Polystyrene	81	T	(89)
Polyindene	85	T	(49)
Polyvinyl carbazole	84	T	(49)
Polyvinyl pyrrolidine	54	T	(49)
Glyptal	83-87	T	(117)
Nylon	47	T	(13)
Ebonite	80-85	T	(96)

^a T, thermal expansion; H, heat capacity.

unvulcanized rubber, and at other fairly well-defined and characteristic temperatures in the case of all high-polymeric materials which have been studied. Coincident with this discontinuity in thermal expansion and heat capacity is a rather marked change in most physical properties. Rubber, for example, on being cooled below the transition temperature, changes from its normal state of toughness and long-range elasticity to a brittle material possessing very little extensibility. In fact, the second-order transi-

tion temperature is a point of reference for all high polymers below which any normal rubberlike material loses such properties and above which any dimensionally stable plastic acquires rubberlike characteristics.

Table I presents second-order transition temperatures for a number of high polymers, ranging from -74° C. for polyisobutylene to 85° C. for polyvinyl alcohol. No effort has been made to choose what might be called definitive values for these transition temperatures. As will become evident later, such diverse factors as heating rate, molecular weight, plasticizer content and stresses in the material influence the transition temperature. Jenckel and Überreiter (51), for example, have reported transition temperatures as high as 108.5° C. for precipitated polystyrene, whereas the usually accepted value for polystyrene is 81° C. Discrepancies of 20° C. between different observers have been noted in the case of other polymers.

Neglecting such variations as the above, there is apparently no simple and far-reaching rule connecting molecular structure and transition temperature. The transition temperature increases roughly in proportion to the intermolecular force constant per unit length of chain (13), but there are many exceptions to this rule. Bulky side groups, as in polystyrene or polyvinyl carbazole, and polar groups, as in polyvinyl chloride, lead to a high T_m . However, polyvinylidene chloride, with its two chlorine atoms, has a low T_m of -17° C., which Baker (5) ascribes to the greater symmetry of C—Cl₂ as compared with C—Cl. As will be seen later (page 26), the transition temperature increases for the series polybutadiene, polyisoprene, polydimethylbutadiene, and then drops back again for polyisobutylene, presumably because of greater symmetry of polyisobutylene. Jenckel (49) has constructed molecular models which indicate that ease of rotation about carbon-carbon bonds is an important factor in determining T_m .

While a second-order transition is not a phase change in the usual sense, it has been likened by Überreiter (118) to an internal melting point above which the polymer preserves the external characteristics of a solid (fixed shape, capable of supporting shear load) while behaving partly like a liquid (constant volume, capable of undergoing large plastic and elastic deformations with a Poisson ratio of 0.5). What appears to happen as the transition temperature is approached from below is that segments of the long polymer chains gradually move further apart, or new "holes" appear (30). Eventually side groups on the hydrocarbon chains, and whole segments of chains, are able to execute more or less free rotations about the long axis of the molecule. This enhanced possibility for vibration and rotation occurring, not at a sharp temperature as with first-order transitions, but over a range of temperature, can likely account for the increase in specific heat

at the transition. Moreover, the ability of the molecule to act as an articulated chain provides the condition necessary for viscous flow according to the Kauzmann-Eyring (53) theory of viscous flow in polymers, and is also essential for the mechanism of long-range elasticity postulated in the kinetic theory of rubber elasticity (70).

Pauling (90) was the first to account for second-order transitions in low molecular weight materials as a change from oscillation to rotation of ions or molecules, or, in the case of organic materials, of certain molecular groups. He established the criteria that high interatomic forces and high moment of inertia favor oscillation, whereas low forces and low moment of inertia favor rotation. He suggested, moreover, that multiple second-order transitions, as in hydrogen bromide, represented rotation about different crystal axes. The field of molecular rotation in the solid state has received considerable attention from the dielectric approach and is well summarized in recent papers by Baker and Smyth (7), Morgan (78), and Smyth (105), who emphasize the role of molecular symmetry in permitting rotation in the solid state. Kirkwood (61) has treated the second-order transition appearing in the pressure-temperature-area relationships of fatty acid monolayers as a problem in hindered molecular rotation.

In regard to amorphous materials Tammann (109) considered a transition interval below which all molecules were frozen in place, above which all molecules could rotate freely. While Müller's x-ray (80) and other studies on *n*-paraffins, ketones and nitriles indicated that such molecules do rotate in the solid state above the transition point, yet it is hardly conceivable that a high-polymer molecule could rotate as a unit. The present tendency, as exemplified by the writings of Alfrey and Mark (4), Fuoss (40), Jenckel (49) and Tuckett (113), over the past few years, is to identify the second-order transition in polymers as the temperature at which rotation of polymer segments, consisting of perhaps as many as forty carbon atoms, begins. Fuller, Baker and Pape have offered additional detailed evidence for rotation of molecular segments in solid polyamides (39). Bunn in particular has presented a comprehensive account of molecular motion in rubber, gutta-percha and chloroprene, although his interest was directed primarily to the question of melting (16).

Just as in the case of first-order phase transitions where, for example, the melting point can be lowered by external pressure or by the presence of impurities, so also is the second-order transition temperature sensitive to external pressure or tension, to plasticizer and to other variables. Continuing the analogy, this internal melting point of a polymer increases at first with molecular weight and then reaches a constant value, just as does the

true melting point of a series of homologous organic compounds. However, this transition involves no latent heat.

There is one other distinct difference—the second-order transition is characterized by marked time effects other than those needed to establish thermal equilibrium. Alfrey, Goldfinger and Mark (3) choose to speak of the “apparent second-order transition in polystyrene” to emphasize that there is no thermodynamic singularity involved. They emphasize that, while the transition temperature appears to be definite for a given polymer, this is simply a consequence of different observers studying the phenomenon at a fairly fixed rate (*i. e.*, the heating rate, rate of deformation, etc.). Richards (93) has also stressed this point of view, pointing out that the temperature of the transition depends on the speed of the test with which it is observed.

It is the purpose of this review to survey in part what has been found experimentally in regard to second-order transitions in rubber, and to interpret the results on the basis of the free rotation principle. It will not always be possible to illustrate some of the points with data on rubber alone; and therefore many examples will be chosen of synthetic rubbers and rubberlike materials. Factors which influence the transition temperature, and the connection between this temperature and related measurements such as the brittle point, will be discussed. The term “transition” will be used to designate a second-order transition, unless otherwise stated; its temperature will be referred to as T_m , while the brittle point temperature will be called T_b . The change in cubical expansion coefficient above and below T_m is called $\Delta\beta$.

The term “free rotation” is used here only in the relative sense, that below T_m any segmental rotation is virtually impossible, whereas above T_m a hindered rotation can occur, even though it consists of many small angular jumps, in the manner discussed by Kauzmann (52) for the orientation of dipoles. This rotation is a cooperative phenomenon which depends on the simultaneous rotation of molecular segments in adjacent chains (7, 37). While the concept of rotation in the solid state appears basic to an understanding of many polymer properties, the analogous situation with low molecular materials still seems controversial. Lawson, for example, after making a detailed study of second-order transition effects in solid ammonium chloride (66), concludes that the data support Frenkel's hypothesis of a change in the character and the amount of vibration above and below the transition, rather than Pauling's ideas on a change from vibration to rotation. Beck, however, has decided that the change in the infrared spectrum of ammonium chloride below and above the transition

is what might be expected if the ammonium group had begun to rotate (8). In the case of polymers, we shall use the term "free rotation" in anticipation of future studies which will demonstrate more precisely what it means.

II. Some Experimental Results on Second-Order Transitions in Rubber

Ruhemann and Simon in 1928 were apparently the first to observe a second-order transition for natural rubber in connection with heat capacity measurements (94). This transition, occurring at -70°C ., was called by them the α -anomaly. They found no appreciable difference for the transition in gel, sol and total rubber or in mildly vulcanized samples. They also measured two methyl rubbers with transitions at 0°C . (methyl H) and -15°C . (methyl W). These types of rubbers may have contained from 6 to 10% of sulfur (74), although this is not clear. In connection with these latter materials, Ruhemann and Simon commented on the mechanical hardening which accompanied cooling below the transition. Shortly thereafter, Kimura and Namikawa reported on the specific gravity of rubber-sulfur compounds over the complete composition range (57). They observed second-order transitions which increased in temperature with increasing sulfur content.

More recently, the fundamental research program on rubber and rubber-sulfur compounds conducted by the National Bureau of Standards has vastly extended such observations to include the effect of confining liquids, experimental techniques, crystallinity and pressure on these transitions as measured by thermal expansion, heat capacity, electrical properties, compressibility and refractive index. These data will enter prominently into the following discussion.

1. Volume-Temperature Curves

Figure 1 shows a curve by Bekkedahl (9) on the relative volume of rubber hydrocarbon in both the amorphous and the partially crystalline states as a function of temperature. A dilatometric method was used with alcohol as the confining liquid. The second-order transition appears in both types at approximately -73°C ., while the first-order transition appears at $+10^{\circ}\text{C}$. for the melting of the rubber crystallites. Figure 2 portrays part of these same data plotted now as cubical coefficient of expansion. It is evident that crystallinity has not altered the location of T_m but has decreased the change, $\Delta\beta$, in expansion coefficient occurring at T_m . Bekkedahl found

that, with acetone as the confining liquid, the transition did not appear at all. This was undoubtedly caused by the plasticizing action of the acetone in lowering T_m , as will be discussed later. With absolute alcohol or alco-

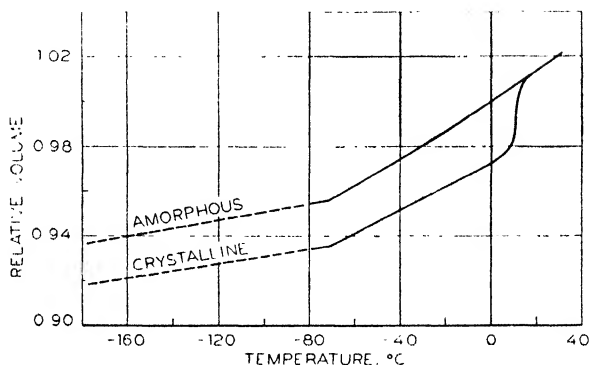


Fig. 1.—Relative volume of amorphous and partially crystalline rubber hydrocarbon as a function of temperature (9).

hol-water mixtures as confining liquids, the transition appeared. Wood, Bekkedahl and Peters (124) later employed an interferometric method for studying dimensional changes in rubber. This eliminated all complications from confining liquids. Moreover, because of its greater sensitivity,

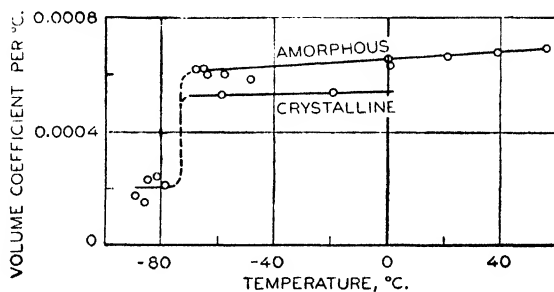


Fig. 2.—Cubical coefficient of expansion of amorphous and partially crystalline rubber hydrocarbon (9).

this method revealed that for stark rubber, at least, the transition was not sharp but occurred over about a 4° C. change in temperature, or from -71° to 67° C.

Figure 3 illustrates the influence of combined sulfur content on T_m over the entire composition range from rubber hydrocarbon to hard rubber. This plot, prepared by Bekkedahl (8a), is distinctly S-shaped. More will be said on page 24 concerning the influence of small amounts of sulfur and other cross-linking agents on T_m . Überreiter (117) has also measured T_m for crêpe rubber to which up to 50% of sulfur was added. His results

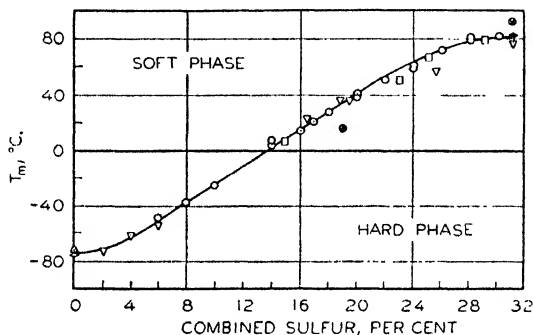


Fig. 3.—Influence of combined sulfur content on second-order transition temperature of rubber: Δ , thermal expansion (9); \circ , thermal expansion (57); \square , softening point (57); ∇ , thermal expansion (96); \oplus , refractive index (75); \otimes , permanent set (17a); \blacklozenge , yield point (17b); \diamond , heat capacity (10).

disagree markedly with the data of Figure 3, since even his highest sulfur content sample had a T_m of only -20°C . He showed, however, that T_m increased with longer times of vulcanization at constant sulfur content, thus suggesting that his samples may not have been completely vulcanized.

2. Heat Capacity Measurements

Figure 4 taken from a paper by Bekkedahl and Matheson (10) shows the discontinuity in heat capacity of amorphous and partially crystalline rubber hydrocarbon near 200°K . Crystallinity shifts T_m to a slightly higher temperature and broadens out the transition region, but its main contribution is in diminishing the height of the discontinuity.

Bekkedahl and Scott (11) investigated the heat capacity of unvulcanized Hycar OR (butadiene - 40% acrylonitrile copolymer) and observed a second-order transition at 250°K . There were no indications of crystallinity in this sample. Rands, Ferguson and Prather (92) later measured synthetic rubber GR-S (butadiene - 25% styrene copolymer) and noted a second-order transition at 212°K , again with no evidence of crystallinity. These authors presented a comparative curve of heat capacity *vs.* tempera-

ture for natural rubber, GR-S and Hycar OR which is reproduced in Figure 5. They also found that values of the specific heat of GR-S below T_m were sensitive to the past history of the sample. Temperature drifts lasting up

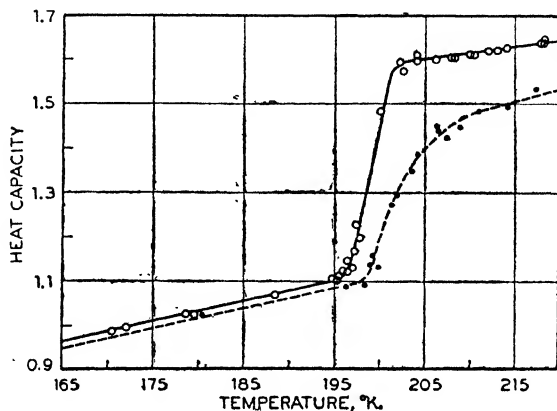


Fig. 4.—Heat capacity in joules per gram per degree C. for amorphous (solid line) and partially crystalline (broken line) rubber hydrocarbon (10).

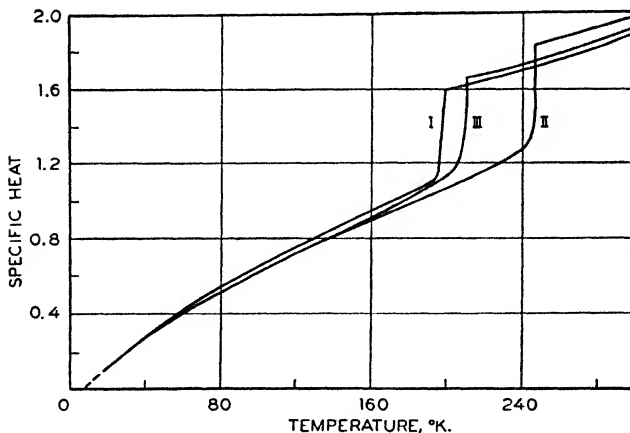


Fig. 5.—Specific heat in international joules per gram per degree K. of amorphous rubber hydrocarbon (I), GR-S (III) and Hycar OR-15 (II) (92).

to one and one-half hours were observed, depending on how rapidly the sample was chilled and how long it remained below T_m . The transition temperature varied from -64° to -59° C. because of such effects.

Ferry and Parks (31) have observed a characteristic discontinuity occurring at 199° K. in the specific heat curve for low molecular weight polyisobutylene. Parks, Huffman and Cattoir (87) found a similar transition in glassy glucose at 8° C. They noted that the time required to reach thermal equilibrium in the specific heat runs was a maximum at the transition temperature (30 minutes as compared with 4 to 5 minutes above and below T_m). Polystyrene also shows a second-order transition in specific heat at about 90° C. (13).

Chang has discussed the specific heats of solids as a problem in molecular rotation, applying Bethe's method for order-disorder phenomena (17). His agreement with experiment in the case of ammonium chloride and ammonium nitrate was not too satisfactory. In this connection it is interesting to note that the specific heat transition accompanying the order-disorder phenomenon in alloys (85), as well as the specific heat transition behavior for materials like ammonium chloride, is a typical lambda point (73) at which the specific heat drops back to a normal value above the transition. In the case of high polymers, as well as the organic glasses studied by Parks and coworkers, the increase in specific heat at T_m persists for all higher temperatures.

In the former instance, the lambda point is apparently connected with a definite process (disordering the lattice, setting ions or molecules into rotation) which, once completed, no longer requires a large increment of energy. This is seen rather well in the case of hydrogen bromide which has three well-defined second-order transitions (lambda type) in close succession, and which Pauling (90) has ascribed to the onset of rotation about the three crystal axes.

For polymers, however, the general complexity of the molecule and the many possible modes of vibration which are conceivable once rotation about carbon-carbon bonds commences, would account for the diffuse nature of the heat capacity transition. It might be permissible to speak of a distribution of lambda point transitions, so many in number and so close together as to give a continuous absorption of extra energy once the transition temperature is reached. This would be in harmony with the concept of a distribution of relaxation times to account for the electrical and mechanical properties of polymers (101). Moreover, just as the maximum loss factor for a polar polymer is much less than is predicted by the Debye theory for a dielectric having a single relaxation time, so also is the specific heat anomaly for a polymer quite small compared with that for a simple molecule. It seems instructive, therefore, to review some of the published specific heat data on simple aliphatic compounds, such as the normal paraf-

fins, where, as Müller has shown, the entire molecule begins to rotate about its long axis at the transition temperature.

Stull (108) observed a low broad anomaly in the specific heat curve of liquid *n*-hexane at 262° K. Ubbelohde (116) observed a rather sharp (about 1000 cal. per mole) transition in the specific heat of pentadecane about 10° C. below the setting point. With hexadecane the transition had fused into the melting point. Cetene, however, exhibited a low (200 cal. per mole), broad, specific heat anomaly about 25° C. below the melting point, although the double bond in this compound introduced complications. Lambda transitions in the specific heat curves of C₂₆, C₃₆ and C₄₄ paraffins were reported by Garner and coworkers, the transition temperature increasing with chain length (42). A similar behavior was noted by King and Garner for the ethyl esters of monobasic aliphatic acids from C₁₈ to C₃₀, where the lambda transition increased regularly from 27° to 62° C. (58).

Even the coefficient of expansion for the normal paraffins gives a lambda anomaly at the transition temperature. Van Hook and Silver reported a rather broad lambda point for C₂₄H₅₀ about 12° C. below the melting point (120). The extensive density studies by Seyer, Patterson and Keays (99) on the even *n*-paraffins confirmed this behavior but also emphasized the complexity. C₁₆ shows no transition; C₁₈, C₂₀ and C₂₂ show the transition only on cooling; while C₂₄ to C₃₄ undergo the lambda transition both on heating and cooling. C₂₉, the only odd paraffin studied, gave a comparatively weak and diffuse lambda transition. The extreme case of a paraffin occurs in the volume-temperature curve for polythene reported by Clash and Rynkiewicz (20). The data suggest a very broad lambda transition ranging from -35° to the melting point at 115° C., which would be consistent with a very broad distribution of molecular sizes. As these authors point out, polythene is unique among all plastics in regard to thermal expansion, although it might be considered as simply a limiting case of the paraffin series, complicated by a distribution of chain lengths. Piper and coworkers have made plots of melting points and transition points for the paraffins from C₂₈ to C₃₄ which indicate that the two curves converge somewhere around C₄₄ and a temperature of 85° C. (91).

Frölich (38) has recently offered a very enlightening interpretation of the lambda transitions in paraffins, along the following lines. A disordering of the lattice begins at the lambda point in which one paraffin chain is rotated and translated with respect to its neighbors. This involves an energy change. However, with further increase in temperature, more and more chains will be involved in such rotations, and the energy difference

between chains will finally vanish. This corresponds to a lambda anomaly in specific heat. The important point, however, is that the above disordering process, in itself, is not able to account for the magnitude of the specific heat anomaly. In addition it is necessary to assume some internal flexibility for each paraffin chain. He calculates that for pentadecane above its lambda point about 50% of all chains are internally twisted.

In the case of polyethylene, there are amorphous areas where internal rotations can occur at temperatures as low as -68°C ., as implied by brittle point measurements which will be shown in Table IV (page 34). With

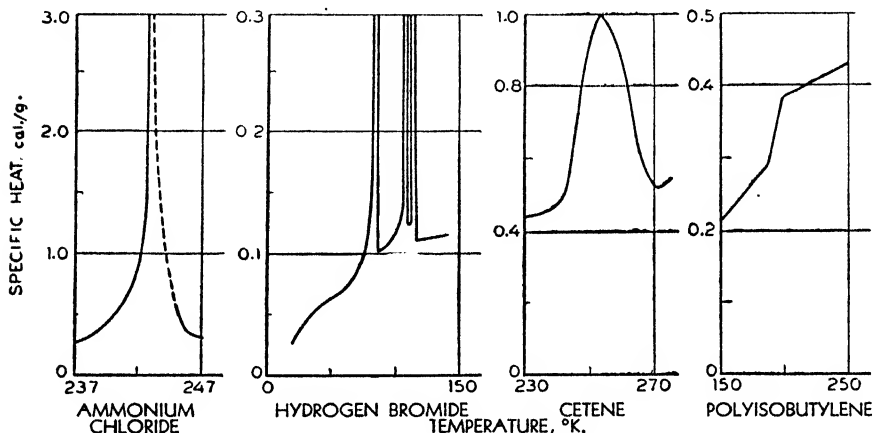


Fig. 6.—Suggested evolution of the specific heat anomaly in polymers as a result of increasing molecular complexity. Ammonium chloride shows a typical lambda transition.

increasing temperature, further transitions then occur in the crystalline areas. This same type of behavior undoubtedly applies to other partially crystalline polymers such as rubber and nylon.

It is realized that the general laws governing such transitions in the paraffins, and their variations with chain length and other structural features, are quite complex and beyond the scope of this review (121). Figure 6 is offered as a suggestion of the development of second-order heat capacity transitions with increasing molecular complexity. Examples were chosen from data on ammonium chloride (66), hydrogen bromide (43), cetene (116) and polyisobutylene (31).

3. Crystallinity and Second-Order Transitions

Parks has commented on the fact that the presence of crystallinity does not appreciably affect T_m but does decrease the magnitude of the break in

the thermal expansion and heat capacity curves (86). He suggests that the second-order transition is confined only to the amorphous regions, and therefore estimates that the "crystalline" sample shown in Figures 1 and 2 was only 20% crystalline, while that listed as the "crystalline" sample of Figure 3 was 29% crystalline.

An analogous situation has been found (13) for vinylidene chloride-vinyl chloride copolymers in which the amount of crystallinity as determined by density and x-ray measurements could be altered, with suitable heat treatment, from zero to roughly 65%. T_m was independent of crystallinity, whereas $\Delta\beta$ decreased almost linearly with increasing crystallinity. This suggested that a completely crystalline sample would not show a second-order transition.

4. Compressibility

Simha (102) has emphasized that the compressibility *vs.* temperature curve for a polymer should exhibit a second-order transition corresponding to T_m . This prediction is verified by Scott's data (96) on the volume of rubber-sulfur compounds from 10° to 85° C. and for pressures up to 800 bars. Compressibility values for 3% sulfur were read from his Figure 12, while the values for 19.5% sulfur were calculated from his data. The results are shown in Figure 7. The volume-temperature curve exhibits no transition in this temperature interval for 3% sulfur, and the compressibility is likewise free of a transition. For 19.5% sulfur, T_m is 35° C., and a definite discontinuity in the compressibility occurs at about this temperature. Adams and Gibson had previously pointed out that soft rubber has the compressibility of a liquid, while hard rubber behaves like a solid (1).

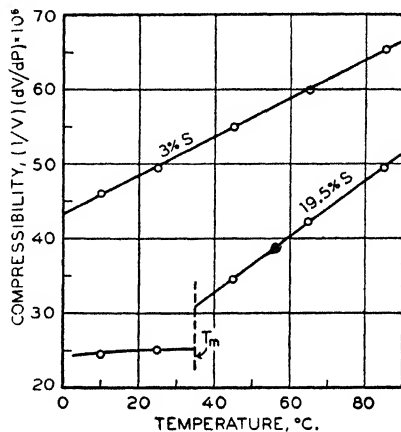


Fig. 7.—Compressibility-temperature curves for rubber-sulfur compounds (data from Scott).

5. Thermal Conductivity

Schallamach (100) observed that the thermal conductivity of rubber at liquid air temperatures was considerably less than its room temperature value. He therefore investigated this property throughout the second-order transition region with the results shown in Figure 8. A sample of

electrodeposited latex containing an unknown but presumably small amount of sulfur was used. A characteristic break occurs around 210° K. on the heating cycle where the lengths of the short horizontal lines represent the temperature difference across the specimen. The behavior on cooling was distinctly different since pronounced supercooling occurred, sometimes to the extent of 100° K. The drop in thermal conductivity was then extremely abrupt and was accompanied by a clicking noise. The sharp increase in thermal conductivity at the transition temperature is presumably connected again with enhanced possibilities for molecular

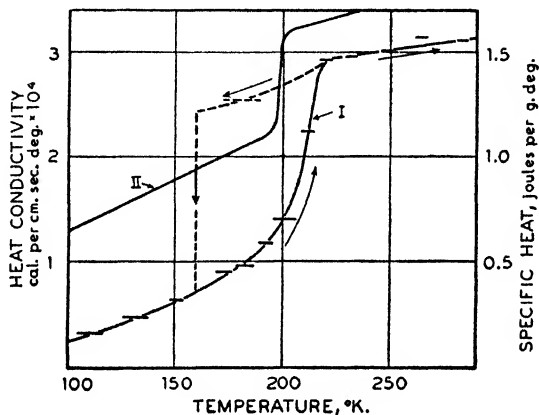


Fig. 8.—Thermal conductivity (*I*) of vulcanized rubber compared with heat capacity (*II*) of amorphous rubber hydrocarbon (100).

motion. One might anticipate a marked anisotropy in thermal conductivity of oriented polymers below T_m , and also some dependence on molecular weight, since vibrations could be passed along the molecular chain even below T_m .

The writers are not aware of any comprehensive treatment of the theory of thermal conductivity in amorphous solids. Bridgman (15) has proposed a simple expression originally developed for liquids but which he found to work reasonably well for hard rubber. A similar expression based on transition state theory has been derived by Kincaid and Eyring (57a), but the original formula by Bridgman is adequate for our immediate purpose. He showed that the thermal conductivity, K , in ergs per degree per cm. per cm.² per sec. is given by:

$$K = 2k \cdot V/\delta^2 \quad (1)$$

where k is the Boltzmann constant, V the velocity of sound, and δ is the cube root of the ratio of the absolute mass of one molecule to the density of the material. Taking one isoprene residue as the kinetic unit, we calculate for vulcanized rubber at 0° C. a thermal conductivity of 0.2×10^{-4} cal. per degree per cm. per cm.² per sec., compared with a value of 3.1×10^{-4} found by Schallamach. V was taken as 5400 cm. per sec. at 0° C. from the Smithsonian tables.

Wood has suggested (122a) that this low value for the velocity of sound in rubber, which is based on some old experiments by Exner (29a), is for a standing wave on a long rubber rod. It agrees with the low value for the Young's modulus of rubber. The velocity of a compressional wave can be calculated from the expression $V = (E/d)^{1/2}$ where E is the bulk modulus and d is the density. Using Scott's data (96) for rubber containing 3% combined sulfur at 10° C., where the density is 0.940 and the compressibility is 46×10^{-12} cm.² per dyne, the velocity of a compressional wave is calculated as 1.56×10^5 cm. per sec. Substitution of this value in the Bridgman formula gives a thermal conductivity value of 5×10^{-4} which is now somewhat greater than the value of 3.1×10^{-4} listed by Schallamach. Incidentally, measured values of sound velocity in rubber are of the order of 1.6×10^5 cm. per sec. for compressional waves in the frequency region from 10 to 50 kilocycles (7a). The general question of sound transmission and sound absorption in amorphous bodies has been treated by Frenkel and Obrastzov (37a).

Any further elaboration on Equation (1) connecting thermal conductivity and sound velocity is probably not justified at this time. It is interesting to note that, if the kinetic unit is taken as two isoprene units, the agreement with Schallamach is extremely good at 10° C. However, it is difficult to see, on the basis of Equation (1), why the thermal conductivity should drop so rapidly as the temperature is lowered through the transition region. According to Figure 7 on page 13 the compressibility decreases abruptly below T_m . The bulk modulus, and hence the velocity of sound, would be expected to increase rather than decrease, and this in turn should lead to an increase in thermal conductivity. Experimental studies on these relationships may reveal some interesting possibilities.

Greene and Parks (44a) have determined the thermal conductivity of glucose glass across the second-order transition region. The observed behavior is similar to that of rubber but the change in thermal conductivity is only 5%.

6. Modulus of Elasticity

Meyer and Ferri have investigated (77) the behavior of the modulus of elasticity of a rubber sample (containing 8% sulfur) in the region of its transition temperature, and at an elongation of 350%. The combined sulfur was probably only 4%. Their results are shown in Figure 9. Starting below T_m , the modulus (expressed as the force needed to maintain a given elongation) decreases with increasing temperature. This is, as Meyer and Ferri explicitly state, the characteristic behavior of an ordinary

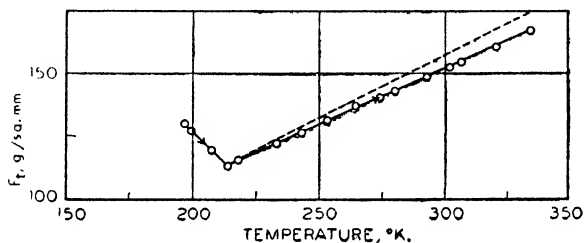


Fig. 9.—Force required to maintain a vulcanized rubber sample (8% sulfur) at 350% elongation (77). Solid line is as measured. Broken line is corrected for thermal expansion.

solid body. Above T_m the force increases in direct proportion with the absolute temperature, which agrees with the kinetic theory of rubber elasticity. X-ray studies showed that there was no interference from crystallinity in this experiment.

7. Refractive Index

McPherson and Cummings have measured the refractive index of rubber-sulfur compounds from 0° to 75° C. (75). The only one of their published curves which shows a second-order transition is that for 19% combined sulfur. Below 17° C., the refractive index is almost independent of temperature, but then gradually starts to decrease. The transition region extends almost to 30° C., where the slope of the curve finally equals that for samples of lower sulfur content. These authors also cited unpublished observations on samples of higher sulfur content which showed a similar behavior. According to Scott's work (96), a rubber specimen of 19% sulfur content has a transition by refractive index at approximately 34° C. It seems curious that the transition by refractive index should be so much lower, since any change in refractive index would presumably result from

density changes. The molar refraction calculated by the Lorenz-Lorentz formula, $(M/d)(n^2 - 1)/(n^2 + 2)$, using Scott's density data, indicated a slight and possibly discontinuous jump between 10° and 20° C. The different samples used for density and refractive index measurements, and slight inaccuracies in reading values from graphs, leave this point in question.

Parks and coworkers have observed (87) changes in both thermal expansion and refractive index for glucose glass in the transition region. Here again there is a suggestion that the refractive index transition begins a few degrees lower than that for thermal expansion ($T_m + 22^\circ$ C.). The molar refraction, however, decreases linearly with temperature on heating, the rate of decrease being three times greater above 23° C. Thus there is a transition in the molar refraction itself.

It may be that the index of refraction anticipates the second-order transition temperature on heating because of some slight change in polarizability of the electrons with decreasing force fields from neighboring molecules. The authors have not been able to locate any further data on polymers to test this point, but the next section, on dielectric properties of rubber, will raise the same question in a different manner. It is interesting to note, in passing, that the aliphatic fatty acids (25) and nitriles (26) also show molecular refractivity *vs.* temperature curves consisting of two straight-line portions with a definite break (40° C. for the acids, 45° C. for the nitriles), which is independent of chain length. These breaks occur in the liquid state. A similar behavior was also found (27) for some of the normal paraffins up to C₁₂ when molecular refractivity was plotted against temperature. The break in this case occurred around 30° C., but was not consistent. It is realized that the Lorenz-Lorentz expression for molecular refraction is not adequate for wide ranges of temperature (65). This sort of objection does not enter here, where the slope of the refractivity *vs.* temperature curve suddenly changes over a narrow temperature interval.

8. Dielectric Properties

Bekkedahl has cited (9) some unpublished observations by Scott and Cummings on the change in dielectric constant of rubber hydrocarbon in the vicinity of the transition temperature. The dielectric constant drops from 2.435 to 2.423 over a 6° temperature rise after correction of the measured values for thermal expansion. This behavior was independent of frequency within the range studied (60 to 300,000 cycles), thus indicating that it was not connected with a dipole effect. Moreover, the usual tendency is for an increase in dielectric constant of polar materials above the transition temperature.

Using Wood's best value (123) of 1.5190 for the refractive index of rubber hydrocarbon (n_D at 25° C.), and a temperature coefficient of 350×10^{-4} per degree C., the calculated refractive index at -65° C. is 1.5505, whose square is 2.404. This is reasonably close to the measured dielectric constant of 2.423, the difference presumably representing atomic polarization. If, then, the dielectric constant increases on cooling below -65° C., the effect would appear to involve some change in the electronic and/or atomic polarizabilities of the rubber molecules. This may be connected with the change from rotation to oscillation, or with a change in short-range force fields, either of which might influence the electronic and atomic polarizability. However, the effect would seem more logical if it were reversed. The usual statement (106) on such questions as this has been that neighboring molecules exert relatively little influence on the polarizability of organic molecules. Such measurements, however, have been confined mainly to the liquid state in which the molecules are already relatively far apart. It would therefore seem that precise studies of the refractive index and the dielectric constant of hydrocarbon polymers in the region of a second-order transition temperature would provide interesting information.

The general dielectric behavior of rubber-sulfur compounds is complex. If pure sulfur is added to rubber, it is without effect on the electrical properties except as a filler. Vulcanization, however, converts the rubber to a polar material which responds in characteristic manner to an electric field. Curtis, McPherson and Scott (23) found that, at fixed frequency and temperature, the power factor and dielectric constant passed through a maximum with increasing sulfur content. This they attributed to the formation of stoichiometric compounds between sulfur and rubber. Kitchin, however, was able to show that the location of this maximum with increasing sulfur content was dependent on both temperature and frequency (62). He interpreted this behavior in terms of second-order transition temperatures, with the suggestion that above T_m the rubber-sulfur compounds acted as liquids in which the dipoles were free to respond to the electric field; below T_m the same compound behaved as a solid in which the dipoles were frozen in place and could no longer contribute to dielectric dispersion and power loss. This is, so far as we know, the first explicit statement of a connection between electrical properties and second-order transitions in polar polymers. Fuoss, of course, has also considered this point in great detail (40).

The extensive series of electrical measurements on rubber-sulfur compounds by Scott, McPherson and Curtis (97) provides ample data on the influence of frequency and sulfur content on the transition temperature.

Field (32) has made a detailed analysis of these data in terms of the Cole circular-arc (21) type of plot. In this method, the loss factor is plotted against dielectric constant to give a circular arc whose center lies below the dielectric constant axis. The parameter α , used by K. S. and R. H. Cole as a measure of the ratio of stored to dissipated energy, has been calculated by Field with the results shown in Figure 10. The parameter α shows a distinct reversal at some temperature which increases with the sulfur content. This temperature corresponds roughly to the maximum in the loss factor curve at 100,000 cycles per second.

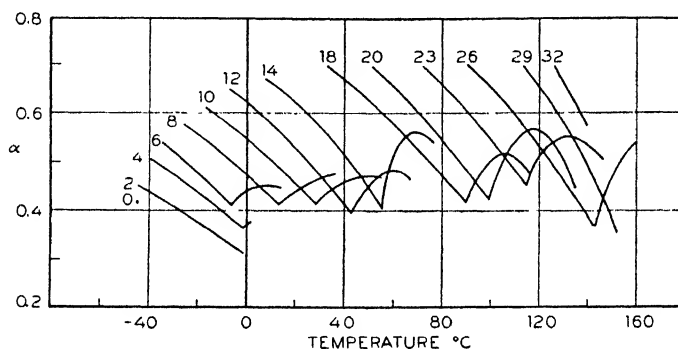


Fig. 10.—Variation with temperature of the Cole circular arc dielectric parameter α for vulcanized rubber. Figures along the curves give the combined sulfur content (32).

Using Field's calculations, the authors have plotted in Figure 11 the temperature corresponding to the maximum in the loss factor curve, as a function of sulfur content. The broken curve shows T_m from volume-temperature measurements as taken from Figure 3 on page 8. As is characteristic for such transition effects, the temperature increases the greater the speed of the test. Kauzmann (52) has also analyzed these rubber-sulfur data in terms of the activated state theory of dielectric dispersion. He shows that both the entropy and the energy of activation for the orientation process increase with sulfur content.

Tuckett has recently clarified the relationship between dielectric and mechanical measurements (115). He indicates that the maximum in the loss factor curve occurs in the temperature range over which high elasticity develops, because both processes depend on a high degree of rotation about carbon-carbon bonds. In many respects dielectric measurements suggest

the most direct interpretation of the basic mechanism of the transition. This is especially seen when the dielectric constant or loss factor of a polar polymer is plotted against temperature. Both quantities are relatively small and comparatively independent of temperature until the transition point is reached. Then both properties rise precipitously (see Fig. 1 of reference 40). Since dielectric behavior is quite well established in terms

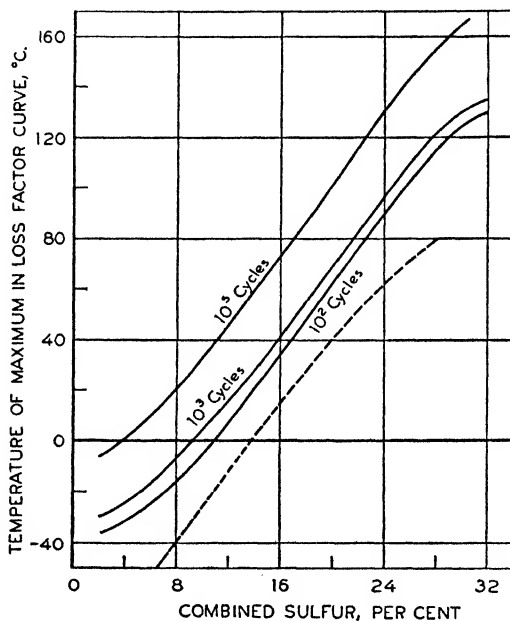


Fig. 11.—Effect of combined sulfur on the temperature of the maximum in the loss factor curve of vulcanized rubber at several frequencies. The dotted line shows T_m from thermal expansion measurements.

of Debye's treatment of dipole rotation, it would appear necessary to conclude that the transition point measures precisely the temperature at which segmental rotation becomes a prominent feature of molecular activity in a polymer.

By contrast, it is not evident from specific heat or thermal conductivity data that rotation rather than oscillation is involved. The thermal expansion anomaly is even more obscure; therefore the following section will attempt to show in some detail that it represents but one more aspect of the segmental rotation problem.

III. Factors Influencing Second-Order Transition Temperature as Determined by Thermal Expansion

1. Effect of Orientation

In order to study the nature of the thermal expansion process of polymers near the transition temperature, specimens of Saran F (a vinylidene chloride - vinyl cyanide copolymer) were oriented by stretching several hundred per cent, allowed to crystallize and then measured for linear expansion parallel and perpendicular to the direction of orientation (14). It was found, as anticipated, that above T_m the linear expansion coefficient was the same in both directions, whereas below T_m the expansion perpendicular to the orientation axis was at least three times as great as in the direction of the chain molecules. There was no marked transition point in expansion at right angles to the chains. The presence of crystallization prevented loss of orientation above T_m . Polystyrene could be studied below T_m with similar results, but, of course, loses its orientation above T_m . F. Muller has reported an anisotropic expansion of rubber with linear coefficients of 1.4 to 2.3×10^{-4} at right angles to the chains, but only 0.7×10^{-4} parallel to the chains. Details of his experiments are not available to us (82). The normal behavior of stretched rubber is a positive expansion perpendicular to the chains, a negative expansion in the direction of stretch. James and Guth have discussed the theory of this effect in detail (46).

The implications of this experiment on the anisotropic expansion of oriented Saran are that, at right angles to the chains, expansion is comparable to that in low molecular weight organic compounds and is relatively free from transition effects. Parallel to the chains, expansion can occur only by a bulk displacement of chains or chain segments parallel to each other. The increased thermal expansion above T_m depends on a new mechanism of expansion. This mechanism is presumably one of viscous flow, which accounts for the time effects that have been noted in connection with such transitions, as well as for the observation that T_m occurs when the viscosity of the polymer is around 10^{13} poises (122). Viscous flow can occur below T_m but its rate soon becomes too small to give an observable effect.

There are materials of low molecular weight showing second-order transitions in thermal expansion which cannot be ascribed to a viscous flow mechanism. Some of these transitions (*i. e.*, the normal paraffins previously discussed, ammonium chloride, etc.) are of the lambda type. Glucose gives a pseudopolymer whose elements are connected by hydrogen

bridges (45), so that viscous flow is probably important. Now Pauling (90) has shown that the force between molecules or ions decreases as rotation sets in, so that this in itself should be sufficient to account for an anomaly in thermal expansion even for unassociated low molecular weight materials. Such a factor may even contribute to a slightly enhanced sideward expansion of polymer chains above T_m .

The second-order transition temperature as connected with thermal expansion might then be defined as that temperature at which enough rotation of polymer segments occurs to permit an observable amount of viscous flow within the time scale of the apparatus used and under the thermal expansion forces acting on the specimen.

If this viscous flow hypothesis is admitted, it then becomes possible to treat second-order transition phenomena in terms of the melt viscosity behavior of polymers. One can thus interpret the time effects, as well as the effect of molecular weight, external forces, cross linking and plasticizers on the second-order transition temperature, in a quantitative manner with equations developed by Flory (34) and by Kauzmann and Eyring (53). Specifically, we employ an observation previously used by Tammann (109), Jenckel (47) and Wiley (122) that the transition temperature corresponds to an isoviscous state. If this is correct, T_m will then shift in response to external influences by an amount which should be predictable from melt viscosity. It is interesting to note that measurements of the viscosity of glucose glass through the transition region have indicated no discontinuity with respect to temperature (88). Similar results have been obtained on glass (67).

2. Time Effects*

Time effects are usually confined to the vicinity just below T_m . At 10° to 15° C. below T_m the rates of volume change are too slow to permit convenient observation, while a few degrees above T_m any rate effects are at least as rapid as thermal equilibrium and hence escape detection. Time effects have apparently not been noted in connection with thermal expansion measurements on rubber, although they have been investigated for other polymers by Jenckel (47), as well as by Alfrey, Goldfinger and Mark (3). Jenckel, for example, quickly changed the temperature of a sample of sele-

* Since this was written, equilibrium volume-temperature curves have been obtained for polystyrene (14a). Such curves exhibit no second-order transition in the temperature range from 20° to 150° C. These data demonstrate conclusively that the second-order transition, at least in polystyrene, involves a rate phenomenon and not a thermodynamic singularity.

nium glass by a few degrees near the transition temperature, and then observed its volume as a function of time. He found that volume change was proportional to the square root of the time.

This problem can be treated in terms of viscous flow by employing an equation given by Tobolsky and Eyring connecting rate of viscous flow with the force producing the flow (112). If one assumes that rate of volume

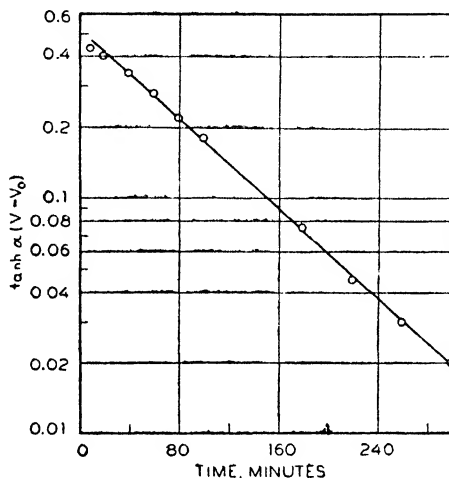


Fig. 12.—Semilogarithmic plot of Equation (2) illustrating the change in volume, V , of glassy selenium with time after being suddenly cooled from 35.23° to 30.7° C. (data from Jenckel).

change measures rate of viscous flow, and that the driving force is proportional to the difference between the instantaneous and the final equilibrium volume, then the volume V at any time t is given by:

$$\tanh[\alpha(V - V_0)] = Ce^{-Kt} \quad (2)$$

where α , C and K are constants, and V_0 is the final equilibrium volume. Figure 12 illustrates how well Jenckel's data on selenium glass follow this type of equation. Small deviations in the beginning may represent lack of thermal equilibrium.

3. Molecular Weight

Jenckel and Überreiter (51) have investigated the influence of molecular weight on T_m for polyisobutylene. They find that it increases rather

rapidly in the region of low molecular weights and then levels off, as shown in Figure 18 (page 41). Polystyrene behaves in an identical fashion. The melt viscosity equation (34, 53) predicts a polymer viscosity which is proportional to the exponential of the square root of the weight average chain length. This in turn means that T_m increases linearly with the reciprocal of the square root of the molecular weight in order to maintain an isoviscous state (114). The available data are not sufficient to test this theory except in a qualitative sense, although they will reappear in the section on plasticizers. Überreiter (119) assumes that the point of leveling off in T_m (at a molecular weight of 20,000) gives the length of the unit involved in the thermal expansion process.

4. *Vulcanization*

It was seen in Figure 3 (page 8) that combined sulfur causes a progressive increase in T_m . Tuckett (113) and Überreiter (119) have suggested that cross linking would inhibit freedom of the dipoles to rotate and that a higher temperature would therefore be needed to give an equivalent amount of rotation. According to the viscous flow concept of transitions it could be said that cross linkage would reduce the tendency of the chain molecules to move lengthwise. It can be seen in Figure 3 that T_m does not begin to increase until more than 2% of combined sulfur is reached. This may be a real effect or may represent experimental error. At any rate, it suggested the problem of what minimum amount of cross-linking agent is needed just to affect T_m . This should give some estimate of the length of the segment involved in the thermal expansion process.

Samples of styrene copolymers containing from 0 to 1.5% of divinylbenzene (a mixture of the six isomers of ethylvinyl and divinylbenzene was used) were prepared and measured for density, swelling and thermal expansion. The equilibrium swelling volume in toluene permitted a calculation of the average number of monomer units between points of cross linkage, according to the theory of Flory and Rehner (36). K_p in their equation (50) was assumed as 0.88, although the results are not sensitive to this constant for small degrees of swelling. The data are collected in Table II.

The samples containing 0.2 and 0.4% of divinylbenzene developed inhomogeneities of the type discussed by Staudinger and Husemann (107), as is evident from their low densities. Swelling and thermal expansion measurements on these samples were therefore impossible. This was somewhat unfortunate; yet a plot of T_m against per cent divinylbenzene indicates that a minimum concentration of roughly 0.4% divinylbenzene is needed to affect T_m . Since a log-log plot of the number of monomers

between cross links as a function of divinylbenzene concentration was linear, an extrapolation to 0.4% divinylbenzene indicated roughly 300 monomer units between points of cross linkage. This, then, is presumably a unit corresponding to the amount of displacement occurring in viscous flow along the chains. Jenckel and Überreiter (51) found that T_m began to level off at a molecular weight of 30,000 to 40,000 for polystyrene, and at about 20,000 for polyisobutylene. In each case this would lead to a value around 300 monomer units.

TABLE II
EFFECT OF CROSS LINKING ON THE SECOND-ORDER TRANSITION TEMPERATURE
FOR STYRENE-DIVINYLBENZENE COPOLYMERS (14a)

Divinylbenzene, %	Polymer density, g./cc.	T_m , ° C.	$\beta_1^a \times 10^4$	$\beta_2^b \times 10^4$	Swelling volume in toluene at 23° C.	Average number of monomer units between cross links
0	1.049	87	2.33	6.22
0.2	0.899	700 ^c
0.4	0.941	280 ^c
0.6	1.048	89.5	2.43	6.29	5.80	172
0.8	1.048	92	2.38	6.60	5.06	101
1.0	1.024	94.5	2.85	7.35	4.59	92
1.5	1.048	97	2.30	8.99	3.68	58

^a Cubical coefficient of expansion below T_m .

^b Cubical coefficient of expansion above T_m .

^c Extrapolated values.

Since the segment length calculated for viscous flow measurements of polymers is usually of the order of 40 carbon atoms (53), it does not seem likely that one cross-linkage point every few hundred carbon atoms would interfere with rotation of polymer segments. It would be interesting to make studies of this type using heat capacity, dielectric and other types of measurements as an indication of the minimum amount of cross-linking agent needed to raise T_m . Eley (29) has pointed out, for example, that a small amount of vulcanization in rubber does not interfere appreciably with rubberlike elasticity, but does have a pronounced effect on viscous flow. We shall examine later (pages 39 and 43) the effect of cross linking on the brittle point.

While crystallinity in a polymer prevents viscous flow above the transition temperature by virtue of its effective cross-linking action, it does not seem to influence T_m even when present to the extent of 65%, as was mentioned earlier. Crystallinity, however, represents highly concentrated and nonuniformly distributed cross links—the crystalline regions are islands in a matrix of amorphous polymer.

5. External Forces

The transition temperature of a polymer can be shifted by external loads on the specimen. Scott (96) showed that T_m for a rubber sample containing 19.5% of combined sulfur increased from 36° to 45° C. as the pressure increased from atmospheric to 800 bars. The density of the sample at the transition temperature decreased about 2% over this pressure interval.

Müller found that an external tension of 2000 g. per sq. mm. lowered T_m for polyvinyl chloride from its normal value around 77° down to 50° C., while T_m for oriented polystyrene decreased with increasing degree of orientation (81). The effect of external tension on T_m for Saran has also been noted (14). These results are at least in qualitative agreement with the idea of an acceleration of viscous flow by an applied force which supplements the forces giving rise to thermal expansion.

6. Copolymerization

Copolymerization produces a continuous but nonlinear change in T_m between the T_m values corresponding to the polymers of the individual

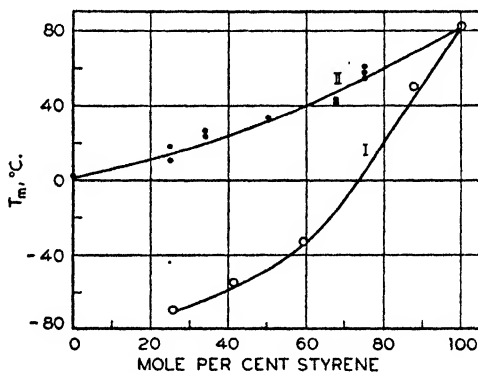


Fig. 13.—Effect of copolymerization on second-order transition temperature of styrene:
 I, styrene-butadiene
 II, styrene-methyl acrylate

monomers. Figure 13 shows the data of Überreiter (I) for the styrene-butadiene system (118) and the results of Jenckel (II) for styrene-methyl acrylate (48). The former curve suggests that polybutadiene might have a T_m of about -85° C. Thus the methyl group of polyisoprene raises T_m about 12° C. above that of polybutadiene, analogous to the case of methyl

acrylate and methyl methacrylate seen in Table I. Judging from the work of Ruhemann and Simon, a second methyl group as in methyl rubber raises T_m to at most -15°C ., although there may have been other complicating factors from vulcanization and fillers in the methyl rubber. T_m for unvulcanized methyl rubber might therefore be between -60° and -50°C .

Tuckett (113) has treated Überreiter's data on the styrene-butadiene copolymers as a case in which the bulky styrene group hinders free rotation. He assumes that free rotation is inhibited whenever two styrene groups occur side by side along the polymer chain. Tuckett calculates that the fraction of C—C bonds which are hindered is X^2 , where X is the proportion of styrene in the copolymer. The data for both sets of copolymers are in reasonably good agreement with this assumption, that is, the transition temperature increases linearly with the square of the mole fraction of styrene. It would be interesting to examine the data for a system such as styrene-vinyl chloride in which the pure polymer species have the same T_m (80°C .) but the size and the polar nature of the substituents vary so markedly. The x-ray, mechanical and moisture absorption studies by Baker and Fuller (6) on nylon copolymers reveal many interesting details about the effect of order and disorder on physical properties.

A certain insight into copolymer behavior is found in the study of the sodium salts of fatty acids (41). Sodium stearate, for example, melts at about 240°C ., but a volume-temperature curve on this material shows a distinct second-order transition at 70°C . which has been ascribed to melting and onset of free rotation in the hydrocarbon portion of the molecule. This transition also shows up in other types of measurements (111). Any copolymer in which highly polar groups alternate with hydrocarbon segments along the molecule (nylon, for example) might be expected to combine flexibility of the polymer and dimensional stability at elevated temperatures as a result of some tendency for crystallization.

7. Plasticizers

When all high polymers are arranged according to a T_m scale, it is immediately evident that the technically important rubbers fall below at least -40°C ., while the important plastics lie above $+50^\circ\text{C}$. Thus, for normal temperatures of usage, arbitrarily set at -40° to $+50^\circ\text{C}$., the rubbers will exhibit high elasticity with viscous flow inhibited by vulcanization; the plastics will exhibit maximum dimensional stability, since cold flow does not occur appreciably below T_m . The crystalline polymers (nylon, polythene, Saran) violate this generality, because a low T_m can be

coupled with a high permissible operating temperature by virtue of the cross-linking action of the crystallinity.

It is possible to pass along the T_m scale in continuous fashion from rubber to plastic by vulcanization or cross linking. Actually, though, only mild or very high degrees of vulcanization find technical acceptance, for in this way the forbidden zone from -40 to $+50^\circ$ C. is avoided. Copolymerization also provides a method of traversing the T_m scale in either direction, by combining, for example, a rubber-forming monomer like butadiene with a plastic-forming monomer like styrene or acrylonitrile. Finally, the T_m scale from plastic to rubber can be followed by plasticization, thus leading to such technically important products as Flamenol, Geon, Koroseal and the Vinylites. The influence of plasticizers on T_m and other mechanical properties of polymers has been widely discussed in the literature. Papers by Russell (95), Clash and Berg (18), Davies, Miller and Busse (24), Fuoss (76) and others (44, 60, 92a) present many pertinent facts.

A thermodynamic approach to the plasticizer problem has been given by Frith and Tuckett, who were concerned primarily with the question of compatibility (37b). For second-order transitions, the main problem is one of efficiency, that is, how far a given amount of a compatible plasticizer will lower T_m . A plasticizer may be thought of as forcing polymer chains apart and thus accomplishing the same effect as does temperature. However, a simple calculation shows that, if this were the only effect, then just a few per cent of plasticizer would lower T_m by as much as 100° . In terms of the isoviscous state, the question reduces to one of how much a plasticizer lowers the melt viscosity of a polymer.

Flory (35) has found, for concentrated solutions of polyesters in liquids of composition similar to the structural units in the polymer chain, that it is possible to use a weight average chain length taken over the polymer and the solvent (treated as monomer). This average value, which is proportional to the weight fraction, W_2 , of polymer in solution, plays the same role for the viscosity of concentrated solutions as does the weight average chain length of a pure polyester. Specifically, he finds:

$$\log \eta = A + B(W_2)^{1/2} \quad (3)$$

where η is the viscosity and A and B are constants. In order to work over a range of temperatures, this equation was modified to give (14):

$$\log \eta = A + B(W_2)^{1/2} + E/RT \quad (4)$$

where E is the activation energy for viscous flow, R is the gas constant and T is the absolute temperature. By assuming that the viscosity remains

constant at the transition temperatures of a polymer containing various amounts of plasticizer, the following expression results:

$$(W_2)^{1/2} = D - (E/B \cdot T_m) \quad (5)$$

where D is a constant. Thus there should be a linear relationship between the square root of the weight fraction of polymer and the reciprocal of the transition temperature. Actually, the energy of activation, E , is not constant as will be evident later from some calculations by Kauzmann. In a study of concentrated solutions of polystyrene in isopropylbenzene, the

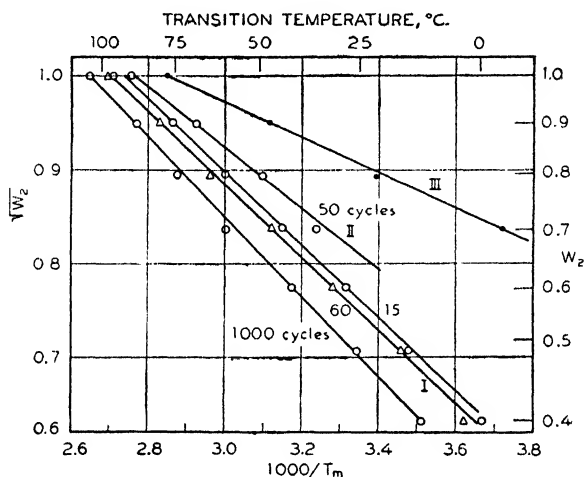


Fig. 14.—Dependence of the transition temperature, T_m , on volume fraction of polymer, W_2 , in the system polyvinyl chloride-tricresyl phosphate. The electrical data represent maxima in the loss factor *vs.* temperature curves. Curve III is derived from thermal expansion data.

authors have noted that E depends on the amount of solvent present while B is temperature dependent.

It nevertheless turns out that Equation (5) does give linear plots for polyvinyl chloride plasticized with tricresyl phosphate, in several types of tests. Figure 14 shows the maximum in the loss factor curve at 15, 60 and 1000 cycles, using the data (curve I) of Davies, Miller and Busse (24), and the peak in the 50-cycle loss factor curve (II) and T_m from volume-temperature measurements (III) as found by Wurstlin (125). The T_m curve is shifted to lower temperatures as compared with the others because it is the slowest test. The polyvinyl chloride samples used by these two groups of

workers are presumably different, as evidenced by the considerable shift of the 50-cycle data of Wurstlin relative to the 60-cycle curve. Similar plots on still other sets of data have been presented elsewhere (14). While this type of representation was suggested by melt viscosity laws, it cannot be considered evidence for the isoviscous state at the transition temperature. In addition to the difficulties mentioned about Equation (5), it is realized that tricresyl phosphate does not obey Flory's assumption of a solvent which is structurally similar to the polymer units.

The most that can be said is that a plasticizer does shift a plastic along the T_m scale in the direction of the true rubbers according to this empirical law. In a broader sense, however, a plasticizer does not convert a plastic into a true rubber characterized by rapid elongation and rapid retraction. For, while a plasticizer can separate polymer chains from each other and permit segmental action of the chains at a lower temperature, it cannot provide kinetic energy which is responsible for rapid retraction. In addition, there are likely to be some thermodynamic complications arising from plasticizer-polymer interactions, which prevent the polymer chain from behaving as a truly random coil.

Eley (29) has resolved the activation energy for the orientation process in a polymer into two parts: The first and larger part is connected with the hindering influence of neighboring chains on segmental rotation in a given chain; the second part involves rotation about carbon-carbon bonds in a single chain. Eley then suggests that viscous flow depends only on segmental action which occurs as soon as the hindrance from neighboring chains is reduced. Rubberlike elasticity depends on the ease of rotation about carbon-carbon bonds, and requires a higher temperature. The behavior of plasticizers in polyvinyl chloride, for example, appears to be in full agreement with these proposals. That is to say, the plasticizer lowers T_m by reducing the interchain barrier to rotation of segments but does not appreciably lower the barrier to rotation about individual carbon-carbon bonds. This intrachain barrier can be overcome only by temperature. Plasticized polyvinyl chloride appears to have some of the attributes of a cross-linked material, possibly by virtue of the highly branched nature of this polymer.

Kauzmann has calculated (52) the energy and entropy of activation for the orientation process involved in dielectric dispersion of plasticized polyvinyl chloride. He finds that both quantities tend to level off once a given plasticizer content is reached. The energy of activation between 0 and 60% tricresyl phosphate decreases from 116 to 49 kcal. per mole while the entropy of activation drops from 263 to 127 cal. per degree C. per mole,

at which point it appears to level off completely. This original dropping off is presumably connected with removal of hindrance to rotation from neighboring chains.

IV. The Brittle Point

The increasing use of rubberlike compositions at low temperatures has imposed severe limitations on the choice of suitable materials, and has brought into vogue many tests simulating operating conditions with varying degrees of exactness. As the temperature is lowered, the rubberlike properties are gradually lost, the material hardens and, finally, a point is reached at which the sample breaks or shatters upon the sudden application of force. The temperature at which such breakage or shattering takes place is known as the brittle point and is of great practical importance, for it represents the lower limit of the useful temperature range of the material.

It has been customary to identify this brittle temperature, T_b , with the second-order transition temperature, T_m . There are, however, several fundamental differences between T_b and T_m which may not show up in the evaluation of commercial polymers of high molecular weight, but which are very apparent for a polymer of low molecular weight. A survey of the experimental results and an analysis of the brittle point test may help to clarify these differences. It has been found, first of all, that the brittle point cannot be specified uniquely, but depends on the manner of testing used in its determination. For this reason many different brittle point tests exist, each designed to give results correlating with previous experience and practice in certain applications. This is important when evaluating and comparing data from different sources.

1. Survey of Brittle Point Tests

In 1928, Kohman and Peek (64) determined brittle points by rapid bending through a 90° angle with a hammer blow. In 1931, Kemp (54) studied a number of rubber samples, using the same method. In 1936, Nagai (84) found that the hardness of rubber samples as measured by a dead-weight penetration test varied hyperbolically with temperature. The temperature corresponding to the intersection of the asymptotes may be regarded as a sort of "hardening point," and was found to be raised by increasing sulfur content in rubber vulcanizates. Kemp, Malm and Winspear (56) have pointed out that hardness values, as such, cannot be taken as reliable indications of low-temperature serviceability, for they found

that a number of varied compositions had different hardness values at the brittle point. In 1940, Koch (63) determined the brittle points of different rubbers by measuring the resistance to bending at various temperatures. He defined two characteristic temperatures, a stiffening point, at which a marked change in modulus was encountered, and a freezing or brittle point, at which the sample broke under applied stress. In the same year, Russell (95) determined brittle points of polyvinyl chloride compositions by observing the lowest temperature at which a bar of the material could be bent double without breaking. He also defined brittle point in terms of the stress-strain curve as the highest temperature at which a sample broke under applied load without observable elongation, *i. e.*, the stress-strain curve was a single point.

In 1943, Selker, Winspear and Kemp described a simple and accurate method for determining brittle points by rapid bending of strips of the samples being tested (98). They found that, if desired, their method could be made to give results reproducible to 0.1° C. With this apparatus, they studied the brittle points of natural and synthetic rubber compositions and observed the effect of state of cure and molecular weight. Several other brittle point tests first appeared during this year, among them those of Martin (72) and of Clash and Berg (18). Martin proposed a simple apparatus for flexing rubber specimens by forcing the ends together between two parallel plates. Clash and Berg proposed a torsional test and defined a "flex" temperature as that temperature at which a standard specimen would undergo a given amount of torsional deformation during a specified time interval under the preferred test conditions. With this test they studied various high polymer-plasticizer systems.

Myers (83) observed in 1942 that the brittle point depends on the rate of application of stress. In 1943, Kemp, Malm and Winspear (56) studied rather extensively the effect on brittle point of both the rate of application of stress and the amount of deformation, and found that faster rates or larger deformations result in higher brittle temperatures. These conclusions were confirmed later in the same year by King (59) and by Morris, James and Werkenthin (79).

Liska (68), early in 1944, reported on the effect of low temperatures on Young's modulus and presented a bibliography of papers dealing with the effect of low temperatures on various mechanical properties of rubbers. He also made brittle point measurements on tread stocks of GR-S and natural rubber and found that, for the relatively low amount of sulfur present (3%), the brittle point was essentially independent of the curing time.

Tables III and IV show typical brittle point data for natural and synthetic compositions, respectively, from several different authors. As mentioned before, brittle points from different sources are not always comparable, as different testing method will, in general, have been used. It may be noted, however, that most of the synthetic rubbers exhibit brittle points higher than those of the corresponding natural rubber compositions. The only exceptions to this seem to be butadiene polymer and Buna S (butadiene-styrene copolymer). Exact details regarding the composition of the various materials reported may be found in the original papers. We have not attempted to compare numerical values of the brittle point and transition temperature for the same material because of the many factors which influence both T_m and T_b . In general, if the brittle point test involves a slow deformation, T_b will agree with T_m within a few degrees. If the brittle point requires a rapid deformation, T_b will be higher than T_m , the difference depending mainly on the speed of the test and on the molecular weight of the polymer.

TABLE III
BRITTLE POINTS OF NATURAL RUBBER COMPOSITIONS

Material	T_b , ° C.	Ref. No.
Raw rubber:		
Pale crêpe	-58	(64)
Smoked sheet	-57	
Pure rubber hydrocarbon	-55	
Pahang gutta-percha	-28	
Vulcanized rubber	-53	
Balata	-44	
Gutta-percha (cable insulation)	-23 to -36	(63)
Paragutta	-45 to -61	
Balata (washed)	-44 to -52	
Balata (washed and deresinated)	-62 to -67	
Crude rubber	-57 to -58	
Soft vulcanized rubber	-53 to -58	
White gutta, first-grade Tjipetis	-53.5	(98)
Whole-latex rubber, ammonia-preserved, air-dried	-61.5	
Smoked sheet rubber	-60.7 to -61.5	
Brazilian fine para, unmilled	-58.5	
Smoked sheet, milled 6-30 min.	-61.5	
Plantation-softened smoked sheet	-60.5	
Pale crêpe rubber	-62.5	
Pale crêpe heated at 202° C. (mol. wt. 6000)	-48	
Gum stock	-59.5	
Tube reclaim	-52.5	
Tire carcass reclaim	-50.5	
Tire tread reclaim	-49.8	
Shoe stock reclaim	-44.5	
Gum rubber (light load)	-50	(59)

TABLE IV
BRITTLE POINTS OF SYNTHETIC RUBBERS AND POLYMERS

Material	<i>T_b</i> , ° C.	Ref. No.
<i>(a) Rubbers</i>		
Polychloroprene gum stock	-38.5	(98)
Butadiene polymer:		
Gum stock	-65.5	
Tread stock	-71 to -69	
Butadiene-styrene copolymer:		
Gum stock	-65.5	
Tread stock	-66 to -70	
Butadiene-acrylonitrile copolymer:		
Gum stock	-42 to -45	
Tread stock	-46.5	
Thiokol A	+ 7.0	
Thiokol F	-35.3	
Thiokol FA	-35.5	
Thiokol FA	-40	(59)
Thiokol RD	- 7	
Buna S	-58	
Butaprene NM	-35	
Butaprene NXM	-19	
Butyl B-1.5	-45	
Hycar OR-15	-19	
Hycar OS-10	-21	
Hycar OS-20	-58	
Neoprene GN	-40	
Neoprene ILS	-19	
Norepol P-345-D	-12	
Butadiene-37% styrene copolymer	-27	(55)
Butadiene-44% styrene copolymer	-10	
Mechanical mixtures of GR-S (25% styrene) with OS-10 (50% styrene):		
25% styrene	-47	
30% styrene	-40	
35% styrene	-33	
40% styrene	-23	
45% styrene	-14	
50% styrene	- 5	
<i>(b) Polymers</i>		
Polyisobutylene (mol. wt. 1500)	-23	(98)
Polyisobutylene (mol. wt. 10,000, 100,000, 200,000)	-50.2	
Polyethylene (low mol. wt.)	-15	
Polyethylene (high mol. wt.)	-68.5	
Polyvinyl chloride	+81	(95)
Polyvinyl chloride-40% tricresyl phosphate	-17.5	
Polyvinyl chloride-40% dibutyl phthalate	-46	
Polyvinyl chloride-40% dibenzyl sebacate	-41.5	
Polystyrene	80	
Plasticized polyvinyl chloride acetate	-50	(59)
Plasticized polyvinyl butyrate	-20	
Plasticized ethylcellulose	-30	
Methyl acrylate	0 to 8	(33)
Ethyl acrylate	-20	
<i>n</i> -Butyl acrylate	-40	
minimum in brittle point around C ₈		
Myristyl acrylate (softens at)	20 to 25	
Cetyl acrylate (softens at)	35	
Octadecyl acrylate (softens at)	40 to 45	

2. Theory of the Brittle Point Tests

In briefly reviewing the various brittle point tests which have been used, it may be noted that most of them require that a sample undergo a fixed deformation in a given length of time. As compared with a thermal expansion measurement, this deformation is large and the time is short. If the specimen can meet this condition, it passes the test and the temperature is then lowered for further testing; if not, it breaks and fails, indicating that the temperature is below the brittle point. Three mechanisms are available to supply this deformation: an ordinary, almost instantaneous, elastic deformation having a comparatively high modulus; highly elastic deformation resulting from the uncoiling of polymer chains; and viscous flow, which is the slowest of the three processes. These three contribute to an observed deformation in varying amounts, depending on the time and temperature. The ordinary elastic deformation is usually a very small part of the total and will be neglected in the following discussion. Tuckett (114) has shown the contributions of the other two mechanisms in the following equation:

$$D = At \exp(-E_{\text{visc}}/RT) + D_{he}(\infty)[1 - \exp(-t/\tau)] \quad (6)$$

where D is the total deformation, A is a constant, t is the time, E_{visc} is the energy of activation for viscous flow, R is the gas constant, T is the absolute temperature, $D_{he}(\infty)$ is the limiting highly elastic deformation at infinite time, and τ is the relaxation time for high or rubberlike elasticity.

According to this picture, the deformation-time curve of a material at constant temperature would be somewhat as follows: first, there would be a small instantaneous deformation due to ordinary elasticity, followed by highly elastic deformation which falls off in rate until finally only viscous flow is operating and the curve becomes a straight line. The effect of increasing temperature is to tilt the whole curve toward higher deformation. As we have already noted, the brittle point test requires a fixed deformation in a specified time interval and thus we arrive at the following definition: *the brittle temperature is that temperature at which the time interval required by the sample to undergo the necessary deformation is just equal to the time interval of the test method.* (Of course, we are confining ourselves to hypothetical deformation-time-temperature curves which arise from the stress-time relationship specified by the test.) At higher temperatures, the time is more than sufficient and the sample deforms without breaking; at lower temperatures, the sample cannot deform fast enough and it breaks. It has already been mentioned (page 32) that the rate of application of load and the total deformation influence the brittle point; and this

now follows directly from a consideration of the above definition and the deformation-time-temperature curves. Any increase in rate of deformation necessitates a higher temperature if the sample is just to pass the test.

It will be realized that the deformation required by a brittle point test is not necessarily completely defined by the apparatus, but may also depend on the sample thickness. Kohman and Peek (64) found, in 1928, that

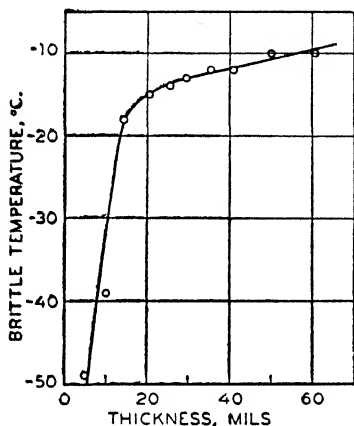


Fig. 15.—Variation of brittle temperature of plasticized Saran* with sample thickness. Spacing on brittle point apparatus was twice the sample thickness. The sharp break in the curve corresponds to the second-order transition temperature.

the brittle temperatures are all lower than the second-order transition of this plasticized copolymer, which we estimate to be around -15° C. Since highly elastic deformation does not occur below T_m , it would seem that the deformation of the thinnest samples arises purely from ordinary elasticity. Increasing thickness of the sample requires more deformation, and the brittle temperature increases (modulus of elasticity decreases) until finally, at around -15° C., high elasticity begins to contribute to the deformation and brittle temperature becomes much less dependent on sample thickness.

* This sample of Saran contains 63.5% by weight of vinyl chloride and 36.5% of vinylidene chloride. The sample then had 10% of a plasticizer added to it prior to making the brittle point measurements.

the brittle temperature of a 70-mil thick sample of gutta-percha was 5° to 10° C. higher than that of a 50-mil thick sample, a result they interpreted as due to the increased strain intensity involved in bending the thicker sample through the same angle. In a recent study on the brittle points of Saran copolymers, the authors observed this same effect, as shown in Figure 15, where it will be seen that increasing sample thickness raises the brittle point. The brittle points were determined by the method of Selker, Winspear and Kemp and the test was run in such a manner as to require almost a right-angle bend for all of the samples. In the interpretation of Kohman and Peek, this would mean increased deformation with increased sample thickness, and hence a higher brittle temperature.

It is interesting to note here that, for sample thicknesses less than 15 mils,

EFFECT OF MOLECULAR WEIGHT ON T_b

The first term in Tuckett's equation, in the form given above (Eq. 6), represents the viscous contribution to total deformation and considers only its dependence on temperature. Three other factors are of great importance in determining the viscosity, namely, the molecular weight of the polymer, the degree of branching or cross linking of the polymer chains, and the amount of plasticizer present. These same variables also affect the second term of Equation (6), although in a different manner, as will be seen from the following discussion.

Mark and Kuhn (71) have shown that, for unit stress:

$$D_{he}(\infty) = M/7RT\sigma \quad (7)$$

where M is the molecular weight, T is the absolute temperature, and σ is the

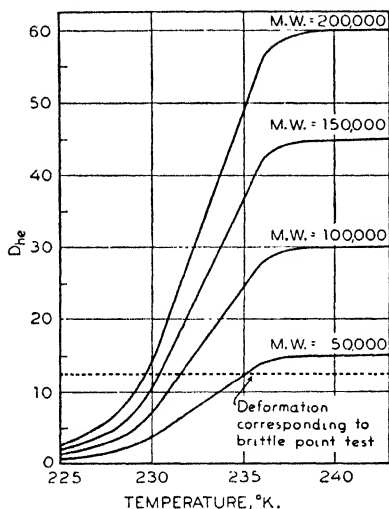


Fig. 16.—Highly elastic deformation in arbitrary units for unit stress after one second as a function of temperature and molecular weight.

density. It is apparent from Equation (7) that, in general, higher molecular weights will permit more highly elastic deformation at any given temperature and, since deformation increases with temperature due to the dependence of τ on temperature, the brittle point (fixed deformation) will be lowered. This may be seen more clearly by referring to Figure 16, in which deformation-temperature-molecular weight curves are shown for unit stress and a time of one second. The relaxation times were calculated from Eley's (29) energy of

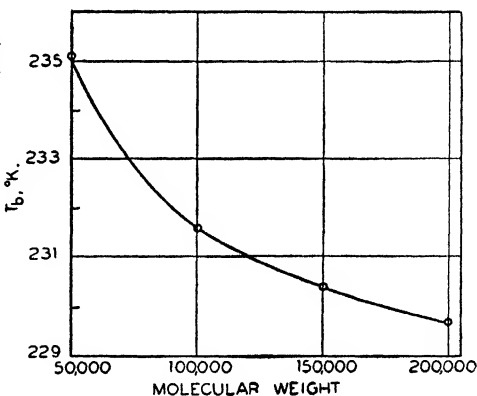


Fig. 17.—Dependence of brittle point temperature on molecular weight when the deformation required by the brittle point test is that shown by the broken line of Figure 16.

activation, which he computed from the data of Alexandrov and Lazurkin (2) on lightly vulcanized rubber. Assuming that the brittle point is now defined as the temperature for a fixed deformation, as indicated by the dotted line, we arrive at the brittle point–molecular weight curve, as shown in Figure 17, which confirms our previous conclusion that increasing molecular weight will lower the brittle temperature. It also suggests that the brittle temperature will tend to level out at higher molecular weights and become essentially constant. The relaxation time, τ , was assumed to be independent of molecular weight. Equation (7), based on the early theories of kinetic rubber elasticity, is not an accurate representation of conditions in an actual rubber sample. Newer theories, such as that of James and Guth (46), predict essentially the same type of variation shown in Figures 16 and 17. These newer expressions do not contain the molecular weight of the polymer since they are concerned with infinite networks. The average molecular weight between network points may be considered in place of M in Equation (7).

Considering Figure 16 again for a moment, we see that, if the molecular weight falls much below 50,000 for our hypothetical case, the entire deformation–temperature curve will lie below the dotted line. This means that high elasticity cannot supply the entire required deformation and the difference must be made up by viscous flow if the sample is not to break. Viscous flow is, in general, a much slower process than rubberlike elasticity because it involves bodily movement of chain segments through the polymer matrix in contrast to mere straightening out of kinks and convolutions in the chains. Therefore, a higher temperature will be necessary to enable this mechanism to produce the requisite deformation in the time interval allowed. With decreasing molecular weight, more and more of the deformation will be viscous and hence the brittle temperature, as previously defined, will be higher.

The dependence of melt viscosity on molecular weight has been given by Flory (34) and introduces a coefficient, $\exp(AM^{1/2})$, into the expression for viscosity, where A is a constant and M is the weight average chain length. By introducing this into equation (6) and making approximations appropriate to the magnitudes of the quantities involved, we obtain the result that the reciprocal of the brittle temperature (degrees absolute) is a linear function of the square root of the molecular weight:

$$1/T_b = AM^{1/2} + B \quad (8)$$

Although this will not apply over the entire range of molecular weights,

it should be at least approximately obeyed over a considerable portion of the lower molecular weight region.

EFFECT OF VULCANIZATION AND PLASTICIZER

Eley (29) points out that a small amount of cross linking will not affect the highly elastic behavior appreciably, but does tend to suppress viscous flow. A larger amount of cross linking increases the energy necessary to free a segment from its neighbors and thereby reduces high elasticity. This is manifested by the necessity of going to a higher temperature to achieve a given amount of deformation in a given interval of time. Tuckett (113) has further emphasized this point of view. Thus, increasing vulcanization or degree of cross linking should not affect the brittle point much at first, but on reaching higher values should raise it and continue to do so as more and more cross-linking agent is introduced.

It is well known that the addition of a plasticizer will lower the brittle point of a high polymer by an amount depending both on the concentration and nature of the plasticizer. The action of the plasticizer consists largely of forcing the chain molecules apart and thereby reducing the interchain potential barrier to rotation. This facilitates the uncoiling of chains in highly elastic deformation and also aids segment motion in viscous flow. The first effect is manifested in a lowering of the relaxation time, at constant temperature, with increasing plasticizer, as reported by Alexandrov and Lazurkin (2) in the case of polymethacrylate, and in a lowering of the energy of activation of high elasticity, as was pointed out by Eley (29). The second effect is merely the lowering of melt viscosity with increasing plasticizer, which is well known, and which was put on a quantitative basis by Flory (35), as seen in Equation (3).

Correcting the viscosity term in Equation (6) to account for the effect of plasticizer, and making suitable approximations, we find that the reciprocal of the brittle temperature should vary linearly with the square root of the weight fraction, W_2 , of polymer:

$$1/T_b = P(W_2)^{1/2} + Q \quad (9)$$

where P and Q are constants. The same objections which were cited against Equation (5) also apply here, namely, a dependence of the activation energy on plasticizer content, and variation of some of the "constants" with temperature. Preliminary studies indicate that a more preferable form of this equation would be as a linear relation between $1/T_b$ and $1/(W_2)^{1/2}$.

EFFECT OF FILLERS

Another factor of importance in determining the deformation, of interest chiefly in connection with rubber compositions, is the amount of filler or reinforcing agent added. It is well known that fillers harden rubber, *i. e.*, increase its modulus; a semiquantitative measure of this effect is the limiting law developed by Smallwood (104):

$$M^* = M(1 + 2.5\Phi) \quad (10)$$

where M^* is the modulus of the reinforced rubber composition, M is the modulus of the rubber matrix, and Φ is the fractional volume loading. If we consider only high elasticity and assume the modulus for this mechanism (limiting modulus for large time intervals) is given by (10) above, then:

$$D_{he}^* = D_{he}(\infty)[1 - \exp(-t/\tau)]/(1 + 2.5\Phi) \quad (11)$$

where $D_{he}(\infty)$ is the full highly elastic deformation for the original rubber matrix, and D_{he}^* is the deformation of the reinforced composition at time t . If we now consider one of the curves of Figure 16, which are plots of $D_{he} = D_{he}(\infty) [1 - \exp(-t/\tau)]$ for $t = 1$, we see that:

$$D_{he}^* = D_{he}/(1 + 2.5\Phi) \quad (12)$$

Our brittle point test requires that D_{he}^* be a constant, for example, the deformation represented by the broken line; and this provides us with a way of calculating the brittle point–filler content curve. The brittle temperature of the original rubber ($\Phi = 0$) is the temperature corresponding to the point of intersection of the broken line and the deformation curve; at every higher temperature there is a corresponding composition having this temperature as its brittle point and which is defined by having $D_{he}/(1 + 2.5\Phi)$ always equal the deformation defined by the broken line. If we construct the T_b – Φ curve in this manner, we find that it is essentially linear over the same range of linearity of the deformation–temperature curve, and that it breaks away at each end, unless the broken line crosses the deformation–temperature curve in its linear portion. This is only a very approximate relationship, of course, being limited by Smallwood's assumption that Φ is small, and the authors' assumption that the deformation is entirely due to high elasticity. It should serve, however, to indicate a rise in brittle temperature with filler content.

3. Some Experimental Results Illustrating the Theory of the Brittle Point Test

The data reported in the literature which illustrate the effects discussed in the previous section may be examined briefly. For those cases in which

information is not available on rubber compositions, data on other high polymers will be used to illustrate the point being made. It is believed that the general nature of the phenomena discussed will hold for all high-polymeric materials.

The first point to be considered is the brittle point test itself, for which we note that the amount of deformation and the time allowed for this deformation must be held constant if comparable results are to be obtained. Kemp, Malm and Winspear (56) studied the effect of these variables by observing brittle temperature as a function of the angle of bend and the rate of bend. Their data on a Buna S composition, typical of all of their observations, are shown in Table V, from which it is seen that increasing the deformation or shortening the time interval raises the brittle temperature. Brittle point determinations by King (59), using a one-second bend, an instantaneous bend, and a shatter test, lead to the same conclusions.

EFFECT OF MOLECULAR WEIGHT

The effect of molecular weight on brittle point was observed in 1942 by Selker, Winspear and Kemp (98). Figure 18 shows their data on polyiso-

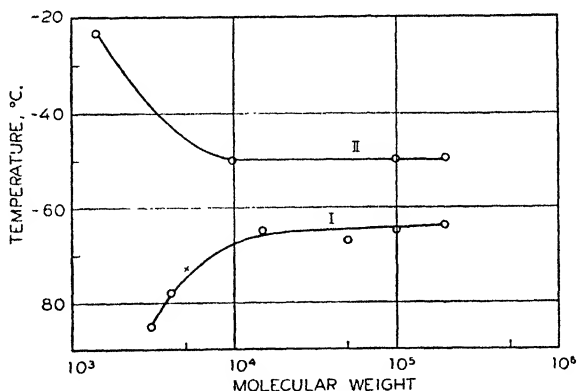


Fig. 18.—Effect of molecular weight on transition point (curve I) and brittle point (II) of polyisobutylene. The datum of Ferry and Parks (31) is represented by \times .

butylene, from Table IV, and, for comparison, the data of Jenckel and Überreiter (51) on the second-order transition temperatures of polyisobutylene. It may be seen that the behavior of T_b and T_m is quite different, the two curves being almost mirror images of each other. The same gen-

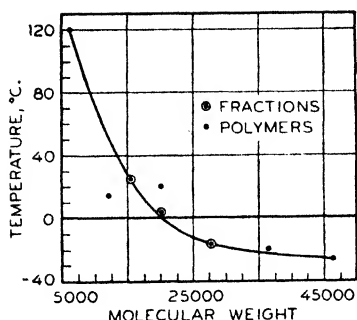


Fig. 19.—Variation with molecular weight of brittle point temperature of polyvinylidene chloride plus 9% plasticizer.

eral type of brittle point behavior was found in rubber by Selker, Winspear and Kemp, when they observed that milling smoked sheet to maximum breakdown (about 30,000 molecular weight) did not alter the brittle point appreciably. However, when they heated it in tetralin at 202° C. for 11 hours, the molecular weight came down to 6000 and the brittle point was raised by 14.5° C. Similarly, high molecular weight polyethylene was found to have a brittle point of -68.5° C., while low molecular weight polyethylene exhibited a brittle point of -15° C.

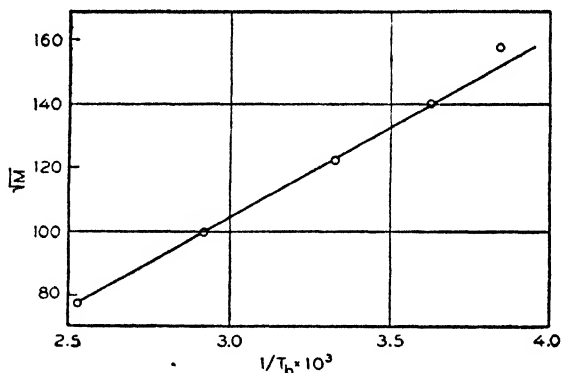


Fig. 20.—Variation with molecular weight of brittle point temperature of polyvinylidene chloride plus 9% plasticizer (data taken from smooth curve of Figure 19).

TABLE V

EFFECT OF RATE AND AMOUNT OF DEFORMATION ON BRITTLE POINT OF A BUNA S COMPOSITION (56)

Rate of deformation	Radius of bend, cm.	T_b , ° C.
150 r.p.m.	Right angle	-51.5
	2.54	-54.5
	3.81	-59.5
75 r.p.m.	Right angle	-54.5
	2.54	-58.5
	3.81	-63.5

The authors have observed the same type of curve in the case of polyvinylidene chloride, as shown in Figure 19. The brittle points were determined by the method of Selker, Winspear and Kemp on samples 10 mils thick and containing 9% of a plasticizer. The molecular weight values are open to question, both on an absolute basis and relative to each other; they were based on the viscosity of 2% solutions of the polymer in *o*-dichlorobenzene at 140° C. and a Staudinger constant of 2.5×10^{-4} . Figure 20 shows the curve from the preceding figure plotted in the manner suggested in the last section, *i. e.*, the reciprocal brittle temperature *vs.* the square root of the molecular weight, and it is seen that a straight line results. The points for Figure 20 were taken from the smooth curve of Figure 19.

EFFECT OF VULCANIZATION

The effect of cross linking on brittle point has been studied largely through the vulcanization of rubber with sulfur. Alexandrov and Lazurkin

TABLE VI
BRITTLE POINTS OF SULFUR-RUBBER COMPOSITIONS (98)

Compound	Cure temp., ° C.	Cure time, min.	T_b , ° C.	Parts per 100 combined sulfur
Rubber-sulfur stock (100 smoked sheet, 10 S)	148	60	-56.5	...
		120	-50.5	...
		180	-44.0	...
		240	-39.5	...
100 smoked sheet +1 sulfur +2 sulfur +3 sulfur +4 sulfur +5 sulfur +6 sulfur	148	720	-58.1	1.00
		720	-55.9	2.00
		720	-52.9	3.00
		720	-51.2	4.00
		720	-48.9	5.00
		720	-46.1	6.00
		720	-58.6	0.00
Gum stock (6 parts S)	142	0	-58.6	0.00
		5	-58.6	0.07
		10	-58.6	0.33
		20	-58.0	1.05
		40	-55.7	2.46
		60	-54.9	3.24
		90	-53.5	3.86
		120	-52.6	4.27
		180	-51.2	5.01
		240	-49.6	5.52
	360	-50.0	5.58	
	720	-48.6	5.97	

(2) found, in 1940, that partly vulcanized ebonite had a very much larger relaxation time than had a lightly vulcanized natural rubber; and Eley

(29) has observed that in this case the energy of activation for high elasticity is almost half again as large for the ebonite as for the natural rubber. He associates this with an increase in the energy required to free a segment from its neighboring chains rather than with any hindrance of the internal rotation of the segment. Selker, Winspear and Kemp observed that cross linking of rubber with sulfur raised the brittle temperature and that the T_b -sulfur curve was linear after the first per cent or so. Their observations are shown in Table VI. Two methods were used: In the first, various amounts of sulfur were added and the mixtures cured under constant conditions long enough for essentially all of the sulfur to combine. In the second method, a constant amount of sulfur was added, the mixture cured for different lengths of time, and the amount of combined sulfur then determined. The results were somewhat the same, the first method leading to slightly higher brittle points. It was found by Selker, Winspear and Kemp and also by Liska (68) that the time of cure of mixtures containing relatively small amounts of sulfur, say up to two or three per cent, had little effect on the brittle point.

EFFECT OF PLASTICIZERS

Plasticizers used in lowering the brittle point have been evaluated in two ways: first, as to the relative efficacy of various plasticizers in lowering the brittle point; and, second, as to the brittle point-concentration relationship for any given plasticizer. Among those who have worked in the first field are Russell (95), who observed the effect of tricresyl phosphate, dibutyl phthalate, dibenzyl sebacate and acetylated castor oil on polyvinyl chloride, and King (59), who reported the brittle points of Neoprene FR compounds containing the same amounts of butyl cellosolve acetate, diisobutyl adipate, dibutyl phthalate, dibutyl sebacate, diamyl phthalate, dicapryl phthalate, plasticizer SC, dispersing oil No. 10, tributoxy ethyl phosphate and TP-10 plasticizer. In the second group are Clash and Berg (18), who studied mixtures of a vinyl copolymer resin with tricresyl phosphate, di-2-ethyl hexyl phthalate, triethylene glycol di-2-ethyl hexoate and binary and ternary mixtures of these plasticizers.

It was stated on page 39 that the reciprocal brittle temperature should vary linearly with the square root of the weight fraction of polymer in the mixture. In order to have more extensive data available for the purpose of checking this relationship, the authors prepared samples of polyvinyl chloride plasticized with varying amounts of tricresyl phosphate and determined brittle temperatures on 30-mil thick samples by the method of Selker, Winspear and Kemp. The square root of the weight fraction of polymer

was then plotted against the reciprocal of the brittle temperature, as shown in Figure 21. A fair straight line resulted over the concentration range studied, *i. e.*, 15 to 60% by weight of plasticizer. This curve has a slope opposite in sign to that of the plot of square root of molecular weight *vs.* reciprocal brittle temperature seen in Figure 20. It also happens that a plot of T_b against plasticizer content, as well as a plot of $1/T_b$ against $1/(W_2)^{1/2}$, is linear. More study is evidently needed to resolve the meaning of these results.

EFFECT OF FILLERS

Because data reported in the literature on the effect of reinforcing agents and fillers on brittle point of rubber are very meager, only the most general conclusions can be drawn from them. Selker, Winspear and Kemp (98) found that channel black and zinc oxide raised the brittle point slightly, while calcium carbonate had much more of an effect, as is shown in Table VII. There are not sufficient data available to test the relationship suggested in the preceding section. Also shown in this table are the observations of King (59) on the Shore hardness and brittle point values of several synthetic elastomer compositions loaded with varying amounts of a semi-reinforcing carbon black; it is seen that, as the hardness goes up with increasing filler content, the brittle temperature does also.

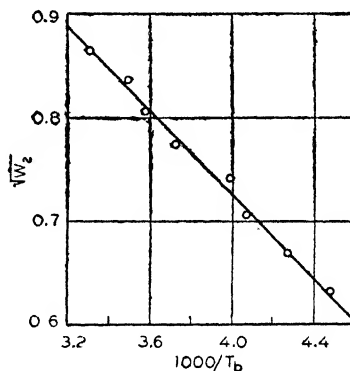


Fig. 21.—Effect of tricresyl phosphate on the brittle point temperature of polyvinyl chloride.

TABLE VII
EFFECT OF LOADING ON BRITTLE TEMPERATURE

Material	Hardness, Shore A	Filler content, parts	T_b , ° C.
(a) Selker, Winspear and Kemp (98)			
Gum stock plus channel black	..	20	-57.5
	..	40	-56.5
Gum stock plus zinc oxide	..	100	-60
	..	200	-59.5
	..	300	-58.5
Gum stock plus calcium carbonate	..	0	-53.2
		27.6	-48.5
		55.2	-41.5 to -43.5

(Table continued on p. 46)

TABLE VII (continued)
EFFECT OF LOADING ON BRITTLE TEMPERATURE

Material	Hardness, Shore A	Filler content, parts	T_b , ° C.
(b) King (59)			
Neoprene FR plus carbon black	40	-62.2
	50	-61.1
	62	-61.1
	70	-60.6
	85	-59.4
Hycar OR-15 plus carbon black	40	-38.9
	50	-34.4
	60	-31.7
	70	-30.0
Neoprene GN plus carbon black	40	-45.6
	50	-44.4
	60	-42.8
	70	-41.1
	80	-37.8

4. Young's Modulus of Unstretched Rubber

There has been a growing tendency during the last several years to rely on Young's modulus measurements of unstretched rubber samples as an indication of low-temperature brittleness (63, 68). It is found, for example, on cooling a specimen of rubber that its modulus begins to increase

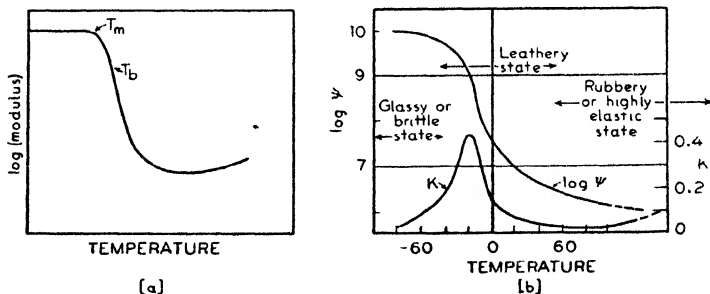


Fig. 22.—(a) Variation of Young's modulus with temperature and the relation of T_m and T_b to modulus (69). (b) Change in firmness, ψ , and time constant, K , with temperature (12).

exponentially at a temperature considerably higher than the brittle temperature, and hence even higher than the second-order transition temperature. Figure 22a, taken from Loughborough, Greene and Harris (69), shows schematically the relationship between T_m , T_b and the modulus—

temperature curve for rubber. Clash and Berg (19) have pointed out a similar situation regarding stiffness (apparent modulus of elasticity) and their flex brittle temperature, T_f , for vinylites.

It is thus seen that, on cooling, the abrupt increase in Young's modulus is a precursor of the impending brittle temperature, which in turn anticipates the still lower second-order transition. Since these modulus measurements involve a small, slow deformation, such behavior is curious in view of our previous explanations of T_b and T_m . Baker and Smyth (7) have noted, on cooling isobutyl or isoamyl bromide, that a mechanical stiffening sets in some 40° above the actual freezing point of this material. This stiffening is explained on the basis that short-range forces are probably beginning to operate and to interfere slightly with the mobility of the molecules as the temperature is lowered and the molecules come closer together. However, rotation does not cease until the freezing point, or, in the case of polymers, T_m , is reached. The authors believe that this suggestion is also a logical one to apply to rubber and other polymers.

Bilmes (12) has recently assessed the rheological properties of plasticized polyvinyl chloride by means of empirical flow equations developed by Nutting and Scott-Blair. His results are summarized in Figure 22b, where $\log \psi$ and K are shown as functions of temperature. ψ is the firmness and measures the resistance of the material to deformation, while K , the coefficient of dissipation, measures the extent to which the time factor influences the deformation, as can be seen in the following equation:

$$\psi = S\sigma^{-1}t^K \quad (13)$$

where S is the shearing stress, σ the strain and t the time. It is evident from Figure 22b that time effects are most important when the $\log \psi$ curve has the steepest slope. There is, moreover, a correlation between the brittle

TABLE VIII
CORRELATION BETWEEN BRITTLE POINT, FIRMNESS AND COEFFICIENT OF DISSIPATION FOR PLASTICIZED POLYVINYL CHLORIDE (12)

Mixture	Brittle point, T_b , °C.	$\log \psi$ at T_b	K at T_b
A	-20	9.71	0.33
B	-10	9.78	0.24
C	-3	9.73	0.27
D	+6	9.62	0.30

point, ψ , and K , as indicated in Table VIII for four different mixtures of polyvinyl chloride. Conant and Liska (22) have measured on rubber compounds some low-temperature creep rates whose behavior with temperature

is similar to the K values found by Bilmes. Their creep constant corresponded very closely to the temperature at which the modulus of elasticity was 10^4 p.s.i.

One other type of correlation might be mentioned. Davies, Miller and Busse made plots of the logarithm of Young's modulus against reciprocal absolute temperature for polyvinyl chloride samples containing various amounts of tricresyl phosphate (Fig. 11 of reference 24). Typical sigmoid curves such as shown in Figure 22a were obtained. They then indicated the contour lines corresponding to the peaks in the loss factor-temperature curves at 15, 60 and 1000 cycles. The 1000-cycle contour corresponded to the bottom knee of the curve, while the 60- and 15-cycle contours fell on the steep part of the curve, *i. e.*, they approached the brittle point indicated on Figure 22a.

It is thus evident from these few examples that the temperature behavior of the Young's modulus, or related quantities, is an important aspect of second-order transition phenomena in polymers. This one type of measurement appears to encompass all of the information on transition temperatures now obtained from thermal expansion, brittle points and electrical tests. It still remains to be seen whether these generalizations, which seem valid for rubbers and rubberlike materials, will apply to all high polymers.

V. SUMMARY

The general features of second-order transition effects in rubbers and other high polymers have been reviewed. It is believed that all of the facts are at least in qualitative agreement with the concept of the onset of a critical amount of rotation about carbon-carbon bonds at the transition temperature. The heat capacity anomaly suggests that there is a distribution in sizes of the segmental units which engage in this rotation. The increase in thermal expansion at the transition is attributed to the occurrence of viscous flow. The brittle point, by contrast, is shown to involve rubberlike elasticity. Various linear relationships connecting transition and brittle temperatures with molecular weight, plasticizer content, etc. have been pointed out. In the absence of more extensive data and a more comprehensive theory, these may be accepted simply as empirical correlations, although the form of the plots was suggested by the theory of melt viscosity and elastic deformation in polymers.

It has been seen that the second-order transition is revealed by a diverse series of tests which in many instances do not appear to have a point in common, that is, thermal expansion, heat capacity, thermal conductivity,

dielectric loss factor, brittle point and Young's modulus. X-ray diffraction and melt viscosity are the only known physical properties which fail to reflect these second-order transitions in polymers. While rotation of segments would seem to link most of these tests together, exact statistical mechanical calculation would have to be made on the actual data to decide

TABLE IX

COMPARISON OF SOME COMMON TESTS FOR SECOND-ORDER TRANSITIONS IN POLYMERS

Test	Linear deformation required	Speed of test ^a	Phenomena responsible for transition
Heat capacity Thermal expansion	Negligible Negligible	Slow (0.01) Slow (0.01)	Rotation of segments Viscous flow made possible by rotation of segments
Young's modulus	Medium	Slow (0.1-1.0)	Effect of short range forces which vary with intermolecular distance and with amount of rotation present?
Brittle point	Large	Rapid (10^2)	Uncoiling of polymer chains in highly elastic deformation
Dielectric loss	Nil	Very rapid (10^2-10^6)	Rotation of dipoles and groups of dipoles
Refractive index (molecular refraction)	Nil	Very rapid (10^{14})	Change in mobility of electrons with intermolecular force fields and intramolecular statistics?

^a Figures in parentheses are approximate frequencies in cycles per second.

these questions in detail. Such theoretical calculations as have been carried out on materials of low molecular weight (17, 61, 103) predict qualitatively the existence of a second-order transition but fail to account for its sharpness. Temperley has suggested (110) that this failure is a result of ignoring long-range order. He believes that the magnitude of the specific heat anomaly at a second-order transition might be a measure of the amount of long-range order involved. In view of the difficulties with simple molecules, a rigorous treatment of polymers might be quite complex.

While these various physical tests probably have the common feature of requiring segment rotation, they differ at least in the demands they make on this rotation, that is, on how fast it must occur, and on the segment length involved in the process. Table IX attempts to summarize some of the characteristic features of the more common tests. Figure 23 depicts some additional aspects of the problem by plotting T_m from volume-temperature curves and T_b from rapid brittle point measurements as a function of

molecular weight. Such a plot might be called a second-order phase diagram for high polymers. In the region below T_m , the polymer is a brittle solid in which the chain segments can oscillate about equilibrium positions at right angles to their length. In the space between T_m and T_b , the polymer behaves internally as a liquid characterized by a sluggish rotation of chain segments. The polymer appears to be tough for a slow deformation, but is brittle when subjected to a rapid deformation. Above T_b , the polymer is an internally tough liquid capable of developing rubberlike elasticity

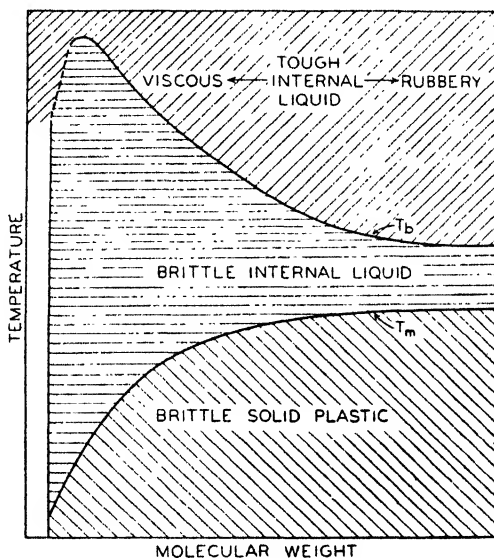


Fig. 23.—Proposed second-order phase diagram for high polymers. The molecular weight scale is logarithmic.

by virtue of a relatively large degree of rotation about individual carbon-carbon bonds. Rubberlike elasticity is confined mainly to the right-hand part of the diagram above T_b , the left-hand side giving way essentially to viscous liquids as species of very low molecular weight are reached.

In the region below T_m , time effects are negligible, the specimen responding instantly to an applied load which produces a relatively small deformation. At T_m , time effects become important for measurements involving slight displacements, such as the thermal lags in heat capacity measurements mentioned earlier, or the slow change in volume shown in Figure 12 or the drift in dielectric properties reported by Fuoss (40). At T_b , the time

factor is quite important for large deformations, thus accounting for the effect of speed and displacement noted on brittle point tests. Somewhere above the T_b line, time again becomes a negligible variable (in the absence of viscous flow), with large, highly elastic deformations resulting almost instantly from an applied load. Below T_m , Young's modulus is high and relatively independent of temperature; above T_b , it is low and again relatively invariant with temperature. Finally, dielectric constant and loss factor are small and insensitive to temperature below T_m (if the dipoles are attached directly to the main carbon chain), but rise abruptly at T_m and reach a maximum somewhere above T_b (depending on the frequency). Thus the area between T_m and T_b is one in which a polymer shows the greatest variation of properties with temperature.

It is recognized that the T_m and T_b lines are not unique since they depend on heating rate, type of brittle point test and many other variables. It would perhaps be appropriate to use bands instead of lines. Moreover, numerous exceptions to the above generalizations might be anticipated for specific polymer and copolymer systems, especially where crystallinity is involved. At least this plot illustrates the type and extent of data needed to characterize the second-order transition behavior of high polymers; and it suggests the contributions from the different molecular weight species to the ultimate physical properties of a heterogeneous polymer.

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CRYSTALLIZATION PHENOMENA IN NATURAL AND SYNTHETIC RUBBERS

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	PAGE
I. Introduction.....	58
II. Methods of Study.....	59
1. Specific Volume.....	59
2. Thermal Measurements.....	60
3. X-Ray Diffraction.....	60
4. Optical Double Refraction.....	61
5. Light Transmission.....	61
6. Mechanical Properties.....	62
Modulus.....	62
Hardness.....	62
Flow and Creep.....	63
III. General Characteristics of Crystallization.....	63
1. Rate of Crystallization.....	63
2. Melting of Crystals.....	66
3. Change of Melting Range with Temperature of Crystallization.....	68
4. Recrystallization.....	71
5. Effects of Crystallization on Mechanical Properties.....	71
6. Fraction of Material in the Crystalline State.....	73
7. Effects of Vulcanization on Crystallization.....	75
8. Size of Crystallites.....	77
IV. Materials Studied.....	78
1. Natural Rubber.....	78
2. Balata and Gutta-percha.....	78
3. Chloroprene Polymers (Neoprene).....	79
4. Organic Polysulfide Polymers (Thiokol).....	80
5. Isobutene Polymers and Copolymers (Vistanex and Butyl Rubber).....	80
6. Polyethylene (Polythene).....	81
7. Vinylidene Chloride Polymers and Copolymers (Saran).....	81
8. Butadiene Polymers and Copolymers.....	82
9. Noncrystallizable Polymers.....	82
10. Other Materials.....	83
V. Interpretation of Experimental Results.....	83
1. Kinetics of Crystallization.....	83

V. Interpretation of Experimental Results, <i>contd.</i>	
2. Range of Melting	85
3. Change of Melting Range with Temperature of Crystallization	87
4. Nature of Crystals	87
Bibliography	88

I. Introduction

Natural rubber, synthetic rubbers, and similar materials are commonly classed as amorphous substances and regarded as distinctly different from those classed as crystalline. It has become increasingly apparent in recent years, however, that under proper conditions some of these mate-

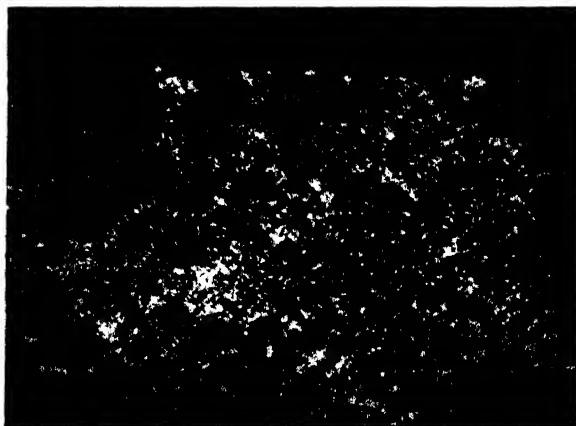


Fig. 1.—Photomicrograph of a thin section of crystalline rubber between crossed Nicol prisms.

rials show the phenomena associated with crystallization and fusion of crystals, while in others such phenomena are completely absent. The purpose of the present chapter is to describe the methods by which crystallization is studied, the general characteristics of the crystallization of high polymers and quantitative details associated with specific materials.

The crystallization may occur in the unstretched material under favorable conditions of temperature and pressure or it may occur during stretching. In the present discussion crystallization during stretching will be regarded as a special case, and stretching will not be implied unless spe-

cifically mentioned. Likewise little emphasis will be placed on the crystallization of rubber from solution (25, 28, 123, 126).

A photomicrograph showing crystals in a thin section of unstretched natural rubber at 0° C. is shown in Figure 1. It was taken between crossed Nicol prisms by Dr. C. P. Saylor of the National Bureau of Standards (125). Further reference to this figure is made on page 61.

The present discussion will include some results of several investigations at the National Bureau of Standards which, because of the pressure of war work, have remained unpublished up to the present.

II. Methods of Study

The change of phase from the amorphous to the polycrystalline state is accompanied by changes in a number of properties any of which may be used to study the conditions under which crystallization occurs. The properties most clearly associated with regularity of atomic arrangement are x-ray diffraction and optical double refraction. Changes in specific volume and enthalpy (heat content) are somewhat better adapted to quantitative measurements of the amount of crystallization. Measurements of mechanical properties such as modulus, hardness or flow are the most closely related to the practical application of the materials.

1. Specific Volume

One of the simplest and most convenient tools for the study of crystallization is furnished by the measurement of specific volume. Often the equivalent properties, density and specific gravity, have been measured. In fact, the earliest data on crystallization appear to be the density measurements of Bunschoten (22) in 1921 and of van Rossem a few years later. Crystallization was suggested by Pickles (108) in 1924 as the probable cause of the density changes observed by Bunschoten and van Rossem. Density measurements have also been made in more recent studies of crystallization (8, 122, 135, 140).

The application of the dilatometer with a confining liquid by Bekkedahl (10) in 1934 was a marked advance in the methods of study of crystallization, since it facilitated the study of time effects and made possible continuous observations (13-15, 29, 72). Holt and McPherson (71) devised an arrangement for direct, continuous measurements of volume changes during stretching (75).

In some instances the measurement of linear dimensional changes is found to be convenient. An interferometer (146), for example, has been applied to a study of the melting of crystalline rubber.

2. *Thermal Measurements*

The thermal effects associated with crystallization were the object of early investigations by Hock (68-70) and van Rossem and Lotichius (115), who measured the heat of fusion as the difference in the heats of swelling of crystalline and amorphous rubber. Bekkedahl and Matheson (11) made extensive direct calorimetric studies of the thermal effects exhibited by the natural rubber hydrocarbon. Similar studies have been published on Hycar OR-15 (12) and on GR-S (112) in which no crystallization effects were noted. Ruhemann and Simon (117) recognized that the "gamma-anomaly" observed in their calorimetric studies was caused by crystallization. More recently their "beta-anomaly" also has been shown to have a similar origin (144). Thermal measurements are also the basis of a recent study of the crystallization of polyethylene (111).

A considerable rise in temperature is found to accompany crystallization by stretching (33, 34). Likewise the heat evolved can be measured calorimetrically (55, 68, 70).

3. *X-Ray Diffraction*

X-ray diffraction, first applied by Katz (77, 78, 80, 82) to the study of crystallization in natural rubber, furnishes much detailed information regarding the arrangement of the atoms in the crystalline state. This type of information serves to supplement the information obtained by other techniques since they are largely concerned with macroscopic phenomena.

A Debye-Scherrer ring pattern is obtained from rubber crystallized without stretching. Such a pattern is of course indicative of the random orientation of the crystalline material (62-64, 80, 127).

The pattern usually obtained from rubber crystallized by stretching is a spot pattern typical of fibers and indicative of alignment with one axis along the direction of stress and the other two in random orientation. By special conditions of stretching, it is possible to bring about in addition an orientation of the two axes normal to the direction of stress and thus to produce "higher orientation." It is usually accomplished (51) by stretching short wide sheets, so that the per cent contraction in thickness greatly exceeds the per cent contraction in width. Some of the spots obtained from rubber in higher orientation are strongly accentuated while others almost disappear. Thus it is possible to identify the planes producing each spot with greater ease. Schallamach (119) has shown how to produce additional orientation in a different fashion.

It should be remembered that the location of the spots is determined by the spacing of the planes in the unit cell of the crystallite, that their

intensity is determined by the number of crystallites and that their sharpness is related to the size of the crystallite.

The application of x-ray methods to natural rubber is treated in an excellent summary by Gehman (50), and the application to a number of synthetic rubbers is treated in articles by Fuller (45) and Mark (92). The reader is referred to these three summaries for more detailed information regarding x-ray studies of crystallization.

4. Optical Double Refraction

The optical double refraction exhibited by crystalline rubber is evident in Figure 1. Since the photograph was taken with the sample between crossed Nicol prisms the light spots are crystalline and the dark portions are amorphous. Similar photographs and a description of the technique involved have already been published by Smith and Saylor (125) who have shown that the crystals are usually small and oriented at random. The crystals are not isotropic and double refraction occurs in each crystal (123, 126). Because of the random orientation it is usually very difficult to make quantitative measurements of the double refraction. However, if the rubber is crystallized from solution (123, 126) or from very thin films formed by evaporation of a rubber solution, it is sometimes possible to obtain needlelike single crystals which may be observed under the microscope and in this manner to measure the two refractive indices of the individual uniaxial crystals.

The double refraction observed in stretched rubber is made somewhat more difficult to interpret because of the superposition of stress-optical double refraction upon the double refraction associated with crystallinity (143). For example, the stress-optical effects observed by Thibodeau and McPherson (130) were for the most part obtained in the absence of crystallization, but the "optical creep" they observed at the higher elongations may be ascribed to continued crystallization. Along the lines indicated by earlier work (49, 85, 102, 150), double refraction has been used to investigate the conditions of formation of crystals in stretched rubber. Thiessen and coworkers (84, 133, 142) conducted parallel studies with double refraction and x-rays, and Treloar (135) conducted parallel studies with double refraction and volume measurements.

5. Light Transmission

The light transmission of amorphous rubber may be relatively large (143). The presence of small crystals, however, gives rise to a white or milky appearance, and the light transmission is much less in the crystalline

rubber, because of the scattering of light by the crystals. Van Rossem and Lotichius (115) found that the transmission of a sheet of crystallized rubber, amounting to less than 1%, increased to about 9% when the crystals were melted. Polyethylene becomes relatively transparent as its crystals are melted (72).

6. *Mechanical Properties*

MODULUS

Crystalline regions in rubber appear to act like particles of a reinforcing filler in stiffening the rubber. Consequently, a study of stress may furnish information about the extent of crystallization. The information is not as readily interpreted as that furnished by some of the other methods since stress is affected by many different factors.

The control of temperature is particularly important because the crystals may be easily melted by the heat generated by stretching or other deformations.

The equipment recently developed in the Firestone laboratories (31, 86) for measurement of Young's modulus of a strip by flexure seems well suited for studies of crystallization of rubbers in the unstretched state.

The effects of crystallization on stress at different elongations are quite evident in a recent study of a pure gum vulcanizate of natural rubber (147).

Messenger and Scott (93) obtained somewhat inconclusive results in an investigation of the effects of a previous crystallization of unvulcanized rubber on its tensile properties.

HARDNESS

The hardness, as evaluated by indentation measurements, is related to the modulus at low elongations. Consequently crystallization may be recognized by an increase in hardness. Van Rossem and Lotichius (115) found the Shore hardness to decrease from about 85 to approximately 30 as the crystals in first latex sheet were melted. Bekkedahl and Wood (14) report an increase of Shore hardness from around 40 to 80 or more during the crystallization of vulcanized rubber. The method has also been used by Yezley and Fraser (149) and by Forman (42) in studies of the crystallization of Neoprene.

The increase of hardness upon crystallization was first noted many years ago. It was the basis for the process of making "cut sheet" (German *Patentgummi*) formerly used in Europe. The sheets were made from unvulcanized rubber which had been crystallized in order to make it suffi-

ciently rigid so that it could be cut into sheets as thin as a few tenths of a millimeter (59).

FLOW AND CREEP

The rate and extent of the plastic flow and creep observed in stretched rubber are considerably affected by crystallization. Treloar (134), Field (40) and Wildschut (141) have utilized such studies to formulate conclusions regarding crystallization and to explain observations of Hintenberger and Neumann (67) and Hauk and Neumann (61).

III. General Characteristics of Crystallization

Most of the phenomena associated with the crystallization of one type of rubber are also observed in the crystallization of other types. This section will be devoted to the general characteristics of crystallization, and the quantitative differences which exist between different types will be discussed later. Most of these characteristics were studied in investigations on natural rubber, which has of course been the subject of more extensive research than any synthetic rubber. Many of the results discussed in this section are taken from an investigation at the National Bureau of Standards by Bekkedahl and the author on the crystallization of unvulcanized natural rubber at different temperatures. Crystallization and fusion were measured by the change of volume of specimens in mercury-filled dilatometers.

1. Rate of Crystallization

The rate of crystallization of a polymer at constant temperature is usually found to be small at first, to increase to a maximum value and to decrease again toward the end of the crystallization. Thus, for example, volume-temperature relations like those given in Figure 2 are obtained with natural rubber.

The time required for one-half the total volume change is much more precisely determinable than the time needed for the volume change to become essentially complete. The reciprocal of the time required for half the volume change is a measure of the average rate of crystallization during the first half of the process. This quantity is plotted as a function of temperature in Figure 3.

It can be seen that crystallization occurs only over a certain range of temperature and is most rapid at a certain temperature in this range. For unstretched natural rubber the range extends from about -50° to

about $+15^{\circ}\text{C.}$, and the maximum rate is observed at about -25°C. At this temperature half the crystallization of unvulcanized rubber occurs in a few hours.

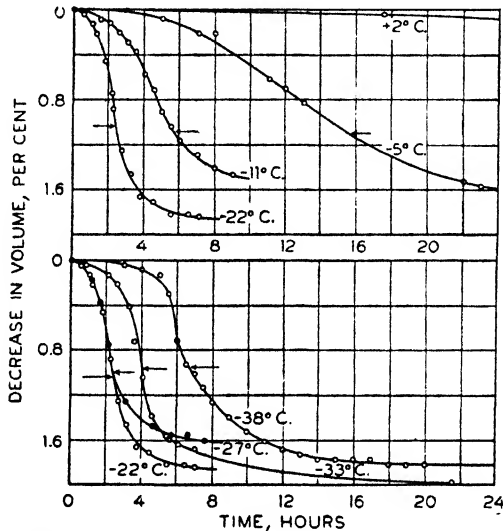


Fig. 2.—Volume-time relations during the crystallization of rubber.

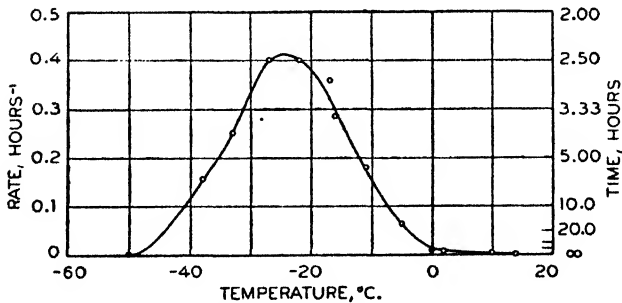


Fig. 3.—The rate of crystallization of rubber as a function of temperature. The ordinate is the reciprocal of the time required for one-half the total volume change.

The absence of crystallization at temperatures below -50°C. is a clear-cut case of the supercooling of an amorphous material to a temperature below which the mobility is insufficient for the formation of crystals. No crystallization was observed in a specimen (10) cooled to -259°C. or

in another (110) held at -190° C. for 8 days. Other specimens (10) were kept between -50° and -78° C. for 3 weeks without the occurrence of crystallization but did crystallize at -35° C. and above. The lower limit of temperature of crystallization in natural rubber is lower than that reported for any other polymer. It is not considered likely that any other rubbers will be found with appreciably lower limits.

The rate of crystallization is affected by external pressure (24). At pressures of 10–30 bars Thiessen and Kirsch (131, 132) found that crystallization of natural rubber just above 0° C. was more rapid than at atmospheric pressure. Others (145) have reported appreciable crystallization in 15 hours at 30° C. under a pressure of 1100 bars. However, at a pressure of 7840 bars Dow (37) could find no evidence of crystallization after 2 weeks at 0° C. Thus it appears that at a given temperature there is an optimum pressure for most rapid crystallization, and that as the pressure is increased beyond this value the decrease in mobility of the chain segments with pressure becomes sufficient to cause a decreased rate of crystallization and to prevent crystallization entirely at the highest pressures studied.

It has been reported (104) that the continued incidence of a beam of x-rays can bring about crystallization of natural rubber at room temperatures.

There are undoubtedly a number of other factors which can influence the absolute magnitude of the rate of crystallization at a given temperature. Katz (79), Gehman (50) and Cotton (32) all state that masticated natural rubber crystallizes more readily than unmasticated. Further study on the general problem of the effects of previous thermal and mechanical history on the rate of crystallization would be very desirable.

The rate of formation of crystals when rubber is stretched has been studied by Davey and coworkers (87), Holt and McPherson (71), Kirsch (84), Thiessen and Wittstadt (133, 142), Field (40) and Treloar (135). X-ray measurements, birefringence and volume changes showed that at moderate elongations much of the crystallization occurs in less than one second after stretching, but if the sample is allowed to remain stretched crystallization continues over a period of days or weeks.

In stress-temperature studies of a pure gum vulcanizate of natural rubber, Wood and Roth (147) found no crystallization effects at elongations below 150% at 25° C. At elongations greater than 500% the crystallization which occurred during stretching and immediately thereafter was so nearly complete that no further crystallization was observed during the entire period of later observation, even when the temperature was

lowered to 0° C. or below. At elongations intermediate between 150% and 500% at 25° C. the crystallization which occurred during stretching was found to be partial, and additional crystallization continued for many hours. At higher temperatures, higher elongations were required for crystallization. At an elongation of 400% at 70° C. there was no crystallization continuing after stretching and presumably no crystallization during stretching. At 40° C. and below there was continued crystallization at this elongation.

Both the sol (126) and gel (123) portions of rubber can be crystallized in both the stretched and the unstretched states (25, 28, 125).

2. Melting of Crystals

When a crystallized polymer is heated it is found that the crystals do not melt at a single temperature, but that melting occurs over a range of temperatures. A family of melting curves for rubber crystallized at different temperatures is shown in Figure 4.

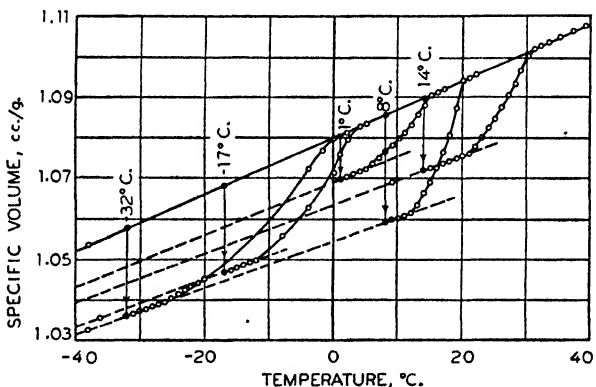


Fig. 4.—The melting of rubber crystallized at different temperatures.

The melting range is not a function of the degree of crystallization since partially crystallized rubber melts over the same range as does rubber in which crystallization is more nearly complete. In three different dilatometer experiments crystallization at 2° C. was interrupted when the volume decrease amounted to 0.085%, 1.0% and 2.7%, respectively. In all three cases the melting range was from 6° to 16° C. within the precision of the determination.

Field (40) has made extensive x-ray studies which yield valuable infor-

mation regarding the formation and melting of crystals in stretched natural rubber. At a given elongation the amount of crystallinity was found to decrease linearly with increasing temperature. At an elongation of 400% about two-thirds of the crystals were melted when the temperature was raised to 90° C. At higher elongations the fraction was smaller. On cooling without retraction the crystals formed again and the amount of crystallinity in vulcanized samples was found to be the same as before the heating. Kirsch (84), on the basis of similar studies of double refraction in specimens held at constant stress, concluded that a temperature of 140° C. was required to melt the crystals formed at the highest stresses.

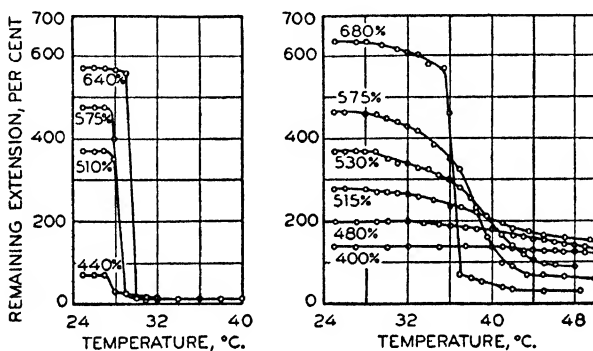


Fig. 5.—Recovery with rising temperature after stretching for one hour to elongations indicated (134).

Studies of recovery after stretching offer additional information about the melting of crystals formed by stretching. Treloar (134), in studying unvulcanized natural rubber, found that after stretching at 25° C. for 1 hour, the recovery following release of the tension was relatively large for elongations up to about 450%. At higher elongations the recovery was relatively small even after 20 hours. It could be made relatively complete by raising the temperature to 29° to 30° C. as shown in Figure 5 (graphs on the left).

Treloar also conducted a similar experiment in which the stretching was carried out for 1 hour at 50° C. and the temperature lowered to 25° C. before the tension was released. The results obtained when the temperature was again raised are shown in the graphs on the right of Figure 5. For the highest extension the range of recovery is seen to be as narrow as in the preceding experiment, but at lower initial elongations the range broadens until it disappears.

Somewhat similar investigations have been made by Feuchter and Hauser (39) whose results have been summarized by Whitby (140). The procedure is very similar to that employed in the T-50 test (54) used as a means of determining the state of vulcanization of natural rubber.

Meyer (94) stretched vulcanized gutta-percha almost to its ultimate elongation at room temperature and studied the melting of the crystals thus formed. He accomplished this by reducing the load and observing the temperature at which retraction occurred for different values of the final load. Melting occurred over a range of about 2° C. and began at 34° C. when the final load was zero. The beginning of melting was as high as 57° C. for the largest final load employed.

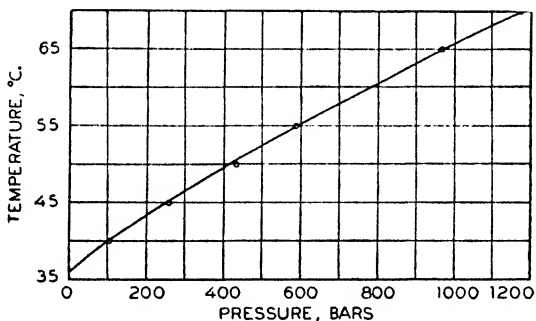


Fig. 6.—Relation between the temperature of melting and the applied pressure for a sample of stark rubber (145).

The melting range of crystalline polymers is altered by a change of pressure. Wood, Bekkedahl and Gibson (145) have found that the crystals in a sample of stark rubber which melted near 36° C. under a pressure of one atmosphere melted near 70° C. under a pressure of 1170 atmospheres and that the relation between the melting temperature, as determined by the disappearance of birefringence, and pressure was that shown in Figure 6. The results can be represented satisfactorily by the equation:

$$\log_{10} (p + 1300) = 5.9428 - 875/T$$

where the pressure, p , is in bars and the temperature, T , in degrees Kelvin.

3. Change of Melting Range with Temperature of Crystallization

It is apparent from Figure 4 (page 66) that the range of melting is a function of the temperature at which crystallization occurred (13). The

nature of the relation is brought out in Figure 7. The lower points represent the beginning of melting, the upper points the ending of melting. The straight line shows the temperature of crystallization as ordinate for easier comparison with the melting range.

It can be seen that the higher the temperature of crystallization the higher are the temperatures at which both the beginning and ending of the melting occur. The beginning of melting occurs at a temperature about 5° C. above that at which the crystals have been formed. The interval may be somewhat larger than 5° if the crystallization temperature is above

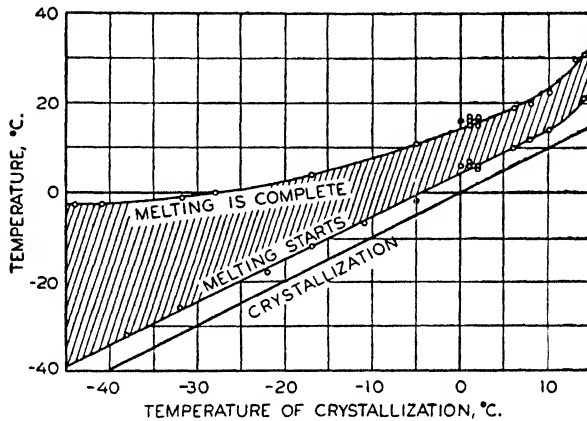


Fig. 7.—Melting range of crystalline rubber as a function of the temperature of crystallization.

10° C. If crystallization occurs between -45° C. and -25° C., the melting ceases just below 0° C. and the temperature at which melting is essentially complete shows only a small dependence on the temperature of crystallization. Thus the range of melting is almost 40° at the lowest temperatures. At the highest temperatures studied the range of melting is about 10° .

Since the line representing the temperature of crystallization does not touch or intersect the shaded area, there is no temperature within the limits studied at which crystalline and amorphous rubber are in equilibrium at atmospheric pressure (13).

It can be seen from the figure that crystals formed at a given temperature melt at a higher temperature and that new crystals of a still higher melting range may then be formed at the temperature at which the first crystals melted. Direct experimental observations of this effect were

made at 0° C. by plunging dilatometers containing rubber crystallized at -30° C. or below into an ice bath. The crystals melted completely within the time required for thermal equilibrium, and shortly thereafter it was evident that new crystals were being formed at the same temperature at which the first crystals had melted.

The presence of crystals melting over a certain range does not interfere with the formation and melting of other crystals possessing a different melting range. The results of an experiment demonstrating this are shown in Figure 8, which represents dilatometer observations on a sample of

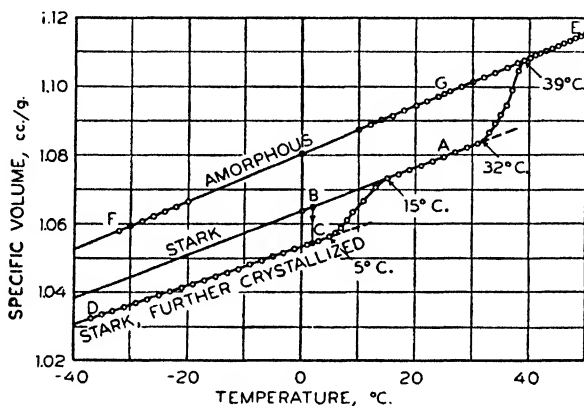


Fig. 8.—Further crystallization and subsequent melting of a sample of stark rubber.

stark rubber, possessing a melting range from 32° to 39° C. The sample was cooled from A to B, where it was crystallized further by holding it at a fixed temperature of 2° C. After a cooling to D and a return to C, the crystals formed at 2° C. were observed to melt between 5° and 15° C. and the specific volume at room temperature was found to be the same as at the beginning of the experiment. Further heating melted the stark rubber crystals between 32° and 39° C. The curve for amorphous rubber EFG was then observed.

This experiment demonstrated the possibility of the coexistence of crystals of several types in a given sample. The different types seem to compete for crystallizable material, since the total volume change has never been observed to be greater than that obtainable in a single crystallization. Rubber containing crystals with a melting range extending above 25° C. was given (108, 140, 146) the name "stark rubber" because it is stiff

and rather rigid at room temperature. The use of such a term is not intended to imply any essential fundamental difference between stark rubber and that melting at lower temperatures. It is to be presumed on the basis of Figure 7 that during the formation of the crystals in stark rubber conditions were such that the rubber was crystallized at temperatures higher than about 10° C.

The change in melting range occasioned by forming crystals in stretched rubber at different temperatures has already been mentioned in the section dealing with the melting of crystals. The retraction experiments of Feuchter and Hauser (39) and Treloar (134) demonstrate the effect. In developing the T-50 test, Gibbons, Gerke and Tingey (54) report that the temperature at which stretching is carried out, if above 20° C., affects the temperature at which the retraction occurs.

4. *Recrystallization*

After a melting of crystals, if the rubber is heated considerably above the upper limit of the melting range a second crystallization at any temperature takes place at approximately the same rate as original crystallization at that temperature. If, on the other hand, the rubber is heated only a few degrees above the upper limit of the melting range, recrystallization occurs in a considerably shorter time and the volume-time relation is not a sigmoid curve like those in Figure 2 (page 64). Instead, the rate of crystallization is greatest at the beginning and continues to decrease. There seems to be no doubt that such behavior is occasioned by the persistence of crystal nuclei, whatever their nature, above the temperature at which the actual melting is complete. The results also make it very probable that the low rate of crystallization normally observed at the beginning arises from the absence of such nuclei.

The melting of recrystallized rubber does not seem to differ in any respect from the melting of rubber crystallized for the first time.

5. *Effects of Crystallization on Mechanical Properties*

Crystallization is accompanied by an increase in stiffness. An increase of at least tenfold in Young's modulus during crystallization is shown in results obtained by Conant and Liska (31) on unvulcanized natural rubber and by Liska (86) on Neoprene GN.

It has been noted on page 62 that the hardness, as evaluated by indentation measurements, is closely related to the modulus at low elongations. During crystallization the value of the Shore hardness is usually observed to rise from the order of 30 or 40 to 80, or above (14, 42,

115, 149). It should be pointed out that crystalline rubbers are not necessarily brittle, however. Brittleness is related to effects accompanying a transition of the second order. Such transitions are discussed in the first chapter of this book.

The progressive crystallization of stretched rubber held at constant length is accompanied by a decreased tension in the rubber (96, 147). In fact, in unvulcanized rubber Smith and Saylor (124, 125) have found that crystallization can continue to such an extent that the stress not only decreases to zero but even becomes negative. If the distance between the ends of the specimen is held fixed the specimen becomes bowed at the center. This effect, named "secondary elongation" by Smith and Saylor, reaches a maximum of about 4% of the stretched length in the region of 200 to 300% elongation (105, 106). This decreased tension of the stretched rubber is, of course, in no way inconsistent with the increased modulus, just discussed, which is effective when the length is changed.

The plastic flow observed in stretched unvulcanized rubber is decreased very considerably by the presence of crystals. As the elongation is increased, the increased flow one would expect to find associated with the greater stress is counterbalanced by the greater rigidity associated with the crystallization so that a maximum amount of flow is observed at an intermediate elongation. In unvulcanized natural rubber at 25° C., Treloar (134) has found that the maximum permanent set occurs at about 300% elongation; at 50° C. it is at about 450% elongation.

The relaxation and creep effects observed in vulcanized rubber are usually not followed by a significant amount of "permanent set" upon removal of the load. Kirsch (84) has shown from measurements of double refraction and permanent set that true flow in vulcanized rubber begins only at temperatures of 80° C. or more. However, he found that creep curves are materially altered by crystallization. Plotting the percentage increase in length of a specimen under constant load for 50 hours as a function of the stress he found a double-peaked maximum which he explained in terms of the formation of crystals. The crystals stiffen the rubber and decrease even the deformation which is recoverable after removal of the load. Hauk and Neumann (61) conducted similar experiments with several different vulcanizates, while Hintenberger and Neumann (67) studied raw rubber. The latter investigators found also that the probability of rupture had a maximum value in the region of stresses where crystallization was just becoming apparent. Field (40), in a creep study of two vulcanizates, one of which contained carbon black, showed that the maximum creep occurs at the elongation at which crystallinity first becomes appreciable.

The most recent studies are those of Wildschut (141), who defines the term "flow" as merely the increase in length at constant tension with increasing time, regardless of any relation to permanent set. Wildschut defines rate of flow as the slope of the straight line representing elongation as a function of the logarithm of the time. At a fixed temperature the rate of flow was found to go through a maximum as the load was increased. The magnitude of the maximum and the stress at which it occurred are shown in the Table I, made up from Wildschut's graphs. The elongation corresponding to 66 kg. per sq. cm. at 20° C. is stated to be about 300%.

TABLE I
MAXIMUM FLOW AND TENSION AT MAXIMUM FLOW ACCORDING TO WILDSCHUT (141)

Temperature, °C.	Maximum flow	Tension at maximum flow, kg./sq. cm.
7	0.224	54
15	0.209	65
20	0.189	66
25	0.145	84
30	0.108	110
40	0.123	127
50	0.152	146
60	0.192	164

Wildschut postulates that the observed flow is made up of a "normal flow," increasing with temperature, upon which is superposed a "pseudo flow" arising from the delayed crystallization occurring following stretching.

Fielding (41) has made a study of the number of cycles of elongation and retraction required for failure when a vulcanizate is given a periodic deformation between two different elongations. He observed that when the number of cycles of elongation and retraction required for failure is plotted against the lower elongation, a maximum is observed at an elongation of about 200 or 300% for those rubbers which crystallize on stretching, while the curve decreases continuously for rubbers which do not crystallize. Natural rubber, Butyl rubber and Neoprene were studied as examples of the first class, while GR-S and Buna N exemplified the second.

6. *Fraction of Material in the Crystalline State*

Only a few of the methods of studying crystallization give results which can be used in a direct determination of the relative amounts of crystalline and amorphous material in a given sample. What is required is an absolute method, whereas most of the techniques already discussed yield only relative values. An absolute method has been developed by Field (40),

who measures the ratio of intensity of an x-ray spot arising from the crystals to that of the halo arising from the amorphous rubber.

In a study of unvulcanized rubber and a number of different vulcanized rubber compounds stretched at room temperature, Field concludes that under the most favorable conditions about 80% of the material is in the crystalline state, in agreement with an earlier study along the same lines by Meyer and Mark (97). More recently, Gehman and Field (53) have investigated samples in which the value was about 90% at the highest elongations.

Similar studies on material crystallized merely by cooling and on material both stretched and cooled might well be undertaken. Such studies have not been made because of the unfortunate proximity of some of the Debye-Scherrer rings to the halo, so that measurements of the intensity of the halo are unreliable (103).

The change of volume on crystallization may be used for comparing relative amounts of crystallization under different conditions but, in the absence of a satisfactory value for the density of the crystals (50, 122), it does not furnish any absolute scale for a determination of what fraction of the atoms are bound in the crystal lattice. Such a scale has already been developed (15) for Saran B (vinylidene chloride-vinyl chloride copolymer). Treloar (137) estimates that, for rubber at the fullest extension at 0° C., the volume change is of the order of 4% and at least 90% of the material is crystalline.

In most cases, the decrease of volume on crystallization without stretching is found to lie between 2.0 and 2.7% as measured with a dilatometer. Values for this quantity calculated from measurements of density or specific gravity reported by previous workers (8, 10, 14, 22, 38, 69, 83, 108, 115, 118, 122, 140) generally lie within the same limits, although a few are somewhat lower. On stretching a specimen of vulcanized rubber to an elongation of 700% at 25° C., Holt and McPherson (71) found a volume change of about 1.85%. Treloar (135), by stretching unvulcanized rubber at 0° C., observed a volume decrease of over 3%, the highest value recorded.

In an earlier paper, Parks (107), on the basis of the magnitude of the second-order transition, had estimated that in the work of Bekkedahl and Matheson (11) on unstretched rubber only 20 to 29% of the material was in the crystalline state. However, estimates based on visual inspection of doubly refracting regions (see Fig. 1, page 58) in material crystallized under similar conditions would lead to values more nearly like those given by Field (40).

Polyethylene at 25° C. has been estimated to be 55% crystalline from volume measurements (72) or 75% crystalline from thermal measurements (111).

7. *Effects of Vulcanization on Crystallization*

Vulcanization decreases very markedly the rate of crystallization of unstretched rubber (14), but apparently does not alter very much the nature of the crystals. Figure 9 represents observations of the change in volume of rubber-sulfur compounds with time at 2° C. Similar curves were obtained when tetramethylthiuram disulfide was used as the vulcanizing agent.

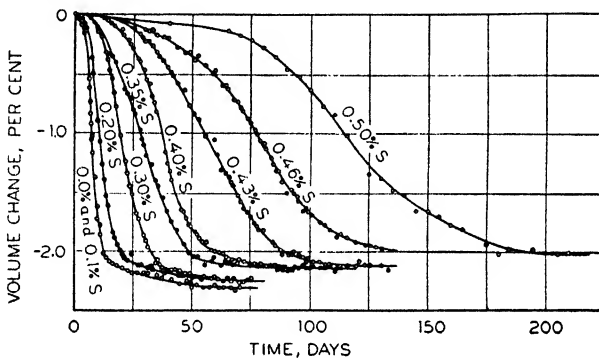


Fig. 9.—Change in volume of rubber-sulfur compounds during crystallization at 2° C. (14).

The melting of crystals formed in this investigation is illustrated by the curves in Figure 10. It is evident that vulcanization does not alter the melting range.

In most practical compounds the rate of crystallization has been so decreased by the decrease in mobility of the chains that crystallization of the unstretched material never occurs. However, under the more drastic displacements arising from stretching, crystals are formed. No differences in the location of the spots in the x-ray pattern have been observed in comparisons of unvulcanized and vulcanized rubber.

When crystals are formed by stretching, it has long been noted that there is no measurable crystallization until a certain minimum elongation is reached. Such observations have been made by many different methods (26, 27, 33, 40, 50, 55, 71, 84, 133, 147). Minimum elongation values between 100 and 250% have usually been found for natural rubber.

The minimum elongation required for a pure gum compound containing a very small amount of sulfur seems to differ little from that required for unvulcanized rubber. However, it is found to be higher the higher the amount of combined sulfur or the longer the time of cure (40). Carbon black in a vulcanizate reduces the value of the minimum for both natural rubber (52) and Butyl rubber (120). At higher temperatures higher elongations are required for a given amount of crystallization (40, 84).

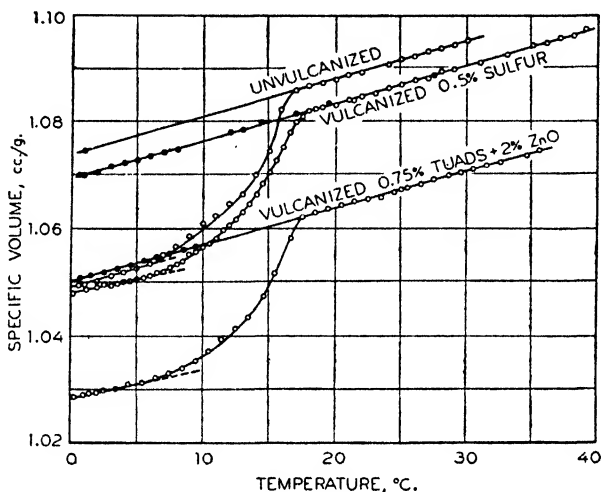


Fig. 10.—The melting of rubber crystallized at 2° C. (14). Open circles represent observations during the first heating following crystallization; dark circles, during subsequent heating.

No evidences of crystallization have ever been reported in ebonite. In this case it seems clear that the decrease in mobility of the chains and the alteration of the constitution of the material have gone so far as to prevent the regularity of structure and alignment necessary for crystallization.

In contrast with the behavior of unstretched rubber illustrated in Figure 10, the melting range of the crystals in stretched rubber is apparently affected considerably by the state of vulcanization. In the well-known T-50 test (54), rubber is stretched at 20° C., cooled to -70° and the tension released. Retraction does not occur until the temperature is raised above -70°. The temperature at which retraction is half complete is usually rather sharply defined and is called the T-50 value. It is found that the T-50 value for unvulcanized rubber is +18° C., with progressively lower

values for vulcanized rubber with increasing amounts of combined sulfur. There would seem to be little doubt that the retraction is associated with the melting of crystals formed during the test, but a satisfactory theory of the T-50 test has not yet been published. The mere connection with crystallization, however, is sufficient to explain the fact that valid comparisons cannot be made between rubber compounds differing in type of accelerator (138) since the ease of crystallization likewise differs with different types of compounds (40, 53). The absence of crystallization in G-R-S synthetic rubber is doubtless the reason for the complete lack of success in applying the T-50 test to it. Treloar (136) has suggested the basis for an explanation of the T-50 test in terms of the internal tensions in the amorphous portions of chains joining two crystalline regions, as proposed by Alfrey and Mark (3). He points out that the higher the state of vulcanization the higher would be these tensions and consequently the more readily would the crystals melt.

8. *Size of Crystallites*

Studies of x-ray data for stretched rubber lead to the conclusion that neither the size of the unit cell nor the size of the crystallite is appreciably altered by stretching or by temperature variations. The most obvious change is an increase in the number of crystallites with increasing elongation and a decrease in their number with increasing temperature (40).

A variation of molecular weight is also found (53) to be without influence on the size of the unit cell and the size of the crystallite. The number of crystallites formed decreases with decreasing molecular weight; and no diffraction spots at all were observed when the molecular weight of the unvulcanized rubber used was much below 100,000. However, vulcanizates made from rubber with a molecular weight of only 25,000 exhibited crystallinity.

From measurements of the sharpness of x-ray diffraction spots it is possible to make estimates of the size of the crystallites involved in the diffraction. Hengstenberg and Mark (66, 97), the first to apply this technique, reported a value greater than 600 Å. in the direction of the fiber axis, 530 Å. for the dimension of the crystal normal to the 200 planes (A_1 spot) and 180 Å. for that normal to the 020 planes (A_2 spot). Gehman and Field (53) in a recent investigation have reported values of 268 to 338 Å. in the 200 direction and 52 to 81 Å. in the 020 direction, without attempting to evaluate the size along the fiber axis. An alternate method of calculation also given by Gehman and Field yields values two or three times as large.

Regardless of the absolute values, certain very definite trends are apparent in the work of Gehman and Field. When the ingredients in the vulcanizate were so chosen as to permit a larger fraction of the material to crystallize, at a given elongation, the dimension of the crystallite in the 020 direction was smaller. Under the same conditions the stress at a given elongation was higher. Probably the stiffening was brought about both by the greater number of the crystallites and by their smaller size.

IV. Materials Studied

1. *Natural Rubber*

A few of the numerical results given in the previous section for natural rubber may well be recapitulated so that they may be compared readily with the corresponding results for other materials. Crystallization of the unstretched rubber is found to be most rapid at about -25°C ., but has been observed at temperatures as low as -45°C . and as high as $+15^{\circ}\text{C}$. The rate of crystallization becomes inappreciable in 8 to 10 hours under the most favorable conditions, but crystallization may continue for years under less favorable conditions.

Crystals may be formed in a fraction of a second when natural rubber is stretched (1, 87), but they may continue to be formed for months or years (71). No evidence has been presented to show that they can be formed at temperatures below -50°C . Melting may occur at temperatures as high as 40° to 45°C . in unstretched rubber at atmospheric pressure (8, 38, 140, 146). Under pressure the melting range may be raised to 70°C . or above (37, 145). Crystals formed on stretching to high elongations are not completely melted at 100°C ., according to the density studies of Holt and McPherson (71) and x-ray studies of Field (40). Kirsch (84) places the upper limit at 140°C . on the basis of measurements of double refraction.

Agreement has not been reached regarding the exact dimensions of the unit cell of the crystal (50, 99), but the most recent results (19) appear to favor a monoclinic cell about 12.5×8.1 (fiber axis) $\times 8.9 \text{ \AA}$. containing four isoprene units.

2. *Balata and Gutta-percha*

Balata and gutta-percha, though obtained from different trees, are essentially identical in structure. They are composed of the *trans*-isomer of the hydrocarbon of which natural rubber is the *cis*-isomer. Like most *trans*-isomers, they crystallize more readily than the corresponding *cis*-

isomers and melt at higher temperatures. They are usually found in a crystalline state at room temperature.

In this case, there appear to be two different crystalline forms (35), which have been named α and β . The α -form, the one which occurs in the tree, melts at about 65° C. and is the form obtained by slow cooling of the amorphous material or by crystallization from solution at room temperature. The β -form, melting at about 56° C., is obtained on rapid cooling of the amorphous material.

The identity period of the α -form along the fiber axis is about 9 Å. (17, 19, 44, 65, 95).

Bunn (19) has assigned to the β -form an orthorhombic unit cell with $a = 7.78$, $b = 11.78$ and $c = 4.72$ Å. Four long-chain molecules pass through this cell parallel to the c -axis. Jeffrey (73), on the other hand, concludes that the x-ray data at present available are insufficient to establish a unit cell.

3. Chloroprene Polymers (Neoprene)

The crystallization which occurs on stretching a chloroprene polymer was recognized in the first paper (23) describing it. The x-ray patterns showed that the orientation is not nearly as perfect as with natural rubber and that the structure corresponds largely to the *trans*-isomer.

Bunn (19) ascribes to it an orthorhombic unit cell containing four chloroprene groups and having the dimensions $a = 8.84$, $b = 10.24$ and $c = 4.79$ Å. (fiber axis). The analysis of Clews (30) yields a cell which is somewhat larger in its longest dimension.

On standing at room temperature and below, the unstretched chloroprene polymers often show a progressive increase in hardness. The hardening has often been noted but has only recently been ascribed to crystallization (42, 76, 86, 149).

Unpublished dilatometric observations at the National Bureau of Standards have shown that different chloroprene polymers in the unstretched state crystallize at widely different rates, but that the amount of the volume change and the range of melting are not appreciably different. Crystallization may occur over the range from about -35° to about +32° C. It is most rapid in the neighborhood of 0° C.

At a given temperature the rate of crystallization of Neoprene CG is more rapid than that in any of the other types. The types studied, in order of decreasing rates of crystallization, were: Neoprene CG, Neoprene E, Neoprene G and Neoprene KC. No evidence of crystallization was ever found in Neoprene FR, which is thought to be a copolymer.

Changes in density occasioned by crystallization in different varieties of Neoprene were observed in the course of measurements reported by Wood, Roth and Bekkedahl (148).

4. *Organic Polysulfide Polymers (Thiokol)*

Crystallization effects are clearly evident in many of the organic polysulfide polymers in both the unstretched and the stretched conditions. The x-ray patterns have been investigated by Katz (81) and Fuller (45). For Thiokol A an identity period of 4.32 Å. along the fiber axis was found. The melting of the crystals formed in the unstretched Thiokol A was reported to occur at about 70° C.

Unpublished dilatometric observations at the National Bureau of Standards have shown that the different polysulfides in the unstretched state at room temperature and below crystallize at widely different rates.

Near 0° C., the rate of crystallization of Thiokol A was found to be more rapid than that in any of the other types. The types studied, in order of decreasing rates of crystallization, were: Thiokol A, D, DX and F. Thiokol RD, which is not a polysulfide, showed no evidences of crystallization under any conditions. It appears likely that among those just mentioned Thiokol A is the only polysulfide rubber which crystallizes appreciably at room temperature. This type also has the shortest repeating unit along the polymer chain. It is considered probable that a short repeating unit is more favorable for obtaining the regularity of position necessary for the formation of crystals (91). Polyethylene, to be discussed later, also illustrates this point. The crystallization of Thiokol A may continue for months or years at room temperature and is one of the factors preventing the more extensive commercial use of this type.

5. *Isobutene Polymers and Copolymers (Vistanex and Butyl Rubber)*

Isobutene polymers (Vistanex or Oppanol B), when stretched sufficiently, show x-ray patterns characteristic of a well-ordered crystalline arrangement (16, 47).

The unit cell is given (47) as orthorhombic containing two chains of eight isobutene groups each. The dimensions were given as $a = 6.94$, $b = 11.96$ and the fiber axis $c = 18.63$ Å. As would be expected, the x-ray pattern of stretched Butyl rubber (4, 120) is found to be rather similar to that for the isobutene polymers.

Dart and Guth (34), from measurements of the rise of temperature on fast stretching of Butyl rubber vulcanizates, have concluded that crystal-

lization begins at elongations of from 500 to 700% at room temperature in agreement with x-ray results (120). Unpublished stress-time studies similar to those on natural rubber (147) have also shown that considerably higher elongations are required to crystallize Butyl rubber than are needed for natural rubber.

No effects ascribable to crystallization have ever been reported for these polymers in the unstretched state. Apparently the mobility is so low or other factors are so unfavorable that crystallization requires the drastic alignment brought about by stretching.

6. *Polyethylene (Polythene)*

Polyethylene in the unstretched state has been shown to be 55 to 75% crystalline at room temperature. Volume measurements (29, 60, 72), thermal measurements (60, 111) and x-ray studies (18) have been made. Crystallization occurs only at temperatures between 60° and 120° C. Although a period of the order of a day is required before crystallization ceases completely, most of the crystallization is so rapid that it has not been found possible to obtain amorphous polyethylene by rapid cooling through this region. The melting of the crystals likewise takes place between 60° and 120° C., with more than half the melting occurring between 110° and 120° C. The upper end of the melting range was found (72) to be somewhat lower than 120° when a polymer of lower molecular weight was investigated. The melting occurs at a temperature somewhat lower than would be expected for a normal paraffin of high molecular weight (89, 114).

The crystals formed in polyethylene by mechanical deformation such as stretching, rolling or drawing have been evaluated by Bunn (18) as having the unit cell $a = 7.4$, $b = 4.93$ and $c = 2.534$ Å. (fiber axis).

7. *Vinylidene Chloride Polymers and Copolymers (Saran)*

Crystallization effects are very striking in the vinylidene chloride polymers and copolymers, and play an important role in the technology of these materials (57, 113). Normally crystalline at room temperature, vinylidene chloride polymers crystallize most rapidly in the region from 50° to 100° C. They may be obtained in the amorphous state at low temperatures if cooled rapidly. On crystallization, a volume decrease of about 2% is observed (57) and a heat of fusion of about 3.4 cal. per g. (113).

The unit cell has been given (57) as monoclinic with $a = 13.69$, $b = 4.67$ (fiber axis) and $c = 6.296$ Å. and $\sin B = 0.8212$.

Increasing amounts of a secondary material copolymerized with the

vinylidene chloride are found to decrease the degree of crystallinity attainable, as would be expected.

8. *Butadiene Polymers and Copolymers*

No such evidences of crystallization have been reported for butadiene polymers as have been presented for the materials already discussed. The only positive results, it seems, are quoted by Mark (92), who states that with a special sample, polymerized in solution, stretching above 300% produced crystal diagrams of medium sharpness and intensity, with most of the material remaining in the unoriented state. The identity period is given as about 5 Å., and Mark points out the likelihood that the polymer is a mixture of *cis*- and *trans*-isomers. Such a mixture, particularly when highly branched, would be expected to be very difficult to crystallize.

Meyer (95), perhaps discussing the same experiments, quotes an observed identity period along the fiber axis of only 2.5 Å., but thinks that the true period may be double this.

In view of what has just been said with respect to simple butadiene polymers, it is not surprising that crystallization effects are not apparent in copolymers of butadiene, where there are additional irregularities associated with the presence of the secondary constituent. Thus, for example only negative results have been obtained in attempts to crystallize GR-S, Buna S and the different varieties of the Buna N type such as Perbunan, Hycar OR, Butaprene N, Chemigum N and the like.

Changes in intensity of portions of the amorphous ring in x-ray diffraction patterns have been interpreted as indicating a considerable degree of alignment of chains in the direction of stretching at high elongations in a butadiene-styrene copolymer (101) and in a butadiene-acrylonitrile copolymer (121). However, such an alignment is not regarded as crystallization.

The stress-strain and stress-temperature relations of GR-S (116) show no evidence whatever of any effects to be associated with crystallization. Recent unpublished measurements by Roth at the National Bureau of Standards in regard to changes of density on stretching vulcanizates of GR-S have shown no changes ascribable to crystallization.

9. *Noncrystallizable Polymers*

For most of the rubberlike materials which have not already been specifically mentioned, no evidences of crystallization have been reported. In a few instances this may arise merely from a lack of knowledge of the proper conditions, but in most cases it may be presumed to arise either

from such irregularities of structure that sufficiently perfect crystalline regions cannot be formed, or from a lack of sufficiently strong interchain forces to preserve the alignment from destruction by thermal agitation.

10. *Other Materials*

The scope of the present chapter has not permitted discussion of crystallization in many other high polymers, which are not quite so closely related to natural and synthetic rubbers as are those already discussed. Some are more closely related to the rigid plastics, and others to fibrous materials. There has been no discussion, for example, of the extensive work at the Bell Telephone Laboratories on polyesters (48) and polyamides (6, 7, 46). Other laboratories have also made studies of the crystallinity of nylon, silk, cellulose and its derivatives, etc. The effects of crystallization, similar to those already mentioned, are often very striking and of considerable importance in the technology of these materials.

V. Interpretation of Experimental Results

1. *Kinetics of Crystallization*

Tammann (128) and others (56, 100, 129, 139) have shown, in comprehensive studies of the nature of crystallization, that crystals originate at certain nuclei and grow outward from such nuclei at a characteristic rate. The rate of crystallization, as measured by the methods described here, is dependent on both the rate of formation of such nuclei and the rate of growth ("linear crystallization velocity") of a crystal once a nucleus has been formed. Quantitative considerations regarding these rates are set forth in several papers by Avrami (5) and others (58, 74).

The rate of nucleus formation and the rate of crystal growth are each strongly influenced by temperature. It has been found for materials of low molecular weight that each rate has a maximum value and that the temperature at which the formation of nuclei is most rapid is lower than the temperature at which the linear crystallization velocity is greatest. Therefore, at least in the temperature region between the two maxima, the ratio of the rate of nucleus production to the rate of crystal growth increases with decreasing temperature. Consequently, the growth of a given crystal is interrupted by interferences from the growth of neighboring crystals at a smaller average crystal size the lower the temperature of crystallization. Direct experimental evidence of this fact is abundant with materials of low molecular weight (128).

According to Avrami's theory of the kinetics of crystallization processes,

there is a certain probability, n , of formation of an active nucleus in a unit time. The temperature dependence of the probability is determined by two factors, one corresponding to diffusion and analogous to collision number in a gas, and a second dependent upon the activation energy necessary for the formation of the nucleus. The latter energy may be expected to decrease with decreasing temperature (9). Consequently n exhibits at an intermediate temperature, the maximum which has already been mentioned.

It seems probable that the slope of the volume-time curve at small values of time, or an evaluation of the induction period required for the crystallization to become measurable, may be regarded as giving an indication of the rate of nucleus formation at a given temperature. An examination of the curves in Figure 2 (page 64) shows that, for natural rubber, the rate of nucleus formation has a maximum value near -25° C. and decreases considerably at lower temperatures. Figure 9 (page 75) shows that, in vulcanized rubber, the rate of nucleus formation decreases with increasing amounts of sulfur.

Nuclei formed in the manner just discussed are capable of growth at a linear rate, G . Avrami discusses in detail the special case of an "isokinetic" range, throughout which the ratio G/n remains constant. With further simplification an equation is derived for V , the volume fraction of the crystalline phase as a function of time, t :

$$V = 1 - \exp(-Bt^k)$$

If the growth of crystallites is three-dimensional, parameter k should vary between 4 and 3, corresponding to the two extremes of small n and large n . For two-dimensional growth or linear growth k should be correspondingly lower. Parameter B is essentially determined by G if n is large but otherwise depends on both n and G .

R. Sinha, in unpublished work, has utilized the data shown in Figures 2 and 9 to study the applicability of Avrami's theory to the crystallization of natural rubber at different temperatures and at different degrees of vulcanization, by plotting $\log \log 1/(1 - V)$ against $\log t$. He finds, for instance, in the case of raw rubber, that between 2° and -33° C. there is always a range over which linearity is obtained and the above equation is valid. Between 2° and -27° C. the exponents k vary between 2.5 and 2.9; at -33° C. k is 4.2. At -38° C. the range of linearity is very short and yields a value of 8.7 for k , which cannot be interpreted in terms of the considerations underlying the above approximate equation.

At large values of time, there is an increasing deviation from linearity

as anticipated in Avrami's work, which does not contemplate that the range of applicability of the equation should extend to complete crystallization. At small values of time, deviations from linearity are also apparent, becoming more pronounced as the temperature is lowered.

The data are not sufficient to make clear the relative importance of n and G in determining parameter B at each temperature. Consequently, one cannot be certain whether, at the time at which the slope of a volume-time curve like those in Figure 2 reaches its maximum value, n is sufficiently large so that the slope depends essentially only on growth rate G . If this should prove to be the case, one could take the value of this slope as an approximate measure of the linear crystallization velocity. It will be noted that the slope increases as the temperature is lowered to -25°C . and changes very little below that temperature. Tammann (128) has shown similar results for the linear crystallization velocity of some materials of low molecular weight. It would be interesting to extend such studies to high polymers. As in Tammann's studies, the effect of the induction period might be varied by experiments in which some nuclei are formed at a given temperature, and growth occurs at a different temperature.

2. *Range of Melting*

There are several possible explanations for the existence of a range of melting instead of the sharp melting point usually found for pure materials of low molecular weight. Alfrey and Mark (2) have discussed several of these possibilities. Since the crystallization and melting of purified rubber are little different from that of the crude material (10), purity is evidently not a major factor. The inhomogeneity of complete molecular chain lengths would also appear to have little bearing, because the chains are, on the average, much longer than a single crystallite (2). A distribution of lengths of the elementary kinetic units is another possibility. Alfrey and Mark discuss this with some favor.

In recent work by Frith and Tuckett (43, 114), the suggestion is made that an explanation of the melting range may be based on the assumption that the temperature of equilibrium between crystalline and amorphous material is a function of the extent of crystallization. At least in its application to rubber this assumption seems open to objection on two grounds. In the first place, it appears from Figure 7 (page 69) that there is no temperature in the range studied at which crystalline and amorphous material are in equilibrium at atmospheric pressure. In the second place, as already stated in the section on melting of crystals (page 66) direct experimental observation not available to Frith and Tuckett indicates that

the range of melting does not depend on the extent of crystallization. It is possible that the theory may be applicable to polyethylene, if not to natural rubber.

Alfrey and Mark (2, 3) have called attention to the stresses existing in the amorphous portions of single chains which pass from one crystalline region to another and to the constrictive effects on the amorphous regions, caused by the growth of the crystalline regions. They point out that the entropy change on crystallization is thus different for the portions of the chain which enter the crystal toward the end of the crystallization of a single crystallite as compared with those which enter the crystal at the beginning. Such a variation in entropy change would then produce a corresponding variation in melting temperature, and give rise to a melting range. This explanation apparently is also regarded with favor by Treloar (136). Should the completion of this process of formation of the single crystal require a period of time comparable with that needed for the over-all crystallization of the material, then the melting range should be different at different stages of the over-all crystallization. This does not seem to accord with the experimental observation that the range of melting is independent of the extent of crystallization.

The same molecular considerations developed by Alfrey and Mark can be used in an alternative explanation based on the distribution of crystal sizes. The entropy change in the formation of large crystals of a high polymer may be expected to differ from that involved in the formation of the same amount of crystalline material in smaller crystals, because of the different magnitude of the entropy effects in the constricted amorphous regions in the two cases. Since the temperature of melting is determined as the ratio of the energy change to the entropy change on melting, with a constant heat of fusion one would thus expect a range of melting to result from a distribution of crystal sizes.

Dostal's earlier suggestion (36) that the temperature of melting of a given crystal depends on the size of the crystal was based upon considerations of free surface energy. With a given distribution of crystal sizes it would apply equally well to materials of low molecular weight. However, it is not likely that such materials would have as wide a distribution of sizes.

Like the other theories mentioned, that based on a distribution of crystal sizes also affords no basis for the observation that the range of melting is independent of the extent of crystallization. It seems highly improbable that any mechanism could maintain the same distribution of crystal sizes from the beginning to the end of crystallization.

3. Change of Melting Range with Temperature of Crystallization

The change of melting range with temperature of crystallization is one of the most fundamental and significant of the experimental relations which have been presented. It deserves careful consideration by those who are developing theories of crystallization of high polymers. Especially striking is the idea that there is no temperature at which the crystalline and amorphous rubber are in equilibrium at atmospheric pressure.

The relation does not appear to be affected by such variables as molecular weight or degree of vulcanization over the range of practical importance. The effect is not limited to natural rubber; it has also been observed in Neoprene. It probably occurs in other high polymers, particularly those in which a low rate of crystallization and a small heat of fusion make it possible to vary the temperature of crystallization. Parks (107) has commented that the heat of fusion of the order of 5 cal. per g. is much lower than the value of 30–50 cal. per g. to be expected for a linear paraffin of high molecular weight.

Any explanation of the existence of a range of melting must be capable of extension to yield the conclusion that both the location of the range and its breadth are determined largely, if not entirely, by the temperature of crystallization.

The distribution of crystal sizes after completion of crystallization is a function of the temperature at which crystallization occurs. Consequently, an explanation in terms of such a distribution would be attractive were it not for the objection mentioned in the preceding section—namely, that the distribution of crystal sizes in an incompletely crystallized material is a function of the time of crystallization, and no dependence of melting range on time of crystallization is observed.

4. Nature of Crystals

The detailed conception of the nature of the crystalline regions in long-chain high polymers has become more definite in recent years. The summaries of Alfrey and Mark (2) and Bunn (20, 21) are particularly useful in expressing the accepted views. A few of the more striking respects in which high polymers differ from compounds of low molecular weight will now be mentioned.

In long-chain high polymers many of the properties are governed not by whole molecules but by kinetic units which are segments of the chains (88, 90, 98, 109). It seems generally agreed that these segments are also the structural units of the crystallites. Consequently, a single chain may

contain segments which are units in two or more different crystallites joined by segments which are to be regarded as part of the amorphous material.

The validity of this conclusion is strengthened by a comparison of dimensions of chains and crystallites. The completely extended length of a single chain in a normal rubberlike high polymer may be between 10,000 and 100,000 Å. Even in the coiled-up state the maximum dimensions are likely to be of the order of one-tenth of the total length. Therefore it can be seen that this molecular dimension of a few thousand angstrom units is appreciably larger than the few hundred angstrom units given in an earlier section (page 77) as the maximum dimension of the crystallites according to x-ray data.

The melting point of a normal straight-chain paraffin hydrocarbon increases with increasing molecular weight but changes relatively little if the molecular weight is high. For polyethylene, the change is said (20) to be inappreciable if the molecular weight is above 10,000. The melting point predicted from theoretical considerations (114) is about 130° to 140° C., whereas the melting of polyethylene is usually observed to be complete at temperatures between 105° and 115° C. Richards (114) suggests that this difference is to be ascribed to imperfections in the crystallization and to the presence of amorphous regions.

The melting of crystalline high polymers, according to Bunn (20), occurs when the temperature is high enough to permit rotation of relatively rigid portions of the chains about the single bonds joining them. He calls this type of motion "molecular wriggling."

In the light of what has been said in the two preceding sections it appears that none of the proposed theories describing in detail the crystallization and melting of the rubber accounts satisfactorily for two experimental observations: one, that the range of melting is not dependent on the extent of crystallization or state of vulcanization; and the other, that it is definitely determined by the temperature at which the crystallization occurs. A theory solidly based on these two observations would have excellent prospects of being adequate to explain many other features of the crystallization and melting of natural and synthetic rubbers.

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THE STUDY OF RUBBERLIKE SUBSTANCES BY X-RAY DIFFRACTION METHODS

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	PAGE
I. The Rubberlike State.....	95
II. The Crystal Structures of Rubberlike and Related Polymers.....	98
1. Methods and Limitations.....	98
2. The Polyisoprene Group—Gutta-percha, Rubber and Poly- chloroprene.....	105
Gutta-percha.....	106
Structure of β -Crystals.....	106
α -Gutta-percha.....	111
Rubber.....	111
Polychloroprene.....	116
3. Butadiene Polymers.....	117
4. Rubber Hydrochloride.....	118
5. Polyethylene.....	119
6. Polyvinyl Alcohol.....	121
7. Other Polyvinyl Compounds.....	123
8. Polyisobutene.....	125
9. Polyesters.....	128
10. Other Rubberlike Substances.....	131
III. Molecular Structure and Physical Properties.....	132
1. The Polyisoprene Group.....	134
2. Rubber Hydrochloride.....	136
3. Polyethylene.....	136
4. Polyisobutene.....	136
5. Polyesters.....	137
IV. Studies of Crystallization and Orientation.....	138
Bibliography.....	141

I. The Rubberlike State

The study of rubberlike substances cannot be isolated from that of chain polymers in general. The substances normally regarded as rubberlike are merely those long-chain polymers which have the familiar characteristics of softness and elasticity at room temperature. But similar properties are

possessed by a number of chain polymers over a particular temperature range which is different for each substance. Indeed, it is likely that with rise of temperature all chain polymers consisting of extremely long molecules (several thousands of atoms long) pass through a rubberlike stage, provided that chemical decomposition does not set in before the appropriate temperature is reached. The position of the rubberlike state in relation to other familiar states of matter is illustrated in Figure 1. Sub-

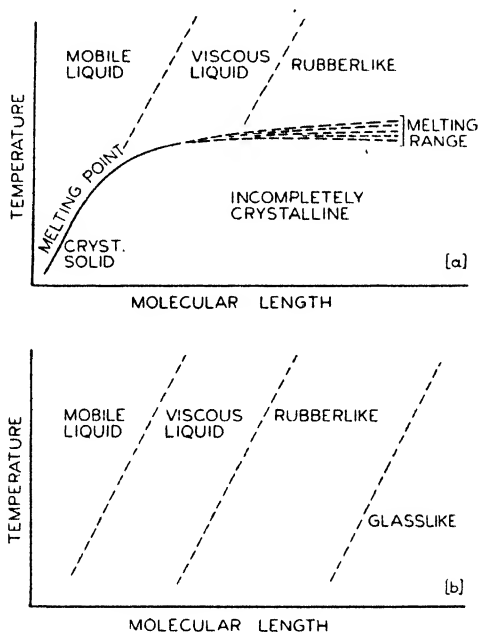


Fig. 1.—The rubberlike state.

stances consisting of small molecules form crystalline solids at low temperatures, and melt sharply to mobile liquids. With increase in the length of the molecule (in a homologous series such as the normal paraffin hydrocarbons), the melting point rises and so does the viscosity of the liquid (Fig. 1a). The melting point does not continue to rise indefinitely with molecular length, but becomes practically constant for very long molecules; the viscosity of the liquid continues to rise until it is so high that the substance has almost the coherence of a solid, and we say it is rubberlike. The limiting melting point is different for each polymer; thus, for polyethylene, it is about 115°C ., for polyhexamethylene adipamide, 250°C .,

and for polyethylene adipate, 50° C. Thus, among very long-chain polymers having a regular molecular structure, the substances having rubberlike properties at room temperature are simply those whose melting points are below room temperature (14).

The melting points of high polymers are not sharp, as are those of micro-molecular substances; and crystallized high polymers are not entirely crystalline but always contain a certain proportion of amorphous material. These special features of high polymers are considered on pages 132-141.

Not all long-chain polymers crystallize at low temperatures. Many interpolymers, for instance, do not crystallize: their molecules have an irregular structure, two or more types of monomer units being linked in indiscriminate succession along the chains. Such molecules cannot be expected to form regular crystalline arrangements (unless the chemically different monomer units happen to be very similar geometrically). Such substances, on cooling from a high temperature, pass through a rubberlike stage and then harden to a glasslike condition. The corresponding type of diagram for such substances is shown in Figure 1b. Some polymers whose molecules appear to be chemically regular fall into this class: polyvinyl acetate, for instance, which is rubberlike above 70-80° C., does not crystallize on cooling, but becomes glasslike. It may be, as Staudinger suggests (82), that left- and right-handed groups occur indiscriminately along the chains; such geometrical irregularities would prevent crystallization just as effectively as irregularities in chemical structure. It is also relevant to mention at this point that some polymers which crystallize if cooled slowly fail to do so when cooled rapidly to temperatures well below the melting point. Rubber itself, if cooled rapidly in liquid air, does not crystallize, but becomes glasslike.

X-ray diffraction methods are capable of yielding detailed information on the structure of crystalline substances. For amorphous substances, their scope is far more restricted. Thus, in the study of long-chain polymers, the principal contributions made by x-ray diffraction studies relate to those substances which crystallize. The most fundamental contributions are conclusions on the configurations of polymer molecules, and the mode of arrangement of these molecules in crystals. In our attempts to understand the properties of rubberlike substances and the relation between these properties and chemical constitution, our policy in x-ray work must be to learn as much as possible by detailed studies of the crystalline polymers; it may then be possible to apply this knowledge to those polymers which do not crystallize. The substances dealt with in this review

are: (1) those natural or synthetic polymers which have rubberlike properties at room temperatures; (2) closely related substances such as gutta-percha and rubber hydrochloride; (3) other polymers which by virtue of their low melting points are theoretically interesting in connection with the problems of rubberlike properties and are potentially useful as constituents of rubberlike substances.

In addition to the fundamental study of molecular structure, there are other applications of x-ray diffraction methods: for instance, the study of the amount and the orientation of crystalline material produced by various types of deformation.

II. The Crystal Structures of Rubberlike and Related Polymers

1. *Methods and Limitations*

The symmetry of high-polymer crystals is usually low—not higher than orthorhombic—and consequently interpretation of the Debye-Scherrer ring patterns given by a mass of randomly oriented crystals (as in frozen unstretched rubber) is scarcely feasible. Single crystals of high polymers (the ideal experimental material for structure determination) have apparently never been obtained. But polycrystalline specimens in which all the little crystals have one particular axis approximately parallel to a line can be obtained; and the x-ray diffraction patterns (“fiber photographs”) of such samples are similar to that given by a single crystal rotated round a principal axis: all orientations perpendicular to the fiber axis are already present in the specimen, so that the effect of rotation is produced. Such specimens are obtained, in the case of substances in the rubberlike condition, by simply stretching a thread of the material (50). The molecules are pulled into parallel alignment and form crystalline arrangements. The specimen must be held in the stretched condition while the x-ray photograph is taken.

Polymers below their melting points can be drawn out to several times their original length; the formerly random crystals are dragged into parallel alignment (19a). The orientation of the crystals in such cold-drawn specimens is usually less perfect than that of stretched rubberlike specimens. It is therefore advisable in making oriented specimens for crystal structure determination to warm a thread of material above its melting point and stretch it in the rubberlike condition, rather than to cold-draw it below its melting point. Crystallization by stretching above the melting point, however, only occurs when the molecules are extremely long ($\sim 10,000$ atoms); when they are shorter (~ 1000 atoms), flow occurs

on stretching, and the tension developed is not sufficient to cause crystallization. Cold drawing is, however, quite effective when the molecules are only 1000 atoms long; consequently, for polymers whose molecular lengths are not sufficiently great to confer truly rubberlike properties, cold drawing below the melting point must be used to produce oriented specimens.

X-ray diffraction photographs intended for crystal structure determination should be taken on cylindrical films. Much work on high polymers is based on flat-film photographs (the film being normal to the x-ray beam), and for many purposes these are adequate; but for structure determination it is very desirable to obtain as much diffraction information as possible. A cylindrical film records a much greater angular range of reflections than a flat film, and the outer reflections, being less spread out on the film, are less likely to be lost in the background. On cylindrical films, reflections at Bragg angles up to 40–45° are sometimes recorded; these may constitute valuable evidence for structure determination.

In addition to the ordinary fiber photographs, in which the x-ray beam is perpendicular to the fiber axis, it is desirable to take another type of photograph: the fiber axis of the specimen is oscillated from the normal position to a position making an angle of 45° to the beam, in order to record reflections from planes normal (or nearly so) to the fiber axis. Photographs taken when the fiber axis is set at definite angles to the beam may be useful for the same purpose, but on such photographs the intensities of the reflections in question may be very misleading (see section on polyisobutene, page 125).

Unit cell dimensions may be deduced from fiber photographs by the reciprocal lattice methods described by Bernal (6) for rotation photographs of single crystals. The unit cell dimension along the fiber axis is given directly by the layer line separation, but the other dimensions and angles of the unit cell must be found by trial.

In addition to the orientation of the molecular axis along the fiber axis, a second orientation can sometimes be imposed: if a thin sheet of a rubberlike substance is stretched, the crystals formed tend to have one particular plane lying in the plane of the sheet (59); this plane orientation is especially marked when the breadth of the sheet is much greater than its dimension in the direction of stretching (40). For crystalline polymers, a similar effect can be achieved by passing a sheet through rollers, whereby it is elongated and at the same time thinned (12). X-ray diffraction photographs of such doubly oriented specimens may be treated as crude oscillation photographs of single crystals (or twinned crystals) so that the indices

of reflections may be checked; or, better still, moving-film photographs may be taken: the reflections are not spots (as they would be for perfectly oriented specimens or single crystals) but streaks showing points of maximum intensity, and these points indicate the orientation of the corresponding crystal planes as in moving-film photographs of single or twinned crystals (89). The second (plane) orientation is, however, usually very imperfect, so that reflections lying on the same layer line and having similar spacings may not be effectively resolved. Some ambiguity in indexing, and some uncertainty with regard to unit cell dimensions, may thus remain. The only course is then to proceed with the later stages of the analysis, accepting provisionally the most probable unit cell; if the cell is incorrect, it will almost certainly not survive the later stages; in particular, it will not be found possible to account for the intensities of the reflections.

The first check of unit cell dimensions is provided by the density of the crystalline polymer. If V is the volume of the unit cell, ρ the density, and M the absolute weight of one monomer unit, then the number of monomer units, n , in the unit cell is $V\rho/M$. For polymers, the measured density is lower than the true density of a crystal, owing to the presence of amorphous material; hence, when the measured density of the polymer is used in the expression $V\rho/M$, the result is not exactly a whole number; it falls below the true number of monomer units in the unit cell by a factor of 0.9–0.95. A figure of 3.6 for n would indicate four monomer units in the unit cell, and would increase confidence in the unit cell dimensions; a figure of 4.0 would cast suspicions on the unit cell dimensions. Figures lying a little below numbers such as 5 or 7 would also raise doubts about unit cell dimensions, since such numbers of monomer units are unlikely to occur in unit cells of crystals.

Consideration of the types of absent reflections, and of those unambiguously present, may lead to conclusions on space group symmetry; but because of the overlapping of reflections, and of the fact that weak reflections may be lost in the general background of polymer photographs, it is well to retain an open mind on the question. It may be necessary to admit the possibility of several space group symmetries, and to consider each in turn in the light of other evidence. To offset this disadvantage, it is sometimes possible to limit the consideration of space groups by special arguments based on the special characteristics of very long chain molecules (see the section on gutta-percha, page 106).

The positions of the atoms in the unit cell must usually be found entirely by trial. The overlapping of reflections bars any attempt to use Fourier series methods, except for the very simplest polymers (10). The procedure

is therefore to postulate particular sets of atomic positions, and to calculate the relative intensities of the reflections for these positions, for comparison with those observed on the photographs. In postulating the configuration of the molecules and the type of packing, use will naturally be made of all existing information on bond lengths and angles, the configuration of chain molecules and the distances between atoms in neighboring molecules.

Owing to the limitations of high-polymer photographs—the limited number of reflections and the overlapping of reflections—we must not expect the same degree of certainty with regard to the general arrangement, or the same degree of precision of atomic co-ordinates, as is attained in work based on single-crystal photographs. But in spite of the obvious limitations there are compensating features which make the study of high-polymer structures not so difficult or uncertain as might be supposed.

These advantages are the result of the fact that one unit cell edge—the fiber axis—is a molecular axis and the length of this edge is a dimension within the molecule—the repeat distance along the chain molecule. This fact has far-reaching consequences, as is clear from the accounts which follow: the repeat distance may, in conjunction with a knowledge of normal bond distances and angles, lead directly to a knowledge of the molecular configuration: the repeat distance of polyvinyl alcohol, for instance, is such that the molecules must be fully extended plane zigzags. When the repeat distance is shorter than that expected for a plane zigzag chain, it is evident that shortening has occurred by rotation around single bonds. If all bond positions attainable by such rotation were equally probable, the number of possible configurations would be large, especially in cases in which the repeat distance is large; but it has been pointed out (13) that in singly linked structures the bonds tend to be in “staggered” positions. This severely limits the possible chain forms. Except in cases in which large deviations from staggered positions may be expected (through overcrowding of side groups, for instance) the “principle of staggered bonds” is likely to be useful in this way; it has already been used successfully in one case (15). It must, however, be emphasized that, except in the simplest cases, such deductions from molecular repeat distances must be regarded, not as definite conclusions, but simply as valuable suggestions which must be put to the test of a detailed consideration of the intensities of all the reflections.

After the consideration of the molecular structure based on the molecular repeat distance, the determination of atomic positions takes a normal course: atomic positions are postulated, and the intensities of the various

reflections are calculated and compared with those on the photographs. Visual estimates of the latter are sufficient, since relative intensities are very sensitively related to atomic positions. Photometric measurements have been made in one simple case, for polyethylene (10), but for most polymers it is not worth while, in view of the limitations of polymer photographs (discussed below). It is usually best to start with the projection along the molecular axis, then to consider other principal zones and finally the general (hkl) reflections. It is necessary to make full use of *all* the reflections on polymer photographs in attempting to place the atoms. It cannot be too strongly urged that the aim should be to account for the entire diffraction pattern.

In view of the comparatively small number of reflections on high-polymer photographs (20 to 40 on an average fiber photograph), it might be thought that this amount of evidence is scarcely sufficient for even the approximate placing of all the atoms. For instance, suppose that, in a particular structure, there are (even when the hydrogen atoms are ignored) 30 variable parameters, and that only 25 reflections are available. It might be thought that a solution is impossible, the number of equations being less than the number of unknowns. But atomic coordinates are not to be regarded as quite independent variables; if normal bond lengths and angles are assumed (even if only approximately), this represents a severe initial limitation of positions.

With regard to the degree of precision in the placing of atoms, it is obvious that this must be inferior to that attained in single-crystal investigations, since single-crystal photographs of substances having unit cells comparable in size to those of the polymers considered here may show several hundreds of distinct reflections. Comparison on the basis of numbers of reflections (49a, 73) is, however, misleading: polymer photographs are not so far inferior as might be supposed from such a comparison. Experience has shown that the 20–40 reflections on the average fiber photograph are remarkably exacting in their demands on atomic positions. There are three reasons for this. In the first place, the main evidence for specific features (particular groupings of atoms) in crystal structures often consists of a few ratios of the intensities of certain reflections (others being insensitive to the particular feature in question, and still others merely confirming the verdict of the “key” ratios)—and such “key” ratios may be displayed quite as plainly on polymer photographs as they would be on single-crystal photographs; provided that the relevant reflections are present, the fact that they are short, somewhat diffuse arcs rather than the sharp spots of single-crystal photographs does not alter the situation.

Secondly, it must be remembered that the weakest reflections on single-crystal photographs are seldom accounted for quantitatively; therefore the loss of these reflections (which fade into the background of polymer photographs) is not necessarily a serious disadvantage. If (the unit cell being settled) a reflection from a certain crystal plane is not seen on a fiber photograph, one knows that its structure amplitude is either small or zero; and if the low structure amplitude is accounted for by a proposed atomic arrangement, this is as much as is achieved in many single-crystal investigations.

Thirdly, in single-crystal work, the atomic positions are usually derived from two or three zones of reflections; the hkl reflections (when they are calculated) being used for confirmation. For polymer structures, *all* the reflections are used in choosing atomic coordinates. The difference thus lies not so much in the amount of basic evidence used in structure determination as in the absence of further confirmation in the case of polymer structures. It is perhaps fair to say that in single-crystal photographs there is far more than enough evidence for placing atoms, while in polymer photographs there is just enough.

This optimistic view of the potentialities of high-polymer photographs must not be carried too far, and it remains true that the amount of evidence available in such photographs is much more scanty than we should like. Consequently, it is very desirable—even more desirable than in ordinary crystal structure work—to study the structures of related polymers. Each structure determined with a fair degree of certainty and precision will provide checks on, and will itself be counterchecked by, the structures of related polymers. If consistent structures are obtained for related polymers, the fact that they are consistent very much increases our confidence in each. Single-crystal studies of the structures of related small molecules may also provide more precise evidence on particular details of molecular structure, and may suggest precise interatomic distances and group configurations which can then be tried in polymer structures. It must, however, be emphasized that the features of related substances must be regarded only as suggestions; such features may not always be exhibited unchanged in the structure under investigation. The evidence for any crystal structure consists of the x-ray diffraction pattern of that crystal; suggestions may be derived from other sources, and the conclusions from the photographs of any one substance may be called in question owing to inconsistency with evidence from other sources; but it remains true that for any one crystal no feature can be admitted unless it accounts for the x-ray diffraction pattern of that crystal. The implications

of x-ray diffraction patterns should be accepted boldly, even if they conflict with stereochemical preconceptions, for only in this way is new knowledge gained.

Of course, there may be, in high-polymer crystals, certain special effects which are likely to confuse the interpretation of the diffraction patterns if their existence is ignored. Probably the most serious possible source of embarrassment in the attempt to locate atoms in rubberlike polymers by calculating the intensities of reflections is constituted by the complex of thermal vibrations in the crystals. In the study of crystals composed of small molecules or ions, especially at temperatures well below the melting points, the thermal movements of the atoms do not lead to any difficulties; the movements are relatively small, and not markedly anisotropic, and their effect is simply to cause the experimental intensities of the reflections to fall away from the calculated values with increasing angle of diffraction: the trend is uniform and can be allowed for. But in crystals of chain polymers, the thermal movements are bound to be markedly anisotropic—the lateral movements of flexible chain molecules are necessarily much greater than movements along the chain; and, since in rubberlike polymers the crystals are near their melting points, such effects are particularly marked (much more so than in the higher melting chain polymers such as cellulose). Anisotropy of this type would not by itself constitute a serious difficulty; its effect would be to diminish the experimental intensities of reflections from planes parallel to the chains, in comparison with those from planes normal to the chains: the effect would be systematic (depending on the orientation of a plane with respect to the chain axis), and could be allowed for. Such an effect occurs in the very simple structure of polyethylene (10), a simple $(\text{CH}_2)_n$ chain. But in more complex polymers thermal effects are not so simple. If we bear in mind that lateral movements of atoms in a chain molecule depend chiefly on rotations around single bonds (see section III) and that in some molecules rotation is easier around some bonds than others, it will be evident that the thermal movements of successive atoms along a chain molecule will not all be equal. (In general, every crystallographically different atom in a crystal has different thermal movements.) Moreover, apart from lateral movements due to molecular flexibility, a type of motion which is likely to occur is partial rotation of a whole molecule around its axis. [Indeed, in comparatively short chains of about 30 carbon atoms, complete rotation around the long axis occurs just below the melting point (68).] The effect of partial rotation for a polymer molecule bearing side substituents (rubber, *e. g.*, with its methyl groups) would be to make the amplitude of movement of the side substituent much

greater than that of the chain atoms, and therefore the relative contributions of these atoms to the intensities of certain x-ray reflections would be modified. The magnitude of these effects is unknown; very few polymer structures have yet been studied in detail. It is a subject for future consideration; we may expect evidence on the matter to turn up as our experience of polymer structures increases. We may also expect valuable suggestions to come from the work that is being done on the "extra" effects (diffuse spots and streaks) which appear on single-crystal photographs of certain substances because of the pattern of thermal vibrations in these crystals (56).

Meanwhile, it has been found possible to account approximately for the relative intensities of the x-ray reflections in a few cases (including rubber itself) without considering possible effects of this sort. (See, however, the discussion on the polyisoprenes on pages 109, *et seq.*)

2. The Polyisoprene Group—*Gutta-percha, Rubber and Polychloroprene*

In view of the historic and practical importance of rubber, the polyisoprene group of which it is a member is given pride of place in this survey, though a more logical course would have been to start with the simplest polymers—polyethylene and the polyvinyl compounds.

Rubber and gutta-percha are isomeric forms of polyisoprene ($-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-$)_n, which cannot be interconverted; it has long been believed that they are *cis* and *trans* isomers. The situation is somewhat complicated by the existence of two different crystalline forms of gutta-percha (48); these will be considered more fully later. For the moment, it may be observed that the molecular repeat distance of the beta form of gutta-percha is 4.7 Å. (44), while that of rubber is 8.1 Å. (59). If molecular models are made, using the normal bond lengths and angles ($\text{C}-\text{C}$ 1.54 Å., $\text{C}=\text{C}$ 1.33 Å., $\angle\text{C}$ $109\frac{1}{2}^\circ$ and $\angle\text{C}$ 125°), it is evident that the length of one

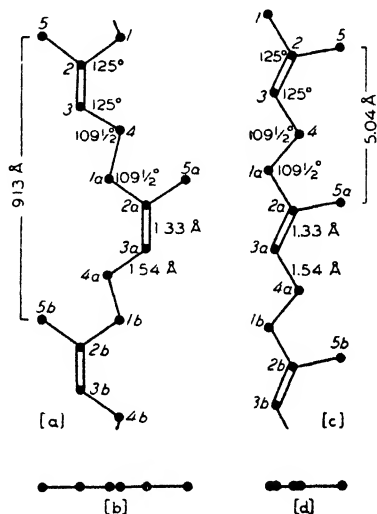
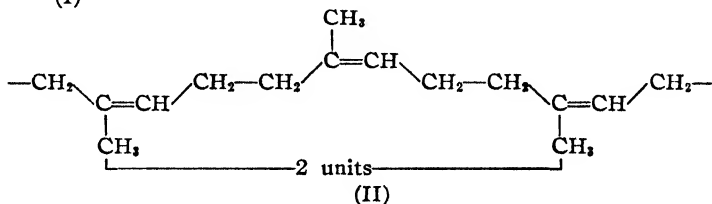
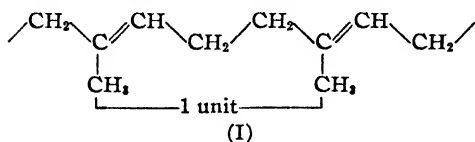


Fig. 2.—Planar polyisoprene models (12): (a) *cis* chain; (b) end view of (a); (c) *trans* chain; (d) end view of (c).

isoprene unit (whether in the *cis* or *trans* form) is 4–5 Å. (Fig. 2); therefore, provided that the chains are not very much shortened (coiled up) by rotation around single bonds, it appears that in crystals of β -gutta-percha the geometrical repeating unit comprises one isoprene unit, while in rubber the geometrical repeating unit comprises two isoprene units. It was pointed out by Meyer and Mark (64), as long ago as 1928, that only the *trans* form (I) of the chain is likely to have one isoprene unit in the repeat distance, the *cis* form (II) having two:



(This embodies the assumption that the bonds of the $\diagup\text{CH}_2\diagdown\text{CH}_2\diagup$ portion of the molecule form a plane zigzag, as in the paraffin hydrocarbons.)

From this point on, the two isomers will be considered separately, gutta-percha being taken first because of the simpler structure of its beta form.

GUTTA-PERCHA

Gutta-percha is amorphous and rubberlike above 70° C. Rapid cooling leads to the crystallization of the beta form, slow cooling (0.5° C. per hour) to that of the alpha form (44). Fiber photographs show that, whereas the geometrical repeat distance in the beta form is 4.7 Å., in the alpha form it is 8.8 Å. [This is the value given by Hauser and Susich (44); Lotmar (61) gives 8.7 Å.] The two crystal forms therefore contain molecules which are stereoisomers having different chain forms; and if both have the *trans* double-bond configuration, they must differ in single-bond configuration (12, 61).

Gutta-percha occurs in the tree in the alpha form; and this form, which has the higher melting point (about 65° as compared with 56° C. for the beta form), appears to be the more stable at all temperatures (61). The beta form is, however, permanently metastable at room temperature (44).

Structure of Beta Crystals.—Unit cell dimensions of the β -form were first

determined by Fuller (32), using cold-drawn fibers, and also stretched threads of slightly vulcanized gutta. (Unvulcanized gutta above its m.p. does not crystallize on stretching; there is so much plastic flow—owing to its comparatively low molecular weight of 30,000 (21, 90)—that not enough tension is developed to cause crystallization. Slight vulcanization links the molecules together sufficiently to prevent plastic flow; and, as in the case of rubber, the x-ray diagram is not changed by this treatment.) Fuller found that all except a few weak doubtful reflections fit an orthorhombic cell having the following dimensions in angstroms: $a = 7.85$; $b = 11.9$; and $c = 4.77$. He considered the possibility of a doubled fiber c -axis, but there is no evidence for this. There were, however, some weak reflections which appeared to demand larger lateral cell dimensions. Electron diffraction photographs taken later by Storcks (83), however, do not show these reflections, though in other respects they correspond closely with the x-ray photographs. It appears therefore, that the extra reflections were due to impurities in Fuller's specimens, and that the cell he suggested is correct.

Bunn (12) obtained doubly oriented specimens by cold rolling a piece of sheet gutta. The x-ray photographs show only reflections consistent with Fuller's cell, though slightly different dimensions are given (in angstroms): $a = 7.78$; $b = 11.78$; and $c = 4.72$. Moreover, the relative intensities of the reflections given by the doubly oriented specimens set at different angles to the x-ray beam were consistent with the indices assigned on the basis of this cell. From the density of gutta (0.945–0.955) and the above cell dimensions, the number of isoprene units in the cell is found to be 3.65. The true number is evidently 4; the discrepancy (due to the presence of amorphous material of lower density) is the same as is observed in other polymers. The true density of a β -gutta-percha crystal is 1.04.

The probable configuration of the chains may be deduced by a closer consideration of the repeat distance. A chain in which all the carbon atom centers lie in a plane (Fig. 2c) would have a repeat distance of 5.04 Å., assuming that bond lengths and angles are normal. This figure is considerably in excess of the measured repeat distance of β -gutta molecules. Since the atoms in the double-bonded group (1, 2, 3, 4 and 5 in Fig. 2c) are expected to be in a plane as in ethylene derivatives (9, 85), the only way of shortening the chain is to rotate around bonds 34 and 1a2a, keeping the two isoprene units 1–5 and 1a–5a parallel to each other so that they remain crystallographically equivalent. There are two ways of doing this (by rotating in opposite directions). Two types of asymmetric molecule, each the mirror image of the other, are obtained; they are shown in Figure 3.

A complete interpretation of the intensities of the x-ray reflections has

been given by Bunn (12): a set of atomic positions was found which give calculated intensities in fairly good agreement with those observed. The derivation of the structure will not be described in detail, but two points are worth noting here. The first is that the molecular configuration suggested by the repeat distance (Fig. 3) was not assumed: in the treatment of the α -projection (in which the molecules are seen end-on), an unprejudiced consideration of possible atomic positions led to the conclusion that no

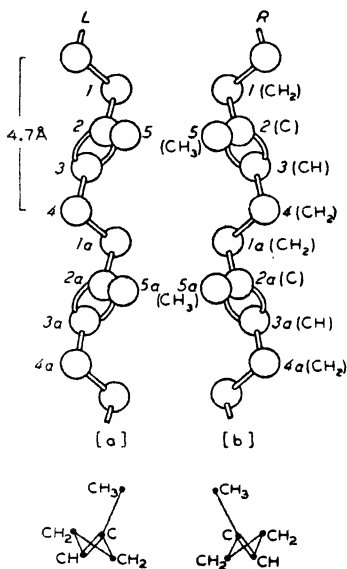


Fig. 3.—Molecular models (12) assuming planar isoprene units (*trans*) and identity period of 4.7 Å. Left- and right-handed molecules.

arrangement of planar molecules can satisfy the intensities of the $hk0$ reflections, and that the only arrangement which *can* account for these intensities has the centers of the carbon atoms of each molecule arranged approximately in the positions shown in Figure 3, with the four chain atoms at the corners of a parallelogram. This agreement with stereochemical expectation, obtained by rigorous consideration of x-ray intensities alone, is a testimony to the exacting nature of even the comparatively small number of x-ray reflections on the equator of a fiber photograph.

The second point is that, in the consideration of the space group, the following argument was used. "Melted" gutta-percha, from which beta crystals are obtained by cooling, is not a liquid but a rubberlike solid; hence the molecules do not move about relative to each other to any great extent. (If they did, the material would be fluid.) Neither can these enormously long molecules turn around to reverse their ends.

Thus, on crystallization, the molecules settle down in an orderly manner while remaining more or less where they happen to be. There are evidently bundles of roughly parallel sections of molecules in the amorphous material; all that happens during crystallization is that the molecules arrange themselves precisely without moving about bodily to any great extent. Since in any bundle there are likely to be approximately equal numbers of "up" and "down" molecules (an "up" molecule being defined as one with the methyl group above the double bond, and a "down" molecule the reverse), it is probable that each crystal contains

equal numbers of "up" and "down" molecules; thus, of the four molecules passing through the unit cell, two are likely to be "up" and two "down." Polar space groups with c as the polar axis were therefore ruled out. This argument might be useful for other polar polymer molecules.

The structure (illustrated in Fig. 4) has the space group symmetry $P 2_12_12_1$. In any one crystal, all four molecules are identical—either all

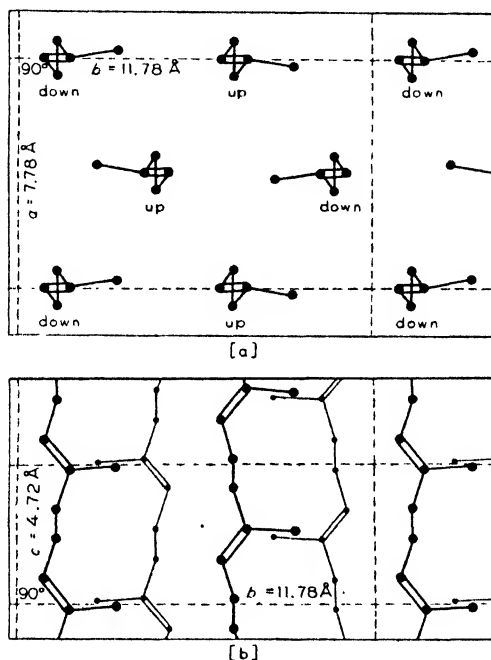


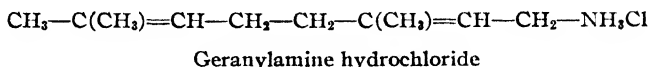
Fig. 4.—Structure of right-handed β -gutta-perch crystal (12), seen along (a) c -axis, (b) a -axis

right-handed or all left-handed, not mixed. Presumably, in any specimen there are equal proportions of left- and right-handed crystals.

The geometrical feature which is of most interest in connection with the physical properties of the substance is the pronouncedly nonplanar character of the chain. This is discussed later, in section III (page 132). A point of more purely stereochemical interest is that the C—CH₃ bond appears to lie 24° out of the plane of the rest of the double-bonded group (see Fig. 5).

This point has been taken up recently by Jeffrey (49b), who, accepting Bunn's structure in all essentials, has reported that the observed intensities

can be accounted for equally well by a slightly different set of atomic co-ordinates based on a strictly planar double-bonded group. Since the measure of agreement between observed and calculated intensities is similar for the two sets of atomic co-ordinates, the issue cannot be decided by the x-ray data on β -gutta-percha alone. It should be noted that a small displacement of the methyl group might be expected because of the repulsion between the methyl group and one of the chain CH_2 groups (4b in Fig. 5). Until the appearance of a preliminary note (5) on the structure of geranylamine hydrochloride (determined from single-crystal x-ray photo-



graphs), direct evidence on the configurations of such groups in other substances was not available. This substance has a *trans* chain like gutta-

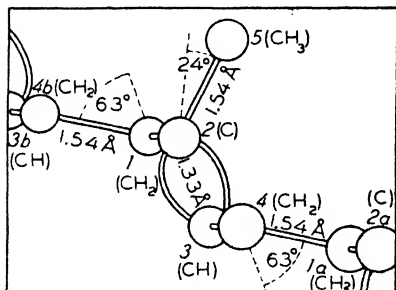


Fig. 5.—Details of structure of left-handed β -gutta-percha molecule (12). Broken straight lines are in the plane 1234.

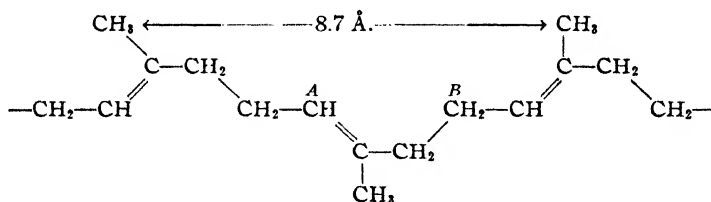
percha and the configuration of each double-bonded group is found to be entirely planar. The single-bond configuration in this substance is different from that in β -gutta-percha; nevertheless, the relations between the methyl groups and chain CH_2 groups are similar; and therefore the data on geranylamine hydrochloride support a substantially planar configuration of the double-bonded group in β -gutta-percha. A comparison of the two sets of atomic co-ordinates proposed for β -gutta-percha will give some idea

of the degree of approximation to be expected at present in structure work on high polymers; it is evident that we cannot hope to determine the finer details of molecular structure, though the general configuration (which is perhaps the most significant aspect for the understanding of physical properties) can be determined with some confidence. Before leaving the subject, it should be noted that in neither of the investigations on β -gutta-percha have thermal motions been taken into account; and that the last word on atomic co-ordinates cannot be said until this has been done. It seems possible that specific unequal thermal movements of crystallographically different atoms might modify the intensities of some of the x-ray reflections in such a way as to lead to the selection of incorrect co-

ordinates for certain atoms when thermal effects are ignored. The examination of such possibilities would constitute a very intricate problem.

α -Gutta-percha.—The structure of the alpha form has not been investigated in detail. All that is known is the molecular repeat distance, which is given by Hauser and Susich (44) as 8.8 Å., and by Lotmar (61) as 8.7 Å.—a length which suggests that there are two isoprene units in the geometrical repeating unit. Knowledge of the configuration of beta molecules, together with the supposition that in alpha molecules the $\text{CH}_2\text{—CH}_2$ chain bonds make the same angle with the plane of the isoprene unit as in beta molecules, has led to the suggestion that alpha molecules have the configuration shown in Figure 6a. There is one other chain, constructed according to the same principles, with a repeating group of two isoprene units. This chain (which may be called the gamma form) is shown in Figure 6b; but in view of its longer repeat distance (9.4 Å.), it is not likely that α -gutta-percha molecules have this configuration.*

Recently, Meyer (61) has suggested for α -gutta-percha a configuration which is a flattened form of Figure 6b, and can be represented as:



In this planar chain, however, carbon atoms *A* and *B* would be only 2.8 Å. apart; it seems more likely that repulsion between these groups would lead to the nonplanar configuration suggested in the last paragraph.

RUBBER

The x-ray study of the crystal structure of rubber dates from the discovery by Katz (1925) that stretched rubber gives an x-ray fiber pattern (50). The spacing of the layer lines immediately gives the molecular repeat distance as 8.1 Å. (It has been variously reported as 8.10, 8.15 and 8.20 Å.) Since the repeat distance of a fully extended chain (Fig. 2a) would be 9.13 Å., it is evident that in the rubber crystal the molecules must be nonplanar.

Several different unit cells have been suggested to account for the fiber pattern. Mark and Susich (59) and Sauter (75) suggested orthorhombic

* It is interesting to note that the chain in geranylamine hydrochloride (5) appears to have this gamma configuration.

four-molecule (eight-isoprene unit) cells of different dimensions, while Lotmar and Meyer (57) proposed a monoclinic four-molecule cell. Morss (66) concluded that all the diffraction spots, except one very weak one on the second layer line, fit a four-molecule orthorhombic cell with sides $a = 12.5 \text{ \AA}$., $b = 8.9 \text{ \AA}$., and $c = 8.1 \text{ \AA}$. better than any other; the very weak reflection which does not fit this cell can be accounted for by doubling the a -axis, giving an eight-molecule cell. The Weissenberg photographs of doubly oriented specimens obtained by van der Wyk and Misch (89) show that the two strongest equatorial reflections are due to planes at 70.4° to each other; this is consistent with Morss's conclusion (the two reflections in question being 120 and 200 for his four-molecule cell), and rules out previously suggested cells, which require different angles between these planes. Morss's larger cell, however, seems unlikely in view of the very high proportion of absent reflections. For this reason, van der Wyk and Misch (89) sought other four-molecule cells but, failing to find a cell of this size which would account for all the reflections, suggest that there may be two different cells (61). Bunn, however, found that, by a small distortion of Morss's four-molecule cell (β being made 92°), all the reflections can be accounted for. It is thus not necessary to postulate the existence of two different crystal structures in stretched rubber. The dimensions of this monoclinic cell are: $a = 12.46 \text{ \AA}$.; $b = 8.89 \text{ \AA}$.; $c = 8.10 \text{ \AA}$.; and $\beta = 92^\circ$. The density of a rubber crystal, according to this cell, is 1.00—a figure which is, as it should be, somewhat higher than the highest observed density of stretched rubber—0.965.

This unit cell survived the subsequent processes of structure determination: it was found possible to account for the relative intensities of all the reflections by an arrangement, in this cell, having the space group symmetry $P 2_1/a$. The derivation of the structure will not be described in detail, but certain points are worth mentioning here.

The first is that, if it is assumed that the single-bond configuration of the chain is similar to that found in β -gutta-percha, and that the double-bond configuration is *cis*, only two chain forms having two isoprene units in the repeat distance are possible; they are shown in Figure 6c and d. Either of these could, by small rotations around the single bonds, attain the correct repeat distance of 8.1 \AA .; both had to be tried. The configuration finally arrived at is a distorted form of Figure 6c.

The second is that, as Morss pointed out, all the equatorial reflections (interpretation of which gives us a projection of the structure in which the molecules are seen end-on) can be accounted for by a cell which has its b -axis halved; and not only that, but this two-molecule cell appears centered;

in other words, when seen end-on, all the four molecules look very similar as regards projected atomic positions and orientation in the cell. This feature simplified the earlier stages of the structure determination, though it was an embarrassment in the later stages.

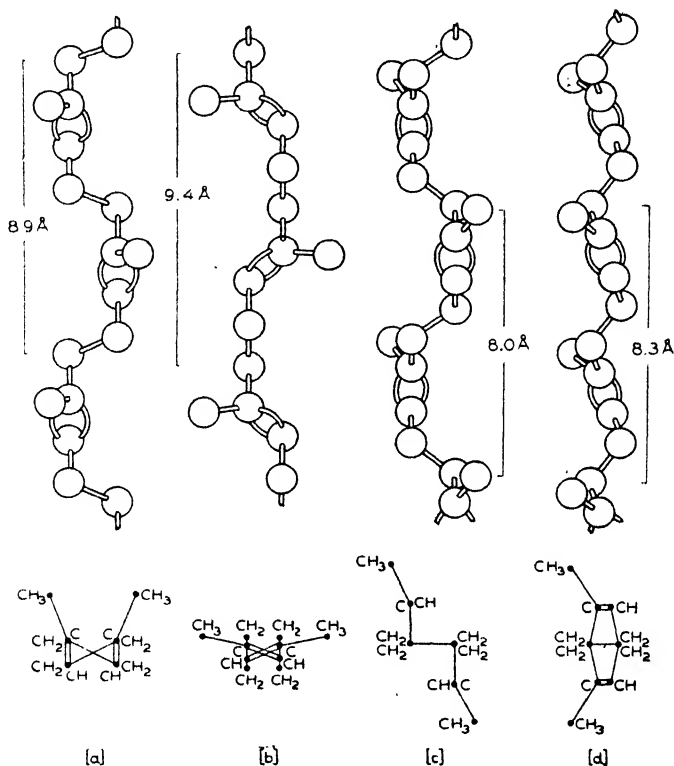


Fig. 6.-(a) Probable structure of α -gutta-percha. (b) Third possible form of gutta-percha (unknown). (c) and (d) *Cis* chains constructed according to the same principle of single-bond orientation. From Bunn (12).

Thirdly, the argument that there are likely to be equal numbers of "up" and "down" molecules in the unit cell was used, as in the case of β -gutta-percha. All these arguments were justified by the final success in obtaining correct calculated intensities.

In attempting to find the co-ordinates of the atoms, the procedure adopted was, first of all, to assume normal interatomic distances and bond angles (and an entirely planar double-bonded group), and then, having ob-

tained a rough fit of intensities, to move the atoms about regardless of anything but the x-ray intensities.

The structure is illustrated in Figure 7, and the details of the configuration of one molecule in Figure 8. The feature which is of greatest interest in

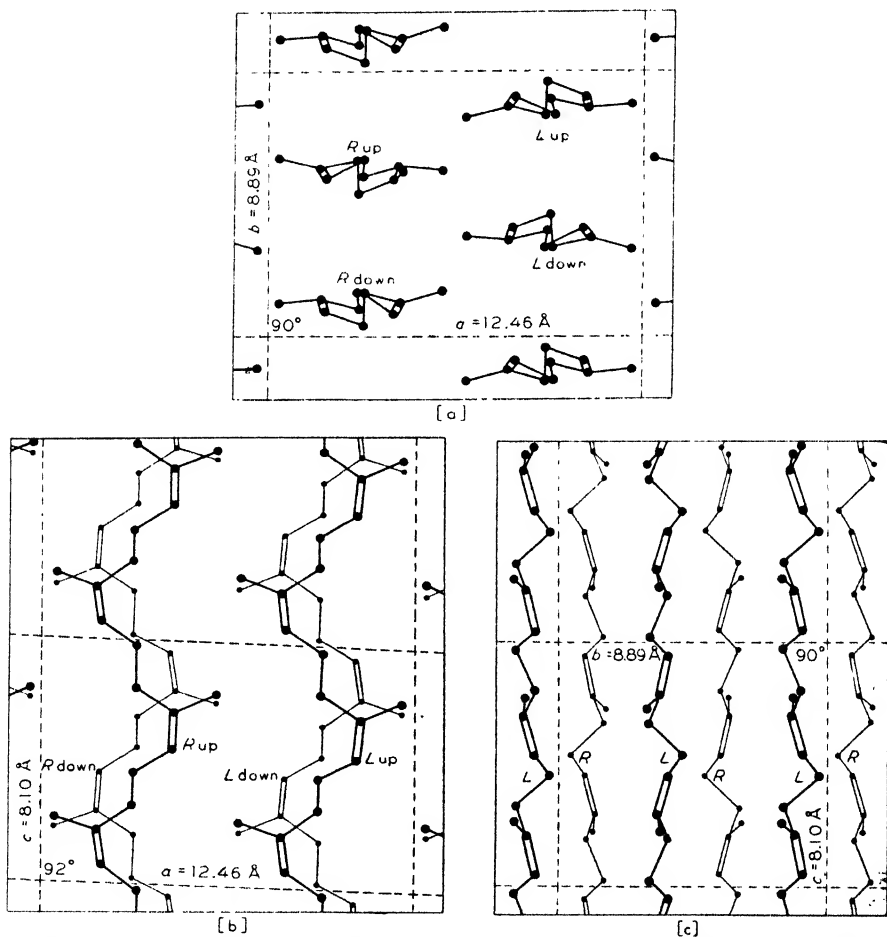


Fig. 7.—Crystal structure of rubber (12) seen along (a) *c*-axis, (b) *b*-axis, (c) *a*-axis.

connection with the physical properties is the nonplanar chain form: as in gutta-percha, the $\text{CH}_2\text{—CH}_2$ chain bonds lie out of the plane of the double-bonded unit. It was, however, found necessary to admit considerable distortions of the "ideal" model (Fig. 6c) to obtain correct intensities:

in the configuration which gives the best agreement between observed and calculated intensities, the two isoprene units which make up the geometrical chain unit are considerably different from each other in the positions of the $\text{CH}_2\text{—CH}_2$ bonds; this indicates considerable freedom of rotation around the single chain-bonds. [The geometrical difference between successive chemical repeating units is formally analogous to the difference between

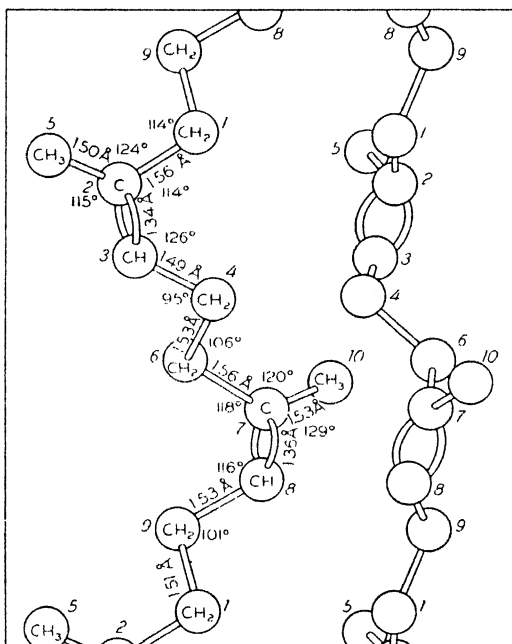


Fig. 8.—Left-handed rubber molecule, seen from two different viewpoints (12).
Bond lengths and angles are necessarily only approximate.

crystallographically different molecules in *trans* azobenzene (29), in which half the molecules are almost exactly planar, while in the others the benzene rings are rotated some 15° about the C—N link.] The chain geometry is discussed in relation to molecular flexibility and rubberlike properties in section III (page 132).

With regard to the details of the structure, it should be remembered that the atomic co-ordinates are necessarily not very accurate; the deviations of the bond lengths in Figure 8 from the normal values (C—C 1.53, C=C 1.33 Å. are not significant though certain deviations of bond angles from the normal values ($\text{>C } 109\frac{1}{2}^\circ$, $\text{>C } 125^\circ$) may possibly have some sig-

nificance. It is also noteworthy that the double-bonded groups appear to be not strictly planar, the methyl groups in particular being displaced in the same way as in Bunn's structure of β -gutta-percha. The question arises (as in the case of β -gutta-percha) whether this feature is genuine. The problem of the simultaneous adjustment of 30 variable parameters, entirely by the method of trial and error, is of course extremely complex; whether it is possible to find a modified set of atomic co-ordinates, based on strictly planar double-bonded groups, which will account for the observed intensities, remains to be seen. It seems to the writer doubtful whether it is worth while attempting this without at the same time attempting to take into account the unequal thermal motions of different atoms.

POLYCHLOROPRENE

This substance, the chemical structure $(-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-)_n$, of which is analogous to that of gutta-percha and rubber, was first prepared by Carothers and his collaborators (20). It is rubberlike at room temperatures. An x-ray fiber photograph of a stretched specimen, published in the original paper, indicates a molecular repeat distance of about 4.8 Å., and this immediately suggests that its chain configuration is like that of gutta-percha rather than that of rubber.

Krylov (53) obtained an electron diffraction pattern, and suggested an orthorhombic unit cell with dimensions 9.0, 8.23 and 4.79 Å. These figures, together with the density figure of 1.23, lead to the unlikely conclusion that there are three monomer units in the unit cell. (Three is an extremely unlikely number for an orthorhombic cell.)

Clews (27) suggested an orthorhombic cell having dimensions 8.90, 4.70 and 12.21 Å. to account for his x-ray diffraction patterns. But this cell does not account satisfactorily for the positions of the reflections. Finding that some of the equatorial reflections could not be given $h0l$ indices (b being the fiber axis), Clews states that "we are not dealing with a single-crystal rotation type of diagram produced by rubber but with a Debye-Scherrer photograph showing preferred orientation," and gives some of the equatorial reflections hkl indices. This is inconsistent with the deduction of the fiber repeat distance from the spacing of the layer lines, which rests on the assumption that all the equatorial reflections have $h0l$ indices, those of the first layer line $h1l$, and so on. (Incidentally, in this paper, the density is given as 1.086. Carothers gives 1.23 and Meyer 1.27.)

Bunn (12) found that all the diffraction spots could be accounted for by a four-molecule orthorhombic cell having dimensions 8.84, 10.24 and

4.79 Å., and showed that the relative intensities could all be accounted for by a structure which is entirely analogous to that of β -gutta-percha (space group $P 2_12_12_1$). The structure is illustrated in Figure 9. The molecular configuration and the type of arrangement are analogous to those of β -gutta-percha, but the orientation of the molecules is considerably different, presumably owing to the different sizes and electrical characters of the chlorine and methyl substituents.

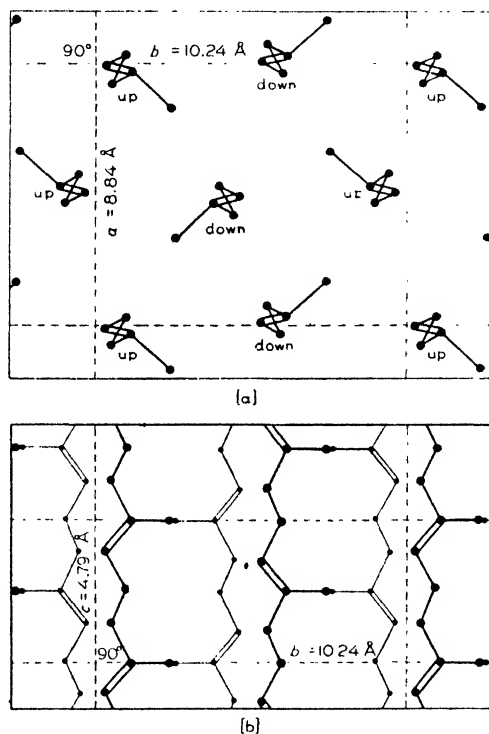


Fig. 9.—Crystal structure (12) of polychloroprene seen along (a) c -axis, (b) a -axis.

The chain configuration rests chiefly on the x and y co-ordinates, which could be deduced satisfactorily from the $hk0$ reflections. On the other layer lines there are very few reflections, and the z co-ordinates are therefore very approximate.

3. Butadiene Polymers

Most of the polymeric materials obtained from butadiene (certain of the "Buna" synthetic rubbers, for instance) do not crystallize on freezing or on

stretching. Probably both 1,4 and 1,2 polymerization, occurring indiscriminately, lead to an irregular molecular structure. But Meyer (61)

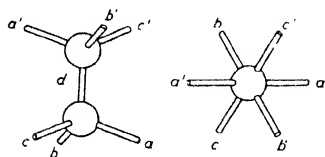
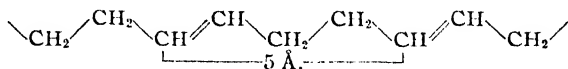


Fig. 10.—Bond positions in saturated molecules (13).

reports one type of emulsion polymer which on stretching gives an x-ray fiber diagram (though evidently it is a very poor one). Although the repeat distance appears to be about 2.5 Å., Meyer suggests that the true repeat distance is twice this length, the material being a 1,4 polymer with a fully extended chain:



The interpolymers of butadiene with other substances (such as styrene), which form the bulk of the synthetic rubber made at the present time, do not crystallize; therefore structural information has not been obtained by x-ray methods.

4. Rubber Hydrochloride

The substance, $[-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)\text{Cl}-]_n$, made by the action of hydrogen chloride on rubber has a melting point (115° C.) much higher than that of rubber itself. Drawn specimens give detailed x-ray fiber patterns, first obtained by Gehman, Field and Dinsmore (41). The repeat distance along the fiber axis (8.95 Å.) indicates that the chains are not fully extended.

A complete interpretation of the fiber pattern has been put forward by Bunn and Garner (15). The probable configuration of the chain had been predicted (13) by the application of a new stereochemical generalization known as the "principle of staggered bonds." In singly linked molecules, the bonds of joined carbon atoms tend to be staggered, as in Figure 10. In chain molecules, any three successive chain bonds may occupy positions $a'da$, $a'db$ or $a'dc$; these configurations will be called *A*, *B* and *C*, respectively. The plane zigzag structure possessed by many chain compounds is an *A* sequence. Other possible regular sequences have characteristic repeat distances, and it is found that

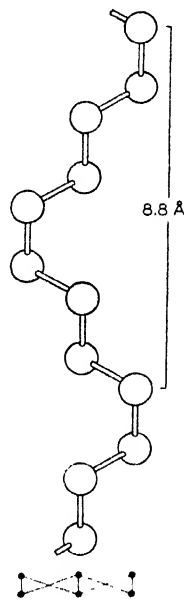


Fig. 11.—Chain type A_2BA_2C (15). At bottom, end view of chain.

the only fairly simple chain having a repeat distance of about 8.95 Å. is $(AAABAAAC)_n$ (Fig. 11). It was therefore assumed that this is the chain configuration in rubber hydrochloride; and, on this basis, attempts were made to account for the intensities of the reflections.

The reflections all fit a rectangular cell having $a = 5.83$ Å., $b = 10.38$ Å. and $c = 8.95$ Å., through which two chain molecules pass. It was found possible to account satisfactorily for the intensities (and thus for the entire diffraction pattern) by an arrangement which is not orthorhombic, but has the monoclinic symmetry $P 2_1/c$, the angle of β being "accidentally"

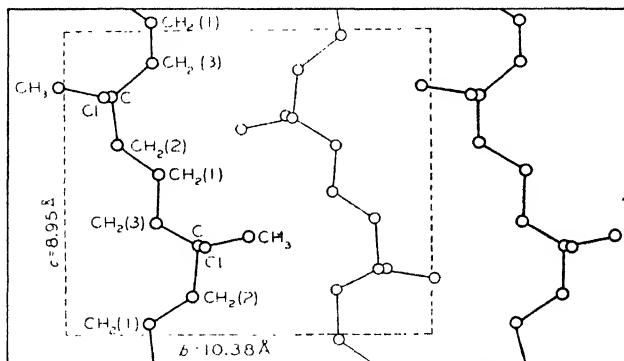


Fig. 12.—Crystal structure of rubber hydrochloride, seen along the a -axis (15).

90° owing to the manner in which the molecules fit into one another. A view of the structure as seen along the a -axis is shown in Figure 12. The molecular configuration is interesting as the first well-authenticated example of a saturated organic chain molecule with a meandering chain configuration.

5. Polyethylene

The substance produced when ethylene is heated to about 200° C. at pressures of the order of 1000 atmospheres resembles gutta-percha in appearance and mechanical properties. It melts at about 115° C., specimens of comparatively low molecular weight giving very viscous liquids, while those of high molecular weight become rubberlike above the melting point (71).

The molecules in this substance are for the most part long CH_2 chains. A description of its structure is included here (in spite of its rather high melting point) for two reasons. First, its features have a bearing on the technique of interpretation of diffraction patterns of high polymers in

general. Second, it is of fundamental importance in the consideration of the relation between molecular structure and physical properties.

X-ray diffraction photographs of cold-drawn threads and rolled sheets show that the repeat distance along the molecule is 2.53 Å., which suggests at once that the carbon chain is a plane zigzag as in the paraffin wax hydrocarbons (46, 67). Interpretation of the complete diffraction pattern by

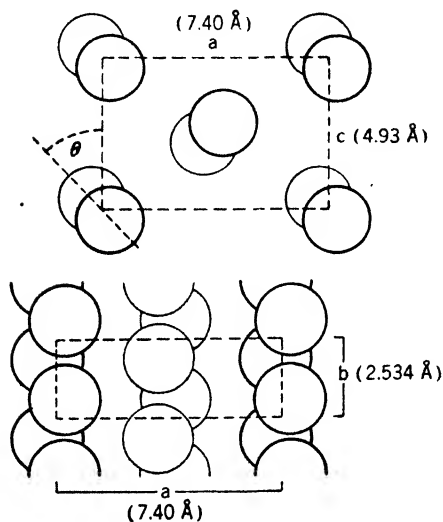


Fig. 13.—Crystal structure of polyethylene (10): above, seen along the b -axis; below, seen along the c -axis.

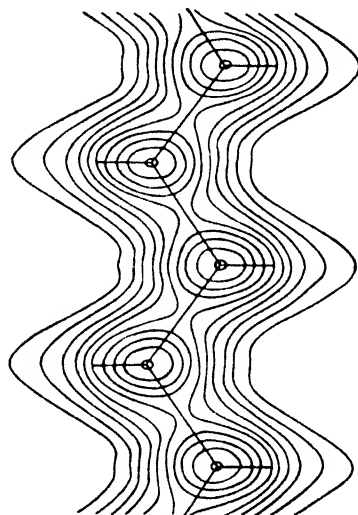


Fig. 14.—Section through the polyethylene molecule showing contours of equal electron density (10).

Bunn (10) confirms this, and leads to the conclusion that the molecules are arranged as in Figure 13. The crystal structure may be described by the following parameters: $a = 7.40$ Å., $b = 4.93$ Å. and $c = 2.534$ Å.; space group $Pnam$. Co-ordinates of carbon atoms: $x, -y, \frac{1}{4}$; $-x, y, \frac{3}{4}$; $-x + \frac{1}{2}, -y + \frac{1}{2}, \frac{3}{4}$; $x + \frac{1}{2}, y + \frac{1}{2}, \frac{1}{4}$, where $x = 0.038 a$ and $y = 0.065 b$. The final parameters of the carbon atoms are based on a Fourier synthesis of the structure amplitudes of all the reflections, which were determined by photometric measurements of powder photographs. This was only possible because of the extreme simplicity of the structure and the fact that overlapping of the reflections was not serious.

An interesting conclusion which came out of this work was that the electron clouds of the CH_2 groups are effectively far from spherical, but are drawn out in the plane of the C—H bonds (the plane normal to the chain

axis) (see Fig. 14). Part of this effect is probably due to anisotropic thermal vibrations in the crystal—the thermal vibrations are much greater in directions normal to the chain axis than they are along the chain. But there is evidence that it cannot be entirely attributed to anisotropic thermal vibrations, or to the combined effects of thermal vibrations and crystal distortions (which would affect the intensities in a way similar to thermal vibrations); a part of the effect seems to be due to a real distortion of the electron cloud of the CH_2 group. The magnetic properties of crystals of chain compounds point in the same direction (55). The significance of this state of affairs, from the point of view of structural studies of chain polymers in general, is that the apparent diffracting power of a CH_2 group is greater for crystal planes parallel to the plane of the three nuclei than for all other planes. In polymer crystals in which all the CH_2 groups are parallel to each other and perpendicular to the chain axis (so that thermal effects are added to that of the real distortion of the CH_2 groups), the apparent diffracting power is about twice as great for the plane parallel to the three nuclei as it is for planes perpendicular to that of the three nuclei; and this should be remembered in calculating the structure amplitudes. For polymer crystals in which planes of the CH_2 groups are not all parallel to each other, it would be much more difficult to allow for the effect; and, so far, attempts have apparently not been made to do so. However, for many crystal planes the effects of the different CH_2 groups may partly neutralize each other, and thermal effects are not likely to co-operate wholly with the "distorted electron cloud" effect. The embarrassing effects on the relative intensities of the reflections would therefore be, on the whole, less than in polymers with parallel CH_2 groups.

It must be emphasized that only the extreme simplicity of the polyethylene structure made it possible to draw conclusions on the finer details of the structure. For most other polymers it will not be possible to do this. Second, because of thermal effects and the "distorted electron cloud" effect (for polymers containing a preponderance of CH_2 groups), we must not expect to be able to account precisely for the relative intensities of the reflections, or to attain any great precision in locating the atomic centers—not at present, at any rate. With the advance of knowledge, it may eventually be possible to take these effects into account quantitatively and to attempt a more precise interpretation of the x-ray diagrams.

6. *Polyvinyl Alcohol*

This substance, which is obtained by the hydrolysis of polyvinyl acetate, is a crystalline solid which softens on warming and may then be crystallized

by stretching (61). The "melting" point does not appear to have been recorded. The fiber photograph shows that the molecular repeat distance is not significantly different from that of polyethylene—it is given as 2.57 Å. by Halle and Hofmann (42), 2.52 Å. by Mooney (65). This means that the carbon chain is a plane zigzag as in polyethylene; and, moreover, the hydroxyl groups must be on alternate carbon atoms and in corresponding stereo positions, as in Figure 15a. Thus the structure of individual molecules is settled by a single measurement (the fiber repeat distance).

All the reflections on the fiber photograph (about 30 in number) were found by Mooney (65) to fit a rectangular cell having the dimensions $a = 7.82$ Å., $b = 2.52$ Å. and $c = 5.60$ Å.

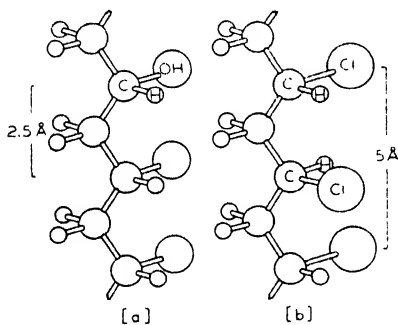


Fig. 15.—(a) Structure of molecule of polyvinyl alcohol. (b) Structure of molecule of polyvinyl chloride.

Two chain molecules pass through this unit cell; the calculated density, accepting this cell, is 1.31, which is a little higher than the measured density of 1.293. The only definite systematic absences are $0kl$ reflections having k odd; if these are genuine space group absences, this means that there is a glide plane normal to a having a translation of $\frac{1}{2}b$. Mooney has suggested a molecular arrangement having the monoclinic symmetry $P 2_1/m$, *i. e.*, containing no glide plane. This arrangement does

not explain the absences mentioned; moreover, the molecular positions suggested would not mean accidental (*i. e.*, non-space group) absences of $0kl$ reflections having k odd; in fact, the intensities given by the suggested arrangement as it stands do not agree with those observed. Mooney, however, presents the following argument: "Planes of the type hkl are experimentally indistinguishable from planes of the type $\bar{h}kl$, though their intensities cannot be the same. If, for convenience in calculating, the viewpoint of approximately equal numbers of oppositely directed chains is adopted, it follows that four quasi-equivalent points are simultaneously involved in the production of a given intensity as observed; namely, xyz ; \bar{x} , $y + \frac{1}{2}$, \bar{z} ; and also $\bar{x}yz$; x , $y + \frac{1}{2}$, \bar{z} . Therefore, the summation for the structure amplitude must include terms for all four points. These, combined trigonometrically, give for each set of atoms the expressions: $F = 4f \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz$ for k even, and $F = -4f \sin 2\pi hx \sin$

$2\pi ky \cos 2\pi lz$ for k odd, which explain the vanishing of planes $0kl$ where k is odd."

It must be observed that, if expressions for the structure amplitude are added together in this way, this implies that waves diffracted by the atoms concerned combine and interfere with each other, and that the atoms actually have the co-ordinates given, in each unit cell. In other words, the amplitudes calculated by these expressions refer to a structure (of orthorhombic symmetry) having half an atom at each of the positions given above. This is clearly unacceptable; and although the calculated structure amplitudes do show a rough agreement with those observed, this agreement must be regarded as fortuitous. [The agreement is actually very rough; if, instead of structure factors, F , the intensities (proportional to F^2) had been listed—this corresponding to a comparison between a theoretical x-ray fiber photograph and the actual photograph—it would be more obvious that there are serious discrepancies.]

The structure of this substance requires reconsideration. Actually, the arrangement suggested by Mooney looks reasonable in respect to clearances between molecules and the association of molecules in pairs linked by hydroxyl bonds; but this arrangement would certainly give appreciable intensities for $0kl$ reflections with k odd, and therefore does not represent the arrangement actually present in polyvinyl alcohol. With regard to the calculation of the intensities for the general planes, it has already been pointed out that it is not permissible to add the amplitudes for hkl and $\bar{h}kl$ planes; the structure amplitudes must be worked out separately, and squared to give numbers proportional to intensities; it is these numbers which must finally be added together to give figures representing the intensities of the composite spots on the x-ray photographs.

7. Other Polyvinyl Compounds

No further polyvinyl compounds have been studied from the structural point of view in detail. And, among those falling within the scope of the present survey, only in one case is there any clear evidence on molecular configuration.

The polymer of vinyl chloride, $\text{CHCl}=\text{CH}_2$, is not rubberlike at room temperature; but plasticized material is much used for insulating sleeving and other purposes for which flexibility or moderate elasticity is desirable; its retraction after distortion is very sluggish compared with that of rubber. The chemical evidence of Marvel (60) indicates that the monomer units are for the most part joined head-to-tail; the structure of the polymer is thus $(-\text{CHCl}-\text{CH}_2-)_n$. Oriented fibers can be obtained, and the x-ray

diffraction pattern shows rather diffuse spots, indicating that the crystalline regions either are extremely small or are very imperfect. The layer line separation gives a molecular repeat distance of $5.0 \pm 0.05\text{\AA}$.—almost exactly double that of polyvinyl alcohol. This suggests that the carbon chain is a plane zigzag but that the chlorine atoms are in alternate stereo positions as in Figure 15b. For the fact that crystallization is far less perfect than in polyvinyl alcohol (or any of the other polymers so far discussed), different explanations might be offered.

(1) There may be occasional monomer units connected head-to-head, tail-to-tail (the chemical evidence does not exclude this possibility).

(2) Even if all the monomer units are connected head-to-tail, there is a possibility of geometrical irregularity; it may be that, although many of the chlorine atoms occupy left- and right-handed positions alternately along the chain, yet in some sections they may be indiscriminately placed; such irregular portions of molecules would not form crystalline arrangements.

Polyvinyl acetate, $[-\text{CH}_2-\text{CH}(\text{O.CO.CH}_3)-]_n$, and polystyrene, $[-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n$, are glasslike substances at room temperature, but soften at about 80° , becoming somewhat rubberlike. They do not, however, crystallize on stretching. The x-ray patterns of the unstretched materials show the very diffuse rings characteristic of noncrystalline substances. On stretching, in each case one of the rings becomes slightly more intense on the equator, indicating that some molecular orientation occurs. The average spacing of the ring affected in this way is 7 \AA . for polyvinyl acetate and 10 \AA . for polystyrene; these spacings represent roughly the average thickness of the chain molecules (51).

Polymethyl acrylate, $[-\text{CH}_2-\text{CH}(\text{CO.OCH}_3)-]_n$, and polymethyl methacrylate, $[-\text{CH}_2-\text{C}(\text{CH}_3)(\text{CO.OCH}_3)-]_n$, are also glasslike substances, giving diffuse x-ray patterns. They have not been obtained in crystalline form. Orientation has not been reported in stretched specimens; but it is relevant to mention here that electron diffraction patterns (28) of multilayers (7) of these polymers indicate some degree of orientation, and that this led Coumoulos (28) to propose a reasonable interpretation of the different diffuse bands in terms of chain spacings and side spacings. According to this interpretation, the glasslike polymers mentioned here (together with some others, but excluding polystyrene which was not studied) have approximately plane zigzag main chains, with side chains alternately in left- and right-handed positions and lying in planes approximately normal to the main chain axis.

In attempting to explain the noncrystalline character of these polymers,

it will be postulated that polymers whose molecules are chemically and geometrically regular will crystallize—if not under normal conditions, then on very slow cooling, or on stretching in the rubberlike condition. If this is so, then the failure of the substances under consideration to crystallize must be ascribed to structural irregularities of some kind in the molecules. The irregularities, which may be of two kinds (see above), are presumably more frequent than in polyvinyl chloride.

Such a view is not inconsistent with the Coumoulos picture; it may be that the majority of the side groups in polymers of this type are regularly placed; a minority of irregularly placed side groups would be sufficient to prevent crystallization altogether.

In the case of polyvinyl acetate, there is some indirect evidence on the question of the type of irregularity. Polyvinyl alcohol, which is made by the hydrolysis of polyvinyl acetate, has a regular structure. Therefore, in the ester the side groups are certainly on alternate carbon atoms; polymerization is evidently consistently head-to-tail. It also appears at first sight (in view of the undoubted molecular structure of polyvinyl alcohol) that the ester groups must all be in corresponding positions as in the alcohol. This, however, does not follow: if, on hydrolysis, the whole $—O—CO—CH_3$ group is detached, there is left (momentarily) a chain carbon atom bearing only one hydrogen atom, the other bond being free; the hydrogen atom might well change over from one stereo position to the other, in response to some local stimulus—for instance, an OH group already established on the next but one chain carbon atom might influence the hydrogen in this way; and thus, it is not impossible that regular polyvinyl alcohol might be produced from irregular polyvinyl acetate. The evidence is consistent with the view that the noncrystalline character of polyvinyl acetate is due to the occurrence of the side groups indiscriminately in left- and right-handed positions, at some points along the chain.

8. *Polyisobutene*

This substance, made by polymerization of isobutene, $CH_2=C(CH_3)_2$, in the presence of boron fluoride at low temperature, is rubberlike at room temperature. Its extensibility (up to 15 times the original length) appears to be even greater than that of rubber, and it crystallizes on stretching, giving a diffraction pattern (8) sharper and far more complex than that of rubber. "Butyl rubber," made by interpolymerization of isobutene with a little butadiene (4), gives the same diffraction pattern on stretching (80). The molecular repeat distance is given by Brill and Halle (8) as 18.5 Å. Fuller, Frosch and Pape (37) have gone further, and have

shown that all the reflections can be accounted for by a rectangular unit cell having the dimensions $a = 6.94 \text{ \AA}$., $b = 11.96 \text{ \AA}$. and $c = 18.63 \text{ \AA}$. The same conclusion was reached independently by the present writer (unpublished work). The $00l$ reflections were recorded by Fuller, Frosch and Pape by taking photographs of specimens inclined to the x-ray beam.

The rectangular character of the cell suggests orthorhombic symmetry. The only systematic absences of reflections are the odd orders of $h00$, $0k0$ and $00l$, suggesting that the space group symmetry is $P 2_12_12_1$. [Electron diffraction photographs by Storks (37) show what appear to be weak 100 and 003 reflections; if these are genuine, there cannot be screw axes parallel to a and c , and the space group symmetry would appear to be $P 22_12_1$.]

The problem of the determination of atomic positions in the unit cell is an exceedingly complex one and has not yet been solved. In the first place, the molecular repeat distance (18.6 \AA .) is remarkably long; since 18.6 is longer than seven times the repeat distance of a fully extended plane zigzag chain ($7 \times 2.53 = 17.7 \text{ \AA}$.), there must be at least eight isobutene units in the geometrical repeating unit; and, since 18.6 is less than $8 \times 2.53 (= 20.2 \text{ \AA}$.), the chain must be shortened by rotation around the single bonds. The principle of staggered bonds is not likely to be helpful in this case, because there is extreme overcrowding of the side groups. If a model is made, and the configuration is varied by rotation around the chain bonds, it can be seen that, whatever configuration is assumed, the distances between methyl groups in neighboring pairs cannot be less than 2.6–2.7 \AA .—much less than the normal distance between unbonded methyl groups (3.6 \AA .). The configuration is therefore likely to be strongly influenced by the repulsions between these side groups.

Fuller, Frosch and Pape have considered what configurations have the repeat distance of 18.6 \AA ., and find that, if, starting with a plane zigzag chain with pairs of methyl groups on alternate chain carbon atoms, rotations are made around the single bonds so that the pairs of methyl groups form a helix around the chain axis, the helix which repeats after eight monomer units has the correct repeat distance of 18.6 \AA . (Fig. 16b). There is another configuration (having about the same repeat distance) resulting from four rotations in one direction followed by four in the opposite direction (Fig. 16a). Now the a and b unit cell dimensions are such that there are likely to be two chain molecules running through the cell; this would mean that there are sixteen monomer units in the unit cell, giving a density of 0.96. This is in satisfactory excess of the measured density of unstretched polyisobutene, 0.915.

In support of this type of helical configuration, Fuller, Frosch and Pape state that the 008 reflection is strong and 004 weak: pairs of methyl groups spaced $\frac{c}{8}$ apart would give a strong 008, if the two molecules passing through the cell have their methyl groups on the same level. It must be pointed out, however, that the estimates of the intensities of the 00 l reflections are based on photographs of stretched fibers set at definite angles to the x-ray beam. Now the orientation of the crystalline regions in polyisobutene is extremely good, so that the 001 planes of all the crystals are almost parallel to each other—the specimen may be regarded almost as a single crystal as far as the 00 l reflections are concerned. Consequently, the intensity of each 00 l reflection depends very much on the exact angle of the fiber axis to the beam; if this angle happens to be just right for any reflection, that reflection will be recorded very strongly on the photograph, even if its structure amplitude is very small. In this work, the fiber axis was apparently set at angles 5° apart (photographs are shown for 15° , 20° and 25°); it so happens that the Bragg angles for 002, 004, 006 and 008 are $4\frac{3}{4}^\circ$, $9\frac{1}{2}^\circ$, $14\frac{1}{3}^\circ$ and $19\frac{1}{4}^\circ$, respectively, and these reflections would be likely to be recorded far too strongly in relation to other reflections. They are also not comparable among themselves. The writer has taken photographs with the fiber axis oscillating at constant speed with respect to the beam; these photographs show 008 extremely weak in comparison with 018 (it is only just visible on a photograph showing 018 very intense), and 004 about the same strength as 008. (Fuller, Frosch and Pape give 004W, 008S, 018VS.) The 00 l intensities therefore do not support the suggested helical configuration. But they also do not disprove it, for pairs of methyl groups on neighboring molecules may not have the same co-ordinates along c ; and in this case we should not expect 008 to be strong. It is therefore necessary to consider other intensities.

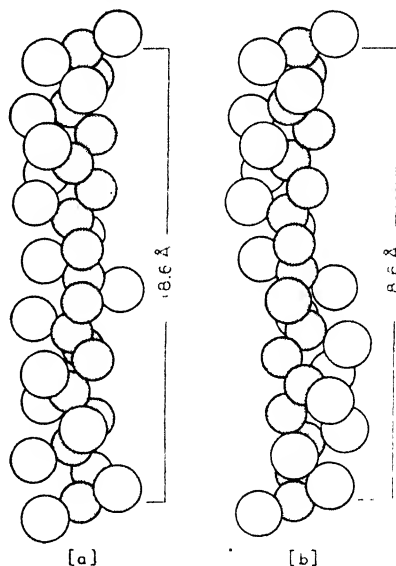


Fig. 16.—Possible molecular configurations of polyisobutylene suggested by Fuller, Frosch and Pape (37).

Detailed consideration of the intensities is rendered difficult not only by the size of the unit cell, but also by another circumstance: the length of the b -axis is exactly $\sqrt{3}$ times that of the a -axis, and for this reason many reflections are superimposed. [Attempts to make doubly oriented specimens for the purposes of separating these reflections failed, though the extremely thin films prepared for electron diffraction work (37) do show some signs of double orientation.] However, in a general way it may be said that the great strength of several reflections on the eighth layer line indicates a subperiod of $\frac{c}{8}$, in support of the idea that there are eight monomer units in the geometrical repeating unit. But by the same type of argument, the great strength of the first few reflections on the fifth layer line is an indication of a subperiod of $\frac{c}{5}$; neither of the helical models in Figure 16 has such a feature. Moreover, in the case of the straightforward helix of Figure 16b, the projection in any direction normal to the chain axis shows the methyl groups lying on a pronounced S curve, a feature which would give rise to some strong reflections on the first layer line. Actually, on the diffraction pattern, all the reflections on the first layer line are weak.

For these reasons, the writer's opinion is that the helical configurations suggested by Fuller, Frosch and Pape are not likely to be correct. It is to be hoped that further attempts will be made to solve this difficult structural problem; the unique character of the diffraction pattern—by far the sharpest and most detailed fiber pattern known so far—indicate remarkably perfect crystallization on stretching, which suggests unique chain flexibility; and the theoretical problems raised by the apparent flexibility of molecules with grossly overcrowded side groups (see section III) make polyisobutene one of the most interesting of chain polymers.

9. Polyesters

The substances made by the condensation of dibasic acids with dihydric alcohols were among the first high polymers made by Carothers and his collaborators (16, 17, 19b). The melting points (18, 38) of members of a series of such substances made from monomer molecules of various lengths—up to decamethylene glycol and sebacic acid, $\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$ —range from 40° to 80° C., with two exceptions: ethylene malonate, $[-\text{O}(\text{CH}_2)_2\text{O}-\text{CO}-\text{CH}_2-\text{CO}-]_n$, which apparently has a melting point below room temperature; and ethylene succinate, $[-\text{O}(\text{CH}_2)_2\text{O}-\text{CO}(\text{CH}_2)_2-\text{CO}-]_n$, which melts at about 108° C.

Most of our knowledge of the crystal structures of these substances we owe to Fuller and his collaborators (33-36). Since the earlier work has been

summarized by Fuller (33), we shall therefore mention only the salient points. The polyesters of the ethylene glycol and decamethylene glycol series which have an odd number of chain atoms in each chemical repeating unit of the chain have fiber repeat distances which indicate that there are two chemical units in the geometrical unit; for instance, polyethylene azelate, $[-O(CH_2)_2O-CO(CH_2)_7CO-]_n$, has $c = 31.2 \text{ \AA.}$, almost exactly twice the expected length of one chemical unit in the fully extended plane zigzag configuration. The even polyesters of these series apparently have only one chemical repeating unit in the geometrical unit; for instance, polyethylene sebacate, $[-O(CH_2)_2O-CO(CH_2)_8CO-]_n$, has $c = 16.9 \text{ \AA.}$, almost exactly the length of one fully extended chemical unit. These lengths are actually a little less than the expected fully extended lengths, so that, unless some of the bond distances or angles are abnormal, the chains must be a little shortened by rotation around the chain bonds. Polyethylene succinate is exceptional: its repeat distance of 8.32 \AA. indicates considerable shortening of the chains and thus a pronouncedly nonplanar configuration.

The odd polyesters of these series apparently have rectangular unit cells, the a and b edges of which are 5.0 and 7.40 \AA. , respectively. These dimensions are almost exactly the same as those of polyethylene, suggesting a somewhat similar molecular arrangement. Fuller has proposed a possible arrangement of the molecules (Fig. 17a) in which the $C=O$ groups lie in planes normal to the c -axis; the symmetry of the arrangement is, however, not orthorhombic, but monoclinic. (If a - and b -axes are interchanged to attain conventional monoclinic orientation, the space group is $P 2_1/a$.)

In the even polyesters, the unit cell is apparently of monoclinic type, with $a = 5.5 \text{ \AA.}$, $b = 7.40 \text{ \AA.}$ and $\beta = 65^\circ$. The arrangement suggested by Fuller for these molecules is shown in Figure 17b; the $C=O$ groups lie in planes inclined to the c -axis. (It should be noted that the symmetry of the arrangement as shown is not monoclinic, but triclinic; but, if the center molecule is rotated through 180° , giving an arrangement which seems equally probable, the monoclinic symmetry $P 2_1/a$ is attained.)

The situation is in some cases complicated by the occurrence of polymorphic forms in the same specimen. Fuller suggests that the polymorphic structures are related to each other by the displacement of neighboring molecules along the c -axis by multiples of the zigzag unit distance of 2.5 \AA. , an application of a suggestion first made by Schoon (79) to account for the polymorphism among chain compounds of molecules containing up to 30 carbon atoms.

More recently, Fuller, Frosch and Pape (38) studied some polyesters of

the trimethylene glycol series, with very interesting results. The repeat distances along the fiber axis are shorter than the length of two fully extended chemical units, by a nearly constant amount of 2.8 Å.; this suggests (on the basis of what has already been said in this account) that the chains are shortened by rotation around chain bonds. Fuller *et al.* con-

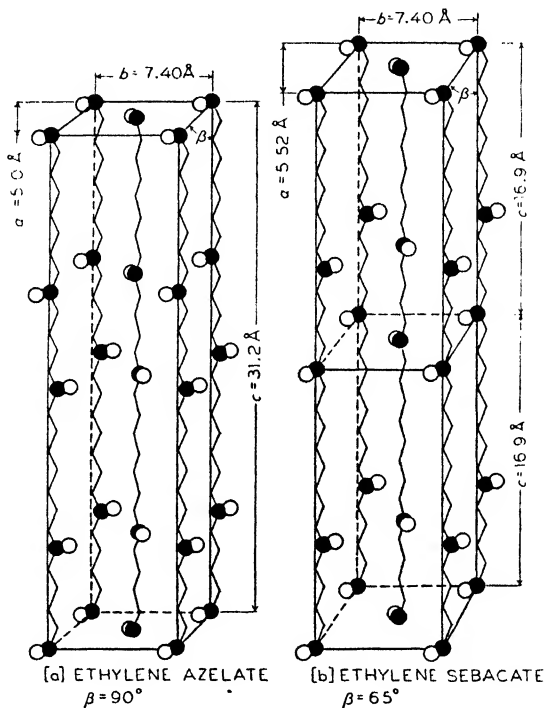


Fig. 17.—Possible structures of polyesters suggested by Fuller (33): (a), odd type; (b), even type. Hydrogen atoms are omitted. ● Carbon. ○ Oxygen.

sider some possible configurations of this sort, but reject them* and take the view that each chain is a planar zigzag tilted with respect to the fiber axis. In support of this suggestion, it is pointed out that, on the fiber patterns, which are quite unlike those of the polyesters previously discussed, there are very strong reflections (suggesting side spacings) not only on the equator but also on upper and lower layer lines. The idea is, however, contrary to the expectation "that the crystallites would follow molecular

* *Note added in proof:* In a later paper which has just come to the writer's attention, Fuller and Baker (33a) express different views, and in fact make the same suggestion as is given here on p. 131.

lines in their habit and would orient with their long axes parallel to the fiber axes"—an expectation which appears to be fulfilled in all other fibers which have been studied in detail. It is therefore desirable to seek an alternative explanation. These authors point the way to what seems a reasonable explanation by their proposal of a structure with alternately tilted repeating units, which "has the advantage of progressing in the fiber direction and in addition more readily explains the fact that the structure repeats every second chemical unit whether it contains an even or an odd number of atoms." But they add: "On the other hand, it is difficult to imagine crystallites constructed of chains possessing such a configuration." The writer can see no difficulty here: chains having a large-scale zigzag configuration would interlock very well—one has only to imagine a chain of the rubber hydrochloride type (Figs. 11 and 12, pages 118 and 119) with the limbs much lengthened. The strong reflections on upper and lower layer lines would be well explained by such a structure; and the writer has found that, if it is assumed that the "kinking" occurs in the trimethylene glycol portion of the chain—giving a staggered-bond configuration of type *ABBA* or *ACCA* instead of the planar zigzag *AAAA* (13)—then chains with appropriate repeat distances (and probably appropriate C=O positions to explain the intensities of 00 l reflections) can be constructed.

The polyesters of the trimethylene glycol series are of great interest for another reason, for Fuller, Frosch and Pape, in the same paper (38), have shown that, on stretching some of the polyesters, the fiber pattern changes completely, and the repeat distance increases. If the configuration suggested in the preceding paragraph is correct, the most natural explanation is that, on stretching, the molecule straightens out by rotation around the chain bonds, a behavior recalling that suggested by Astbury in the case of the hair protein, keratin (2). These are the first synthetic polymers to behave in this manner; it is highly desirable that a detailed interpretation of their fiber patterns be attempted.

10. Other Rubberlike Substances

Several other polymers with rubberlike properties have been investigated by x-ray diffraction methods, among them polyethylene sulfides (the basis of "Thiokol" synthetic rubbers) and the inorganic substances, elastic sulfur and polyphosphonitrilic chloride [probably $(-\text{PCl}_2=\text{N}-)_n$]; but there is no recent work on these substances, and the older work has recently been summarized by Meyer (61). It must suffice to mention that unit cell dimensions have been suggested for both the inorganic substances (62, 63) and for polyethylene tetrasulfide (51), and that none of these chains appear

to be planar. For polyphosphonitrilic chloride, the space group appears to be *Pna* and an arrangement of the molecules has been suggested (63); but intensities have not been calculated.

III. Molecular Structure and Physical Properties

It has been said at the outset that chain polymers of regular structure and very high molecular weight are rubberlike above their melting points. Those which are rubberlike at room temperature are those having melting points below room temperature. Any attempt to explain why one polymer is rubberlike and another crystalline at room temperature must be, first of all, an attempt to explain the melting points in terms of molecular structure. The phenomenon of melting is not at all well understood, except in a broad general way, even in the case of simple molecules. But although the time is not ripe for an attempt at quantitative treatment, it appears that qualitative ideas of some value may be gained by combining a simple kinetic conception of melting with the conception of chain flexibility.

It is first necessary to say a little about the indefiniteness and variability of the melting points of high polymers. These substances do not melt sharply at a definite temperature, but over a range of at least several degrees. This is undoubtedly connected with the fact that crystallization in these substances is never complete; there is always a certain amount of amorphous material, as is shown by the diffuse ring which accompanies the crystalline x-ray diffraction pattern. Any one molecule passes through a number of different crystalline regions; the sections of molecules lying between one crystalline region and the next constitute the amorphous material. The pull of the "tying" portions of molecules must affect the melting points of the crystals to which they are tied, to a degree depending on the size of the crystalline regions and other local conditions (1, 87); thus, on heating, portions of molecules leave the crystals and join the amorphous material at different temperatures; and some crystals melt completely before others; the result is that the proportion of amorphous, melted material increases with rise of temperature.

The melting points of some polymers (the polyesters, for instance), though not sharp, are not reported to be very variable; but for rubber itself the melting point varies considerably with its past history. Most specimens of raw rubber melt between -5° and $+16^{\circ}$ C. (23), but specimens kept in a crystalline condition at a low temperature for a long time melt at a higher temperature, the highest melting point recorded being 43° C. (3). Specimens of smoked sheet rubber are sometimes partly

crystalline at room temperature and only become completely amorphous at about 40° C. The question is: what is the true melting point of *cis* polyisoprene? Although it is possible to suggest causes for either the raising or the lowering of the melting point (11), it does not appear possible to judge how far each of such factors modifies the melting point. But the doubt about the true melting point of *cis*-polyisoprene should not deter us from considering in a qualitative way why rubber melts at a lower temperature than gutta-percha, why both melt at a much lower temperature than polyethylene and why polyisobutene apparently has a lower melting point than any of these.

A crystalline solid melts when the amplitude of the thermal motions of the atoms, ions or molecules of which it is composed becomes great enough to destroy the regular arrangement in the crystals. The Lindemann equation (54) embodies the assumption that, for atomic crystals, melting occurs when the amplitude of vibration of the atoms becomes comparable with the distances between them, and for a few crystals it has been shown that this equation leads to vibration frequencies in agreement with those calculated in other ways. For hydrocarbon crystals composed of rigid molecules, the amplitude at a given temperature decreases with rising molecular weight, and this is reflected in the general rise of melting point with molecular weight. But when one part of a molecule can make large movements with respect to another part, the melting point, which depends on the weight of the moving parts, is likely to be much lower than that of a substance composed of rigid molecules of the same molecular weight.

The flexibility of chain polymer molecules arises chiefly from rotations around the single bonds, the amplitude of movement due to such rotations being much greater than that arising from distortion of bond angles or bond lengths. Ease of rotation, however, varies considerably in different situations, and the melting points of crystals composed of molecules in which rotation is easy are likely to be many degrees lower than those of crystals composed of more rigid molecules.

Molecular flexibility is not, of course, the only factor influencing the melting points of chain polymers. The presence of strongly polar groups must tend to hold molecules more firmly in position, and thus increases the melting point. This is presumably the reason why polyamides have much higher melting points than hydrocarbon polymers. Among hydrocarbon polymers in which there are no such effects, the melting point may be influenced by the efficiency of packing of the molecules in the crystals: when molecules pack badly because of awkwardness of shape, the melting point is likely to be lower on that account. Gross inefficiency of packing would

probably be indicated by an abnormally low density; but quantitative treatment of this factor would appear to be difficult. A more subtle effect arises from the behavior of the molecules on melting. Because of rotations around the single bonds, there is a tendency for the molecules to curl into random configurations, a tendency which will not be the same for different molecules—it will depend on molecular geometry as well as on the forces between the molecules. The more random the configuration in the liquid (other things being equal), the lower is the melting point. From the kinetic point of view, the more random the configuration in the liquid, the less chance there is of molecules straightening out to form crystals, and therefore the lower the freezing point. From the thermodynamic point of view, the randomness of configuration forms part of the entropy term in the expression $T_f = \Delta H/\Delta S$, where T_f is the melting point, ΔH the latent heat of fusion, and ΔS the change of entropy on fusion; the larger ΔS , the lower is T_f .

It does not seem possible at present to assess the part played by each of these factors in individual cases. The correlation of the thermodynamic and the geometric-kinetic points of view should yield valuable results; but this correlation is difficult, since the two terms, ΔH and ΔS , in the thermodynamic expression do not correspond with the two factors in the geometric-kinetic approach, which may be called the crystal structure factor and the molecular flexibility factor, respectively. The thermodynamic and the geometric-kinetic methods of approach represent two different methods of dividing the problem; the boundaries between the divisions made in these two ways do not wholly correspond. For instance, the latent heat of melting of a crystal (ΔH) may be considered as made up of the energy required to separate the molecules to a greater average distance apart (the difference between the densities of liquid and solid being a measure of this separation) and the energy required to start the molecular motions which characterize the liquid state—these motions, in the case of high polymers, including changes of configuration by rotation around the single bonds; ΔH thus includes both packing and flexibility factors.

The remarks made here will be confined to suggestions arising from the x-ray study of the substances concerned.

1. *The Polyisoprene Group*

It is instructive, in the first place, to realize that the low melting points of these unsaturated substances are in line with those of shorter chained unsaturated substances. The hydrocarbon squalene, which may be re-

garded as a low polymer of isoprene having a chain 24 carbon atoms long, has a much lower melting point (45) (below -20° C.) than the normal saturated hydrocarbon of the same chain length, $C_{24}H_{50}$ (54° C.). Mack (58) points out that the acid $C_8H_{17}-CH=CH-(CH_2)_7-COOH$, which has a double bond in the middle of the chain, has a much lower melting point (16° C.) than stearic acid $C_{17}H_{35}-COOH$ (69.3° C.), and that acids of the same chain length with two or three double bonds in the chain have still lower melting points. The presence of double bonds in chain molecules thus has the effect of lowering the melting point. The effect might be due either to bad packing (the double-bonded group being geometrically different from the remainder of the chain), or to molecular flexibility caused by the presence of the double bond. With regard to the latter, the double-bonded group itself is expected to be more rigid than the saturated parts of the chain, and therefore any additional flexibility in the chain must be attributed to additional ease of rotation around the single bonds adjacent to the double bond.

Evidence on the ease of rotation around single bonds in various small molecules has been obtained from data on the specific heats of gases (74, 86). It appears that the potential barrier to rotation around a single bond is lower when there is an adjacent double bond, as in propylene ($CH_3-CH=CH_2$), than in comparable saturated molecules such as propane ($CH_3-CH_2-CH_3$). This fact appears to give some support to the idea that the low melting points of the unsaturated chain compounds under discussion are at any rate partly due to additional ease of rotation around single bonds adjacent to double bonds. It is not certain, however, that information on the small molecules can be applied directly in this way; much depends on the origin of the potential barriers—whether they are due mainly to some bond-orientation effect (13, 52) analogous to that which keeps the four bonds of one carbon atom tetrahedrally disposed, or solely to forces between the groups held by the bonds. If the former is correct, then the figures for the potential barriers in the small molecules may be assumed to apply to the polyisoprenes, modified to some extent by the forces between groups which have to pass close to each other on rotation; but, if the latter is correct, then the potential barrier in rubber is likely to be very different from that in propylene.

The configuration of the rubber molecule in the crystal certainly indicates considerable freedom of position of the CH_2-CH_2 chain bonds, since alternate bonds of this type (bonds 4-6 and 1-9 in Fig. 8) occupy considerably different positions with respect to the planes of the double-bonded units. The difference represents a rotation of some 50° . Since this is brought

about by the weak van der Waals' forces in the crystal, it appears that rotation around the single bonds is easy, at any rate through this angle.

With regard to the comparatively small differences between the melting points of rubber, gutta-percha and polychloroprene, it has been pointed out (14) that the hindrance to rotation presented by the methyl group is likely to be less for *cis*-polyisoprene (rubber) than for the *trans* isomer (gutta-percha); this is consistent with the fact that rubber melts at a lower temperature than gutta-percha. Similarly, the substitution, in the *trans* type of molecule, of a chlorine atom for a methyl group would be likely to increase molecular flexibility; and this again is consistent with the fact that polychloroprene melts at a lower temperature than gutta-percha.

2. Rubber Hydrochloride

In this molecule, the hindrances to rotation presented by the side groups are similar to those in rubber (15). The much higher melting point of this substance may be caused by higher barriers to rotation due to the saturated character of the chain, or by increased dipole effects or inertia effects due to the presence of the chlorine atoms.

3. Polyethylene

The fact that the melting point of polyethylene is much higher than that of rubber has given rise to much discussion. It has been suggested (87) that the cause is better packing of the simple polyethylene molecules in the crystals; but there is no necessary connection between chemical simplicity or molecular symmetry and efficiency of packing. There is no obvious waste of space in either crystal structure; and the densities of the two crystals (calculated from the unit cell dimensions) are both equal to 1.00.

The potential barriers to rotation in simple molecules such as propane and propylene suggest that a saturated molecule like polyethylene should be less flexible than a comparable unsaturated molecule; but whether the differences in flexibility are sufficient to account for the large difference of melting point is not clear.

4. Polyisobutene

The melting point of polyisobutene is unknown, but it is clearly far below room temperature. At first thought it might be supposed that, because of the presence of many side groups in close proximity, the hindrances to rotation around the chain bonds would be much greater than in polyethylene, and that this would mean reduced molecular flexibility and a

higher melting point—in contradiction to the facts. This view is, however, superficial and fallacious. Ease of rotation around single bonds depends on the *difference* between the energy contents of the continuously variable configurations attainable by rotation. If a model of the polyisobutene molecule is made, it is seen that the methyl groups are overcrowded, whatever configuration is assumed,* and that they are overcrowded to much the same extent for a wide range of configurations. The greatest clearance is obtained when adjacent pairs of methyl groups are placed in positions like those suggested by Fuller, Frosch and Pape (Fig. 16, page 127), the distance between carbon atom centers being 2.6–2.7 Å.; but this is not very different from the distance between these atomic centers when the chain has a staggered configuration such as a plane zigzag (2.53 Å. if the bond angles are normal). Both these distances are far less than the sum of the effective radii of two methyl groups (3.6–4.0 Å.). However, they are so similar that there may be little difference between the energies of the different configurations attainable by rotation around the chain bonds. Therefore, the molecules are expected to be highly flexible, which may account for the low melting point.

A further consideration would arise if there were any bond-orientation effect such as we have discussed previously. The bonds themselves (let us suppose) prefer staggered configurations. But the side groups, as we have seen, prefer nonstaggered configurations to attain greater clearance—configurations like those in Figure 16. The opposition between the two tendencies may have the effect of reducing the energy difference between different configurations to a negligible quantity (depending on the relative magnitudes of the energies associated with each factor) (14).

5. Polyesters

The low melting points of the polyesters—decreasing, on the whole, with increasing proportion of ester groups per unit chain length—are in line with the fact that monomeric chain esters such as hexadecyl stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2)_{16}\text{CH}_3$, have lower melting points than paraffin hydrocarbons of the same chain length (45). It appears that the presence of an ester group in a chain either gives additional flexibility at that point, or else gives rise to inefficient packing of the molecules in the crystals. The presence of $\text{C}=\text{O}$ dipoles might be expected to increase the melting point. Indeed, monomeric chain ketones all have higher melting points

* This state of affairs—considerable overcrowding of side groups—is reflected by the abnormally low heat of formation of this substance (30).

(76) than the corresponding paraffins (69). Evidently, in the esters, this tendency is more than counterbalanced by the flexibility or packing effects. In looking for any causes of bad packing, any possible effect of the presence of the side (carbonyl) oxygen atoms may be discounted, since the monomeric chain ketones have higher melting points than the corresponding paraffins. Moreover, the effective cross-sectional area of a polyester molecule (given by the unit cell dimensions of the crystals) is almost exactly the same as that of a paraffin molecule. The oxygen atoms in the chain, since their radius (1.35 Å.) is considerably smaller than that of a CH₂ group (~ 2.0 Å.), might be expected to give rise to gaps in the crystal structure. It does not appear possible to decide whether it is this effect, or a flexibility effect, which is responsible for the low melting points of the polyesters.

The fact that the polyesters do not all have the same chain configuration suggests that different bond positions in the region of the ester group are almost equivalent energetically; for flexibility, however, it is not enough that different bond positions shall be energetically similar—the transition between the bond positions must be easy. A possible hint in this direction is given by the phenomena which occur when fibers of certain polyesters of the trimethylene glycol series are stretched; if the interpretation suggested previously is correct—that the chain configuration is changed by stretching—then it does appear that rotation around the single bonds (since it is brought about by mechanical means) is comparatively free.

IV. Studies of Crystallization and Orientation

“Crystalline” long-chain polymers are not entirely crystalline—there is always a certain proportion of amorphous material; and when they “melt,” they do so over a range of temperature. Although the proportions of amorphous and crystalline material change most rapidly at temperatures just below what is commonly referred to as the “melting point,” it is likely that minor changes in the proportions of crystalline and amorphous material occur over a considerable range of temperature below this. It is also likely that the proportions change with time. The proportions can be determined from x-ray diffraction photographs by measuring the relative intensities of the diffuse amorphous bands and the sharper crystalline reflections. It is highly desirable that such studies should be undertaken, to widen our knowledge of the phenomenon of melting in chain polymers, and to correlate the results with the changes of physical properties with time and temperature. Quantitative studies of this type on the substances dealt with here do not appear to have been reported.

The progress of crystallization during the stretching of rubber has, however, been studied quantitatively by Field (31). It has long been known that, when rubber is stretched, sharp "crystalline" x-ray reflections are not formed by gradual sharpening of the diffuse "amorphous" reflections. What happens is that sharp reflections appear superimposed on the diffuse bands, at first faintly, but increasing in intensity with increasing elongation (43). Field measured the intensity of the principal diffuse band given by a known thickness of unstretched rubber at a fixed temperature for a definite x-ray exposure, and then repeated this measurement for different

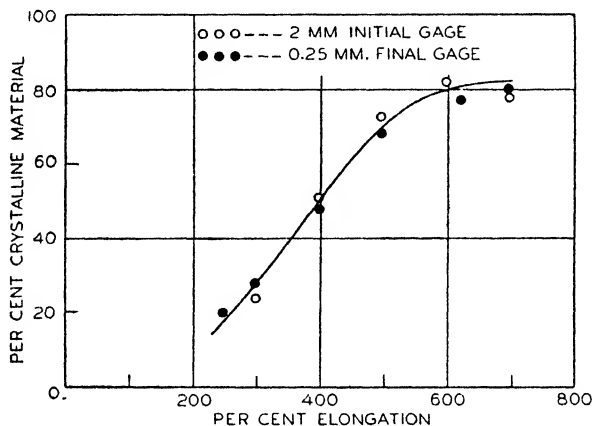


Fig. 18.—Crystallization of stretched, unvulcanized rubber (31).

degrees of stretching. The results are shown in Figure 18. Evidently, in a piece of rubber there are local variations (on a submicroscopic scale) of stress or of parallelism of molecules, so that crystallization in different regions occurs at different stages of stretching. Field also measured the proportion of crystalline material in specimens stretched at temperatures up to 90° C.; at a given elongation, the proportion of crystalline material decreases with a rise in temperature. He also studied the effect of vulcanization, and showed that for a particular rubber compound the degree of vulcanization which results in the optimum crystallization for a given elongation is the "best cure" for general purposes.

The amount of crystallization in stretched rubber depends to some extent on the past history of the specimen and the rate of elongation. Earlier work on hysteresis effects has been summarized in a review by Gehman (39). More recently, Clark and his associates have measured the intensities

of the crystal reflections and correlated these measurements with tension and elongation, for varying degrees of vulcanization, following the process in this way through several cycles of stretching and relaxation (24, 25).

The crystalline x-ray reflections given when rubberlike substances are stretched or crystalline polymers are cold-drawn are not perfectly sharp spots, but short arcs, somewhat diffuse in comparison with the reflections given by large single crystals, though sharp compared with the reflections of amorphous substances. The length of the arcs, which is a measure of the degree of dispersion of the crystal axes from the fiber axis, varies with the chemical nature of the polymer and its past history; quantitative measurement and correlation with physical properties (in the case of the substances dealt with here) do not appear to have been reported. The breadth of the arcs also varies with the nature of the substance and with the history of the specimen. It has usually been taken as an indication of the size of the crystals. Hengstenberg and Mark (47), on the basis of measurements of the breadths of the reflections of stretched rubber, gave the dimensions of the crystals as approximately $500 \times 150 \times 600 \text{ \AA}$. Small crystal size is, however, not the only possible cause of the broadening of reflections. Crystal distortions and imperfections as well as thermal vibrations in the crystals are other possible causes; and it is difficult to distinguish between the different possibilities. Generally speaking, the reflections given by polymers stretched above their melting points are both sharper and of shorter arc length than those of polymers drawn below their melting points. But much depends on the temperature and rapidity of stretching or drawing. And different substances vary greatly in these respects: polyisobutene, for instance, gives with great readiness shorter and much sharper reflections than rubber, the reason being unknown, though it is possibly connected with the greater extensibility of polyisobutene, and with the fact that at room temperature this substance is further from its melting point than is rubber.

The plane orientation obtainable by stretching thin short sheets of rubberlike substances has already been mentioned. Schallamach (77) reports that the plane orientation alone (that is, without any longitudinal orientation) is produced, as would be expected, when a rubber balloon is inflated. Various interesting observations on double orientation and freezing effects in rubber are reported by Gehman and Field (40).

In conclusion, we may note some miscellaneous applications of x-ray diffraction methods to rubber problems. Clark, Gross and Smith (22) showed that rubber crystallized from solution at low temperature (81) has the same structure as stretched rubber. The same authors measured the

crystallization points of various rubbers (23). Schallamach (78) showed that long spacings (36–50 Å.) given by certain specimens of rubber are due to crystals of impurities which become oriented on stretching. Trumbull (88) showed that rubber from the plant *Cryptostegia grandiflora* gives the same pattern on stretching as the common *Hevea* rubber. Jeffrey, as described in a paper by Roberts (73), showed that certain fractions extracted from ordinary rubber give identical patterns when stretched, but that one fraction containing oxygen, on freezing, gives a pattern somewhat different from that of ordinary rubber. Cyclized rubber, made by the action of stannic chloride or chlorostannic acid, has been studied by Thies (84) and photogells by Bunn [in a paper by Naunton (70)]. The orientation of crystals of fillers (such as calcite and zinc oxide) and “accelerators” in stretched rubbers has been noted by Clark, LeTourneau and Ball (26).

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THE THERMODYNAMIC STUDY OF RUBBER SOLUTIONS AND GELS

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	PAGE
I. Introduction.....	145
II. Experimental Study of Thermodynamics of Rubber Solutions....	147
1. Vapor Pressures of Rubber Solutions and Gels.....	147
2. Swelling Pressure.....	150
3. Osmotic Pressure.....	151
4. Cryoscopic Measurements.....	153
5. Free Energy of Dilution.....	154
6. Heat of Dilution.....	155
III. Statistical Calculations.....	156
1. Entropy of Mixing.....	156
2. Heat and Free Energy of Mixing.....	162
IV. Comparison of Theory and Experiment.....	165
V. Applications of Thermodynamics to Specific Problems.....	169
1. Molecular Weight of Rubbers from Osmotic Data.....	169
Micellar Theory of Rubber Structure.....	173
2. Solubility of Rubbers in Different Liquids.....	174
3. Limited Swelling of Rubbers in Liquids.....	179
4. Solubility of Solids in Rubbers.....	188
5. Fractionation of Rubbers.....	190
6. General Conclusions.....	193
Bibliography.....	194

I. Introduction

The behavior of rubber* toward solvents constitutes one of its most striking characteristics. Whereas a typical low-molecular substance dissolves readily in suitable solvents to a sharply defined maximum concentration, rubber first swells, imbibing liquid without being itself dispersed. In nonsolvents this is the final state of the system, while in true solvents

* Throughout this chapter "rubber" is intended to include any rubberlike high polymer; natural rubber will be so designated when necessary.

the rubber gradually loses its form and ultimately disperses. The ordinary thermodynamic theory of solutions has proved quite incapable of accounting for these phenomena. It is the purpose of this chapter to discuss where the ordinary theory breaks down, to describe the attempts which have been made to formulate an amended theory and to apply it to a number of specific problems.

The problem of the thermodynamic properties of rubber solutions and gels may be approached either theoretically or experimentally. We shall describe the latter first, and then consider how far it has been possible by statistical mechanical methods to produce a theory capable of accounting for the experimental results.

Considering the process of adding one mole of liquid to a large bulk of rubber solution or gel, the increases in Gibbs' free energy, entropy and heat content are denoted by ΔG_0 , ΔS_0 and ΔH_0 and are termed the free energy, entropy and heat of dilution, respectively. The reverse process, of adding one mole of rubber, is termed solution, and is denoted by subscript r . If p_0^0 and p_0^m are the vapor pressures of the pure liquid and of the solution, then, provided the vapor behaves as a perfect* gas:

$$\Delta G_0 = RT \ln p_0^m/p_0^0 \quad (1)$$

Thus the free energy of dilution may be calculated from experimental measurements of vapor pressure, or of any other property which can be thermodynamically related to vapor pressure. The most important of these for the present purpose is the osmotic pressure, or swelling pressure.

If a rubber solution or gel is separated from the pure liquid by a membrane permeable only to the liquid, the osmotic pressure or swelling pressure may be defined as the hydrostatic pressure which must be applied to the solution in order to prevent liquid from flowing through the membrane. If this pressure is denoted by Π , then it may be shown that

$$\Delta G_0 = -\Pi V_0 \quad (2)$$

where V_0 is the partial molar volume of the liquid in the solution. The vapor pressure of a solution may also be related to the freezing point, by the approximate expression:

$$\ln p_0^0/p_0^m = \frac{L_f}{RT_f^2} \theta \quad (3)$$

where L_f is the molar latent heat of fusion of the solvent, T_f is its melting point and θ is the freezing point depression produced by the solute.

* If the gas is imperfect the vapor pressures must be replaced by fugacities.

Several experimental methods are thus available for the determination of the free energy of dilution.

The heat of dilution may be determined calorimetrically, or from the temperature coefficient of the free energy by means of the thermodynamic relationship:

$$\Delta H_0 = \frac{\partial(\Delta G_0/T)}{\partial(1/T)} \quad (4)$$

The entropy of dilution then follows at once from the well-known relationship:

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (5)$$

II. Experimental Study of Thermodynamics of Rubber Solutions

1. Vapor Pressures of Rubber Solutions and Gels

A number of workers have measured the vapor pressures of rubber solutions, although the accuracy attained in most cases appears to be rather

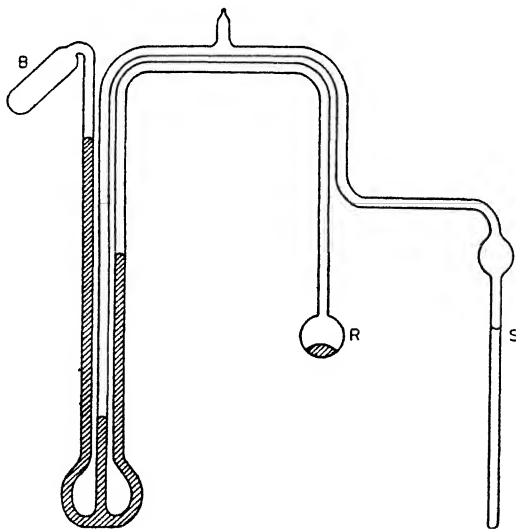


Fig. 1.—Apparatus for the measurement of vapor pressures of rubber gels (21).

low, judging from the scatter of the experimental points. The essential precautions to be observed were clearly pointed out by Stamberger (50), but later workers have modified his procedure so as to make it both more

precise and more convenient. Careful outgassing of the rubber and purification of the liquid are the main points to be observed. The quantities to be measured experimentally are the vapor pressure and the concentration of the solution. The latter may be determined either by analysis of the solution, or by transferring a known amount of liquid from a reservoir on to the rubber. Stamberger used the former method, while later workers have preferred the second procedure, which is more convenient experimentally.

Probably the simplest type of apparatus which has been described is that used by Gee and Treloar (21) (Fig. 1). The apparatus, containing a

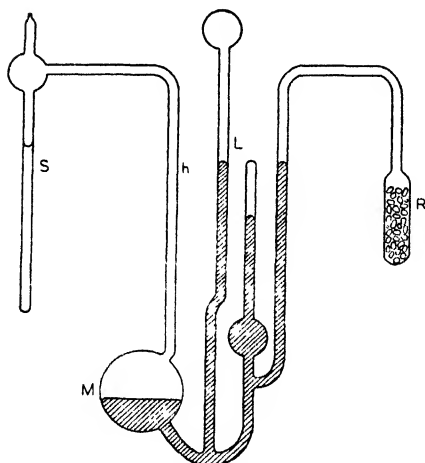


Fig. 2.—Apparatus for low vapor pressures (21).

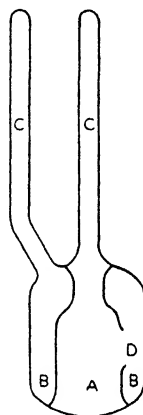


Fig. 3.—Apparatus for small vapor pressure lowerings. *A*, rubber solution; *B*, reference solution; *C*, calibrated tubes; *D*, large hole blown in side of rubber compartment.

weighed quantity of rubber in bulb *R*, is sealed on to the vacuum line, the rubber outgassed, and the liquid distilled from a subsidiary reservoir into calibrated tube *S*. After careful evacuation the apparatus is sealed off from the line, and is then a self-contained unit in which are known amounts of rubber and liquid. As shown in the figure, these are separated by the mercury manometer, but contact between them may be made by tilting the apparatus so as to pour the mercury into bulb *B*. Any part of the liquid may then be distilled on to the rubber and the two sides then isolated again by pouring the mercury back into the manometer. The apparatus is then thermostated, and in the course of a few hours the mercury levels in the manometer become constant; from them may be read the

difference of vapor pressure between the liquid and the rubber. The concentration of liquid in the rubber may be calculated from the height of liquid in the calibrated tube, due allowance being made for vapor. The main experimental difficulty arises from the possibility that the liquid used may not be quite homogeneous, so that each distillation of the liquid effects a partial separation; any such tendency is quickly reflected in a lack of reproducibility of the results. This method was applied by Gee

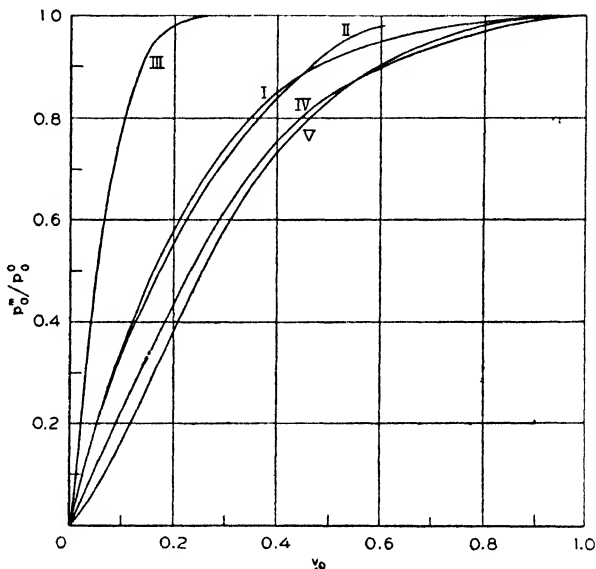


Fig. 4.—Vapor pressures of natural rubber solutions and gels. Curve I, benzene (21); II, toluene (2); III, acetone (33); IV, chloroform (33); V, carbon tetrachloride (33).

and Treloar to the system natural rubber hydrocarbon plus benzene. It fails when either the vapor pressure of the solution or the amount by which the vapor pressures of the liquid and the solution differ becomes too small to measure accurately.

Measurements of very small vapor pressures have been carried out by Gee and Treloar, using a small McLeod gage. The apparatus is shown in Figure 2, its dimensions being such that when the liquid reservoir *S* is at the thermostat temperature, mercury level *h* is just level with the top of the McLeod capillary, *L*. When the liquid in *S* is frozen in liquid air, the mercury level falls to *M* and thus puts the McLeod gage in contact with the rubber in bulb *R*.

Small vapor pressure differences between the solution and the gel are most conveniently measured by allowing the rubber solution to come into equilibrium with a solution, in the same liquid, of a solute of known molecular weight. Experimental methods of doing this have been described by Stamberger and by Gee and Treloar. The author has recently devised an improved form of apparatus, shown in Figure 3, in which the two solutions are contained in coaxial vessels, and the rate of distillation is measured by inverting from time to time, so as to drain the two solutions into calibrated side tubes. Vapor pressure curves for a number of liquids in natural rubber are plotted in Figure 4.

2. Swelling Pressure

The determination of swelling pressure affords another possible experimental approach to the region of small vapor pressure lowering. The only

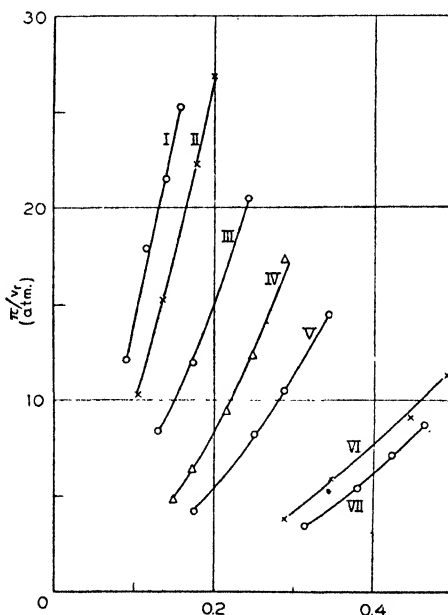


Fig. 5.—Swelling pressures of natural rubber gels (41). I, carbon tetrachloride; II, chloroform; III, dichloroethylene; IV, thiophene; V, benzene; VI, ethylene dichloride; VII, ether.

measurements recorded for rubber were obtained by Posnjak (41) using an earthenware cup as a semipermeable membrane. Samples of crude natural

rubber were confined in the cup by mercury, through which a measured hydrostatic pressure could be applied. Swelling of the rubber occurred when the cup was immersed in liquid, and could be followed by having the free surface of the mercury in a capillary tube, where its movement was readily observed. Some of Posnjak's results are shown in Figure 5. The swelling pressures were found to be independent of temperature, within the normal variation of room temperature.

3. *Osmotic Pressure*

Although there is no thermodynamic distinction between swelling pressure and osmotic pressure, the two may be arbitrarily distinguished by the different techniques employed. Osmotic pressure measurements are confined to solutions and may be extended to a fairly high dilution, thus covering a part of the concentration range not otherwise accessible. Osmometers suitable for use with rubber solutions have been described by various workers (14, 34; see also 6, 10, 12, 21, 46). A typical example is the author's modification of the design of Meyer and Boissonnas, shown in Figure 6, the diagram on the left being a longitudinal section of the right-hand side. The membrane is held vertically between two brass blocks and is supported by the grid arrangement shown at *C*. The cells are each 1 in. in diameter by $\frac{1}{8}$ in. deep; the upper part of each communicates, through a copper-glass seal, with a glass tube for the measurement of the pressure head. The cells are filled through tubes *E*, and sealed by closing screw valves *F*. Other workers have used somewhat larger cells, and this is probably a considerable advantage in increasing the rate of osmosis to be measured.

Suitable semipermeable membranes may be purchased ready for use, made by controlled denitration of nitrocellulose (38), or prepared by swelling commercial Cellophane sheets (6, 10). The author has found the purchased membranes to be the most satisfactory, but has also successfully employed membranes prepared from nitrocellulose, as described by Montonna and Jilk (38). The ideal membrane would contain a large number of pores of uniform size so as to give the highest degree of permeability to the liquid consistent with the necessity of holding back the rubber.

Measurements of osmotic pressure may be made in two ways: (1) by the static method, in which time is allowed for osmotic equilibrium to be attained, the osmotic pressure being read off as the difference in hydrostatic pressure developed between the two cells; (2) by the dynamic method, in which a series of fixed hydrostatic pressures are applied across the membrane and the rate of osmosis measured as a function of the pres-

sure head, the osmotic pressure being then the interpolated hydrostatic pressure at which osmosis just ceases. Both methods have their advantages and there is probably little to choose between them. The dynamic method requires considerably more attention, but is capable of giving an answer in a shorter time from the start. The time required for equilibrium

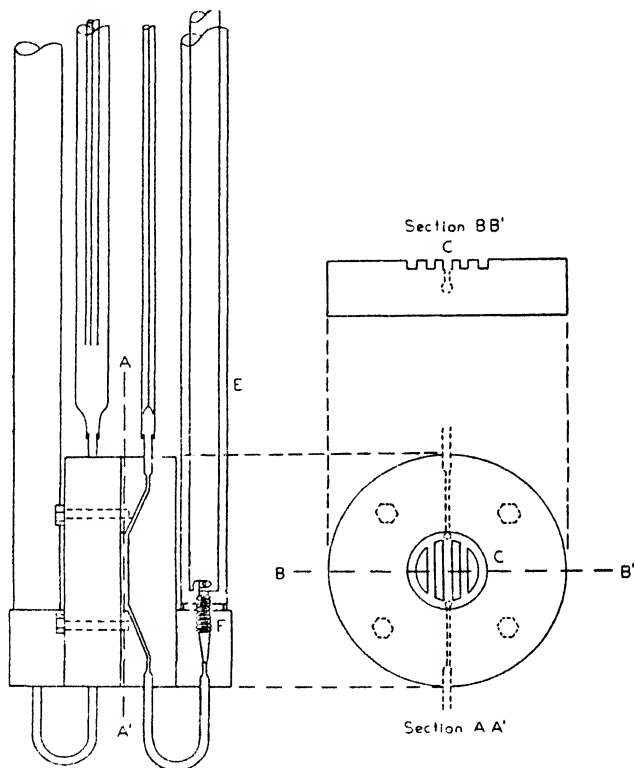


Fig. 6.—Modification of the Meyer and Boissonnas osmometer (14, 34).

to be attained varies with the molecular weight of the rubber and the permeability of the membrane, but is seldom less than 24 hours and may well be more. Fuoss and Mead (12) have described an interesting method in which the membrane is permeable to both solvent and solute, but measurements are made rapidly, before serious penetration of the membrane by the solute has taken place. Before adopting this very rapid method as a standard, it would be desirable to show that it gave the same results as the slower methods which employ a truly semipermeable membrane. The

advantages of the method appear to be considerably reduced by the difficulty experienced in washing the polymer out of the membrane after use.

The results of osmotic pressure measurements will be discussed in a later section (pages 169–173).

4. Cryoscopic Measurements

The freezing point of a dilute solution of rubber in benzene is not measurably different from that of pure benzene, but the cryoscopic method has been applied to very low molecular rubbers, principally by Kemp and

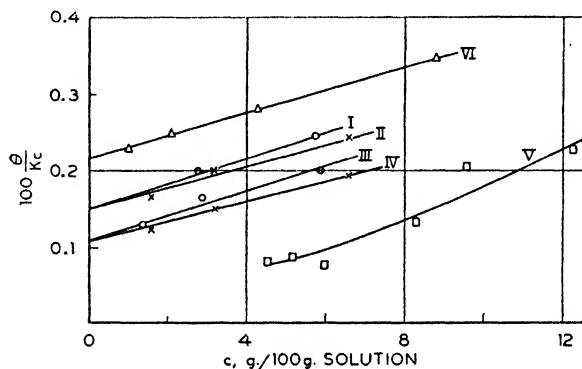


Fig. 7.—Cryoscopic measurements on rubber solutions. Thermally degraded natural rubber in benzene (curves I and III), in cyclohexane (II and IV), in camphor (half-scale) (V). Curve VI, polyisobutylene in cyclohexane (subtract 0.1 from ordinates).

Peters (29). The materials examined were obtained by a rough fractionation of thermally degraded natural rubber and polyisobutylene. The natural rubber products contained a considerable proportion of oxygen, and their behavior in solution may therefore be somewhat different from that of pure rubber hydrocarbon fractions of the same molecular weight. Kemp and Peters found that θ/c was only independent of c for the lowest molecular weight fractions, so that the apparent molecular weight depended on concentration c . Some of their results for the higher fractions are plotted in Figure 7, c being expressed in g. per 100 g. of solvent, while K is the cryoscopic constant for the solvent.

Cryoscopic measurements with total natural rubber were carried out by Pummerer and coworkers (43) using the Rast method with camphor as solvent. The author (16) showed that rubber undergoes severe degradation on heating with molten camphor in air, and found that, if the experiments were carried out *in vacuo*, the freezing points of camphor solutions

of rubber which were sufficiently dilute to be fluid were indistinguishable from that of camphor. He has, however, recorded measurements of the freezing points of camphor solutions of a degraded rubber of osmotic molecular weight 38,000; these are included in Figure 7.

5. Free Energy of Dilution

All the above measurements can be used to calculate the free energy of dilution of rubber by various liquids, using Equations 1 to 3. The results

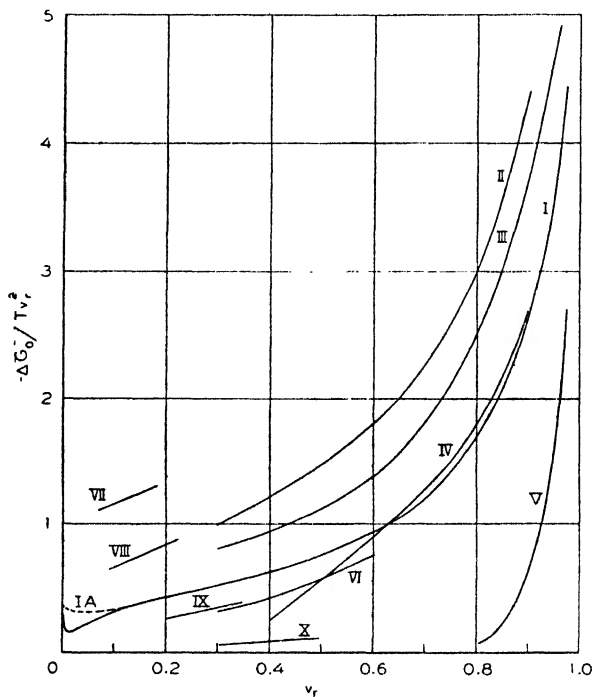


Fig. 8.—Free energies of dilution for natural rubber in various liquids. Curve I, benzene from smoothed data of Gee and Treloar (21); IA, theoretical form of curve for dilute solutions. Curves II–VI, vapor pressure data: II, carbon tetrachloride (33); III, chloroform (33); IV, toluene (2); V, acetone (33); VI, carbon disulfide (50). Curves VII–X, swelling pressure data (41): VII, carbon tetrachloride; VIII, chloroform; IX, toluene; X, ether.

of these calculations are given in Figure 8 in which $-\Delta G_0/Tv_r^2$ is plotted as a function of v_r , the volume fraction of rubber, *i. e.*, the ratio of the volume of the rubber to the total volume of the mixture.

6. Heat of Dilution

Few calorimetric measurements have been made of the heat of mixing of rubber and liquids. The problem is a difficult one, owing to the slowness with which liquids are imbibed by rubber, and the smallness of the heat to be measured. The fragmentary data of Hock and Schmidt (23) are summarized in Table I. These workers found that the results obtained

TABLE I
INTEGRAL HEAT OF SWELLING OF NATURAL RUBBER (23)

<i>A. Heat of Swelling of Milled Raw Rubber and Vulcanized Rubber</i>		
Liquid	Heat absorbed, cal./g. rubber	
	Raw	Vulcanized
Benzene	1.36	2.4
Dichloroethylene	0.5	-0.8
Toluene	0.37	0.6
Petroleum ether	0.1	...
Carbon tetrachloride	-2.3	-1.2
Chloroform	-3.0	-2.0

<i>B. Effect of Aging on Heat of Swelling of Milled Rubber</i>		
Hours aging	Heat of swelling in	
	Benzene	Petroleum ether
50	0.36	0.09
100	0.59	0.08
200	0.87	0.08
400	1.16	0.09 _s
700	1.42	...

were highly dependent on the history of the specimens examined. It is not clear how far this dependence results from oxidation of the samples, and how far it is a reflection of the physical state of the rubber (*e. g.*, partial crystallization of the rubber resulting in the inclusion in the measured heat of a part of the heat of fusion). Heats of dilution of rubber by benzene and toluene have been estimated from the temperature coefficient of vapor pressure and osmotic pressure, but the temperature coefficient is so small that no great quantitative significance can be attached to the results. The figures which appear to be most reliable are summarized in Table II.

Two important conclusions may be drawn from this experimental study: first, that the heat of mixing is small and generally positive (heat absorbed). The heats of mixing per cubic centimeter of mixture are of the same order as those found for the mixing of two low-molecular liquids, and considerably smaller than the heat of solution of a solid in a liquid. This means

that rubber in its solubility behavior resembles a liquid rather than a solid, and this is indeed to be anticipated in view of the mechanical properties of rubber. It is clear that rubber cannot be adequately described either as a liquid or as a solid in the ordinary sense of these terms. Its elastic properties require, however, a very large degree of freedom of the molecular chains to slide over one another; and in this rubber resembles a

TABLE II
HEATS OF DILUTION OF NATURAL RUBBER FROM VAPOR PRESSURE
AND OSMOTIC PRESSURE DATA

<i>A. Benzene (21)</i>		
v_r	ΔH_0 , cal./mole	$\Delta H_0/v_r^2$
0.99	250 ^a	250
0.945	120 ^a	135
0.92	80 ^a	95
0.78	80 ^a	130
0.59	0 ^a	..
0.0254	0.03 ₁	50
0.0218	0.02 ₃	50
0.0179	0.01 ₆	55
0.0131	0.01 ₂	70
<i>B. Toluene (34)</i>		
0.0443	0.04 ₅	23
0.0331	0.02	18

^a These figures differ from those of the original paper, owing to the application of a correction for the departure of the benzene vapor from perfect gas behavior.

liquid. The second conclusion from the experimental work is that the entropy of mixing is far larger than can be accounted for by the usual expression valid for mixtures of small molecules. This may be seen most strikingly by expressing the heat of mixing as the molar heat of solution of the rubber. For natural rubber in benzene a figure of approximately 500,000 cal. per mole is obtained, which is far larger than can be accounted for by the so-called "ideal" entropy of solution. We have therefore to consider how the "ideal" entropy of solution is calculated and to inquire where this method requires modification for application to rubber.

III. Statistical Calculations

1. Entropy of Mixing

The statistical calculation of the entropy of mixing of n_1 molecules of type 1 and n_2 molecules of type 2 may be carried out in the following ap-

proximate manner. We consider a lattice containing $n_1 + n_2$ sites each capable of accommodating one of either type of molecule. The number of ways of arranging $n_1 + n_2$ molecules on the lattice is evidently $(n_1 + n_2)!$ According to Boltzmann's equation (11a), the entropy S of this assembly is $k \ln (n_1 + n_2)!$ This represents the entropy of a random mixture of n_1 type 1 molecules and n_2 type 2 moles. If these molecules are now separated, the type 1 molecules being confined to n_1 specified lattice points, the number of ways of arranging the molecules is $n_1! n_2!$ so that, again using Boltzmann's relation, the entropy of the system with the molecules separated is $k \ln (n_1! n_2!)$. Hence the increase of entropy on mixing is:

$$\Delta S^m = k \ln \frac{(n_1 + n_2)!}{n_1! n_2!}$$

Using Stirling's approximation for the factorials, this may be reduced to the more usual form:

$$\Delta S^m = -k \left(n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right) \quad (6)$$

The entropy of mixing calculated in this way has been shown to agree fairly well with experiment for mixtures of low-molecular liquids (22). It is easy to see, however, that the model is not even an approximate description of the mixture of rubber molecules and solvent molecules, for its application to such a system involves the assumption that a lattice point is capable of accommodating either a molecule of solvent or a molecule of rubber. Since the latter may be some 5000 times larger than the former, this is obviously not the case. The way out of the difficulty is to allow the rubber molecule to occupy a large number of lattice points, while the solvent molecule occupies only one. We therefore regard the rubber molecule as made up of a large number of segments, each approximately equal in size to the solvent molecule, and calculate the number of ways of arranging the two types of molecules on a lattice. Since the rubber molecule is flexible, the only restriction on the lattice points it may occupy is that successive segments must occupy adjacent points.

Three workers have produced approximate solutions, using two different methods of approach. Flory (9) and Huggins (25) have attempted a direct calculation of the number of configurations of a mixture of n_0 solvent molecules with n_r polymer molecules, each containing x segments equal in size to a solvent molecule, on a lattice of $(n_0 + xn_r)$ sites. Flory's treatment is very simple, the essential steps being as follows: The polymer

molecules are introduced first, the fraction of sites filled by the first n_i polymer molecules being given by:

$$i = xn_i/(n_0 + xn_r) \quad (7)$$

The number of sites available for the terminal segment of the next polymer is evidently $(1 - i)(n_0 + xn_r)$, and on the average $Z(1 - i)$ will be available for the second segment, where Z is the coordination number of the lattice. Then $(Z - 1)(1 - i)$ points are available for the third segment, since the first segment blocks one otherwise available site.* For the more remote segments, complications arise from the possibility that two or more neighboring sites may already be occupied by segments of the molecule being introduced. Flory neglects this factor and takes as the number of sites available for each succeeding segment $(Z - 1)(1 - i)$. The number of configurations, ν_i , of the $(n_i + 1)$ th polymer is thus found to be:

$$\nu_i \simeq 1/2 (1 - i)^x (n_0 + xn_r) (Z - 1)^{x-1} \quad (8)$$

and the total number of configurations, W , of the system:

$$W = \frac{1}{(n_0 + xn_r)!} \prod_{n_i=0}^{n_r-1} \nu_i \quad (9)$$

Algebraic simplification, followed by substitution into Boltzmann's equation, gives for the entropy of mixing:

$$\Delta S_{\text{mixing}} = -k \left[n_r \ln \frac{n_0}{n_0 + xn_r} + n_r \ln \frac{n_r}{n_0 + xn_r} \right] + k(x - 1)n_r \{ \ln(Z - 1) - 1 \} - kn_r \ln 2 \quad (10)$$

This expression requires correction for the configurational entropy of the polymer alone, and reduces finally to:

$$-\Delta S^m/k = n_0 \ln v_0 + n_r \ln v_r \quad (11)$$

where v_0 and v_r are the volume fractions of liquid and rubber, respectively. The partial molar entropies of dilution (ΔS_0) and solution (ΔS_r) are obtained from (11) by differentiation:

$$\begin{aligned} \Delta S_0 &= R \left[\ln \frac{1}{v_0} - v_r \left(1 - \frac{1}{x} \right) \right] \\ \Delta S_r &= R \left[\ln \frac{1}{v_r} + v_0(x - 1) \right] \end{aligned} \quad (12)$$

* A more accurate expression would be $Z(1 - i) - 1$.

Huggins' analysis follows the same general lines as Flory's, but makes a more serious attempt to compute the number of sites p_{ij} available for the j th segment of the n_i th polymer molecule. The result, f_0 being a small constant, is:

$$p_{ij} = \frac{(Z-1)(1-f_{ij})}{1 - \frac{2(x-1)}{xZ} f_{ij}} \quad (13)$$

where:

$$f_{ij} = f_0 + \frac{(n_i-1)x(1-f_0)}{n_0 + xn_r} \quad (14)$$

Proceeding from these expressions in the same way as Flory, Huggins obtains for the entropy of dilution:

$$\Delta S_0 = R \left[\ln \frac{1}{v_0} + \frac{1}{2} Z' \left(1 - \frac{1}{x} \right) \ln \left(1 - \frac{2v_r}{Z'} \right) \right] \quad (15)$$

where Z' is very nearly equal to Z .

Miller's (37) approach to the problem is less direct, and consists in applying Bethe's approximation to calculate the number of configurations of mixtures of: (a) single and double molecules, and (b) single and triple molecules. The entropies of mixing thus obtained are then compared, and used to extrapolate to the case of single plus very long molecules. In the Bethe method (11c), the number of configurations is evaluated by considering, instead of the whole lattice, a representative site and its immediate neighbors. Various approximations are possible, according to the number of neighbors considered; and, within the limits imposed by this approximation, the number of configurations can be computed exactly. Miller's calculations were carried only to the first approximation (central site plus nearest neighbors) and would probably be somewhat modified if higher approximations were used. His results for the entropy of mixing $\Delta S_{1,2}$ and $\Delta S_{1,3}$ of single and double, single and triple molecules, respectively, are:

$$\frac{\Delta S_{1,2}}{k} = \left\{ (Z-1)n_r + \frac{1}{2} Zn_0 \right\} \ln \left\{ \frac{\frac{2(Z-1)}{Z} n_r + n_0}{2n_r + n_0} \right\} - n_r \ln v_r - n_0 \ln v_0 + (Z-1)n_r \ln \frac{Z}{Z-1} \quad (16)$$

$$\frac{\Delta S_{1,s}}{k} = \left\{ \frac{3Z-4}{2} n_r + \frac{1}{2} Z n_0 \right\} \ln \left\{ \frac{\frac{3Z-4}{Z} n_r + n_0}{3n_r + n_0} \right\} - n_r \ln v_r - n_0 \ln v_0 + \frac{1}{2} (3Z-4)n_r \ln \frac{3Z}{3Z-4} \quad (17)$$

By comparing these equations it is possible to see how the chain length, x , of the polymer is involved and thus to write down for the entropy of mixing ΔS^m of polymer plus solvent:

$$\frac{\Delta S^m}{k} = \left\{ \frac{1}{2} (xZ - 2x + 2) n_r + \frac{1}{2} Z n_0 \right\} \ln \left\{ \frac{\frac{xZ - 2x + 2}{Z} n_r + n_0}{x n_r + n_0} \right\} - n_r \ln v_r - n_0 \ln v_0 + \frac{n_r}{2} (xZ - x + 2) \ln \left(\frac{xZ}{xZ - 2x + 2} \right) \quad (18)$$

whence the entropy of dilution is found to be:

$$\Delta S_0 = R \left[\ln \frac{1}{v_0} + \frac{Z}{2} \ln \left\{ 1 - \frac{2v_r}{Z} \left(1 - \frac{1}{x} \right) \right\} \right] \quad (19)$$

It is evident that, in the extrapolation from short polymers to a long one, no account is taken of the complications arising from the interference of different parts of the same molecule, so that the calculated entropy will be too high on this account. The effect of considering too restricted a group of sites is probably to reduce the number of configurations, and the two errors may therefore partially cancel.

Comparing the three methods of calculation, Huggins' should clearly be more precise than Flory's, but it is difficult to find any real basis of comparison of either with Miller's. Since x is large it is readily seen that Equations 15 and 19 are nearly identical, while both reduce to Equation 12 as $Z \rightarrow \infty$. In practice, therefore, any of these equations may be taken to include the essential terms in the entropy of mixing, as deduced from the assumed model. The remaining question is as to whether this model is in fact reasonable. The assumption of a lattice is in itself highly artificial, but the fact that a similar assumption leads to the correct entropy of mixing of small molecules gives one confidence that no serious error can be introduced here. The further assumption that a polymer molecule may always be divided into segments each equal in size to a solvent molecule is more open to question. It has been examined by Flory and Huggins in different ways, and with very different conclusions. Flory considered the case in

which each lattice point can accommodate either one polymer segment or β solvent molecules, and concluded that the entropy of dilution (Eq. 12) should be divided by β . Huggins employed a lattice in which each point could accommodate a solvent molecule, while p colinear points were required for a segment, and found that the entropy of dilution was the same

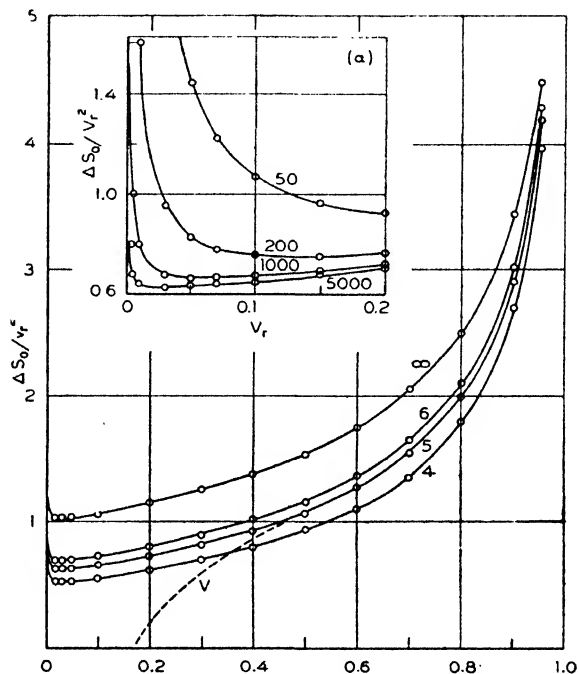


Fig. 9.—Theoretical entropy curves from Equation 19, with $x = \infty$, and the values of Z shown on the curves. The broken curve (V) is for vulcanized rubber.

Fig. 9a (inset).—Curves for $Z = 5$ with x values shown on the curves.

as in the simple case (Eq. 15) provided that x was interpreted as the ratio of the molar volumes of rubber and solvent V_r/V_0 . He therefore suggested (without proof) that the equation is valid for polymers of any segment size and flexibility. In the author's opinion, Huggins' analysis is to be preferred to Flory's, in which it appears likely that the low entropy of mixing calculated results from the undue restriction involved in allocating more than one solvent molecule to a single site.

Figure 9 gives a plot of $\Delta S_0/v_r^2$, calculated from Equation 19 for $Z = 4, 5, 6$ and ∞ . The last is equivalent to Equation 12, while Equations 15 and 19 give practically indistinguishable plots. It will be noted that these curves are very similar in form to those of $-\Delta G_0/Tv_r^2$ for rubber solutions given in Figure 8. The significance of the dotted curve, for vulcanized rubber, will be discussed later (page 181).

The limiting form of the entropy of dilution as v_r becomes small may be obtained by expanding the log terms of Equation 19, when we find:

$$\Delta S_0 \underset{(v_r \text{ small})}{\approx} R \left[\frac{v_r}{x} + \left(\frac{1}{2} - \frac{1}{Z} \right) v_r^2 \right] \quad (20)$$

2. Heat and Free Energy of Mixing

The calculations of the entropy of mixing which have been outlined above involve the implicit assumption that the heat of mixing of the two species is zero. If this is not the case, different configurations will not all have the same energy and will therefore be of different probability. In considering a real mixture we should therefore strictly revise this calculation so as to allow for the effect of the heat of mixing on the randomness of mixing. This has been done in the case of low-molecular liquids (11b), but no similar calculations for polymers have yet been published.* It is therefore necessary to assume that the entropy of mixing will not be seriously affected by a nonzero heat term; and we do this with more confidence since it has been shown that, in the case of low-molecular liquids, a similar procedure leads to free energies which are not greatly in error (11b). The heat of solution ΔH_1 of a low-molecular liquid (1) in a second liquid (2) can be represented as a function of the volume fraction v_2 of the latter by a simple power series in which the first term of the series is the square; and it is frequently unnecessary to consider any higher terms (22):

$$\Delta H_1 = k_2 v_2^2 + k_3 v_2^3 + \dots \quad (21)$$

Before applying this equation to a rubber plus liquid system, it is neces-

* Since this chapter was written, the free energy of mixing of polymers with liquids has been calculated by Orr (38a), and by Guggenheim (21a). Their conclusion is that the entropy and heat of mixing are both reduced *slightly* by nonrandom mixing, leaving the free energy almost unaffected. In the author's opinion, the correction introduced by this more accurate treatment is not large enough to be significant in comparison with approximations inherent in the model. The discussion presented in this chapter is therefore still considered to give a fair estimate of the value of the theory in the interpretation of experimental results.

sary to examine the assumptions on which it is based. The mixing of two molecular species, 1 and 2, involves: (a) the separation of type 1 molecules from one another; (b) the separation of type 2 molecules from one another; and (c) the bringing together of type 1 and type 2 molecules which have already been separated from their neighbors. If e_{11} , e_{22} and e_{12} are the respective energies per molecular contact, then the increase of energy, ΔE , on making N 1-2 contacts is:

$$\Delta E = \frac{N}{2} (2e_{12} - e_{11} - e_{22}) \quad (22)$$

where e_{11} and e_{22} are properties of the separate liquids, measured by their cohesive energies, while N and e_{12} are properties of the mixture. N depends on the degree of mixing, which is assumed, as in the entropy calculation, to be completely random. Denoting by E_{11} , E_{22} and E_{12} the cohesive energy densities (cal. per cc.) of the two liquids and of a hypothetical liquid in which all contacts are 1-2, the increase of energy ΔE on mixing v_1 cubic centimeters of 1 with $1 - v_1$ cubic centimeters of 2 is given by:

$$\Delta E^m = (E_{11} + E_{22} - 2E_{12})v_1(1 - v_1) \quad (23)$$

If the binding forces involved in the three types of molecular contact are similar in nature (dispersion forces in the case of nonpolar molecules), we may write E_{12} as approximately equal to the geometric mean of E_{11} and E_{22} , when Equation 23 becomes:

$$\Delta E^m \simeq (\sqrt{E_{11}} - \sqrt{E_{22}})^2 v_1(1 - v_1) \quad (24)$$

whence the molar heat of solution of 1 in 2 is:

$$\Delta E_1 = (\sqrt{E_{11}} - \sqrt{E_{22}})^2 V_1 v_2^2 \quad (25)$$

Higher terms of Equation 21 may be regarded as empirical corrections for the approximations involved in the above treatment.

This analysis has been worked out for the mixing of two liquids, but it is clear that, insofar as the solubility behavior of rubber is essentially that of a liquid, the same treatment should apply to solutions of rubber. The main difficulty arises in estimating the cohesive energy density of the rubber. For a liquid, the cohesive energy density is simply the latent heat of evaporation per cubic centimeter at constant volume. An approximate value for rubber may be obtained by considering its molecular structure. The cohesive energy densities of the paraffins $C_n H_{2n+2}$ increase with chain length, and appear to tend to a limiting value of ca. 60 cal. per cc. as n be-

comes large.* The presence of the methyl side groups in rubber would reduce this value somewhat, while the double bonds would cause a small increase. We shall describe below a method of obtaining a quantitative estimate from the swelling of rubber in a range of liquids: this method gives for natural rubber a value of 63.7 cal. per cc. Assuming this value, one may calculate the heat of dilution of rubber by any liquid of known latent heat of evaporation by means of Equation 25, without the use of any arbitrary constant. A correction should be applied for the volume change of mixing, since we have calculated ΔE_0 instead of ΔH_0 . In the case of mixtures of two liquids, this correction is often considerable, and may well be of the same order for rubber plus liquid. No accurate data are available for the volume changes on mixing rubber with liquids, but Posnjak (41) has shown that the volume change in the case of rubber plus benzene does not exceed 1%.

In the following pages, we make the approximation that $\Delta H_0 \approx \Delta E_0$, and write:

$$\left. \begin{aligned} \Delta H_0 &\approx \beta V_0 v_r^2 \\ \Delta H_r &\approx \beta V_r v_0^2 \end{aligned} \right\} \quad (26)$$

where:

$$\beta \approx \left(\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}} \right)^2 \quad (27)$$

Combining these equations with Equation 19 gives a complete expression for the free energy of a rubber-liquid system, containing only one unknown, namely the coordination number, Z , of the lattice. In practice, exact quantitative agreement cannot be expected, since 27 holds only approximately for liquid mixtures. The free energies of dilution and solution should, however, be given by equations of the form:

$$\begin{aligned} \Delta S_0/v_r^2 + \Delta G_0/Tv_r^2 &= \beta V_0/T \\ \Delta S_r/v_0^2 + \Delta G_r/Tv_0^2 &= \beta V_r/T \end{aligned} \quad (28)$$

where ΔS_0 and $S_r \Delta$ are given their theoretical values, from Equation 19. For dilute solutions, the approximate expression (Eq. 20) for ΔS_0 may be used, when the free energy of dilution becomes:

* There is some evidence (24) that the latent heat of evaporation per cubic centimeter falls again for large values of n , owing to the growing tendency of the long molecules to coil in the vapor phase. This does not of course mean that the cohesive energy density would show any corresponding decrease.

$$-\frac{\Delta G_0}{RT} \cong \frac{v_r}{x} + v_r^2 \left(\frac{1}{2} - \frac{1}{Z} - \frac{\beta V_0}{RT} \right) \quad (29)$$

IV. Comparison of Theory and Experiment

A complete test of the theory developed above requires the measurement of ΔG_0 and ΔH_0 over the whole concentration range. The only sys-

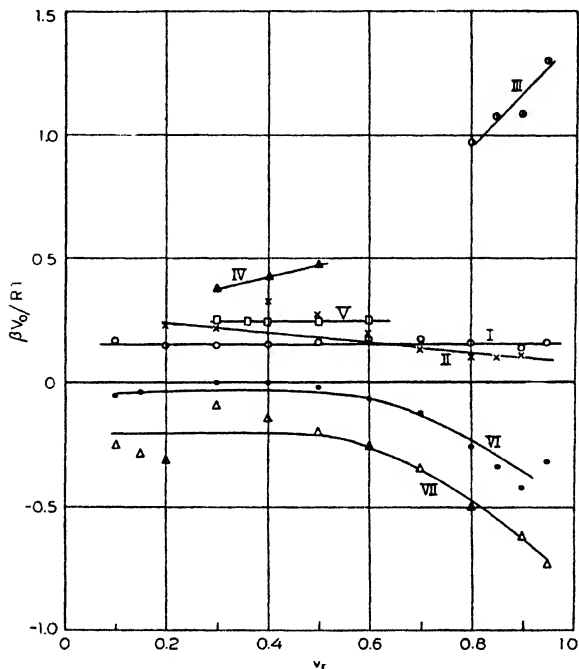


Fig. 10.—Values of $\beta V_0/RT$ obtained from Figures 8 and 9. I, benzene; II, toluene; III, acetone; IV, ether; V, carbon disulfide; VI, chloroform; VII, carbon tetrachloride.

tem for which this has been attempted is natural rubber plus benzene, and we shall therefore begin by considering in some detail the data of Gee and Treloar for this system (21). It is evident from Table II that ΔH_0 is only very approximately known, but the data suggest that $\Delta H_0/v_r^2$ is not quite constant, increasing from *ca.* 50 cal. per mole at infinite dilution to *ca.* 150 cal. per mole as $v_r \rightarrow 1$, the corresponding values of $\beta V_0/RT$ being 0.08 to 0.25. By employing Equation 28 it should be possible to derive

$\beta V_0/RT$ from ΔG_0 by substituting in it the theoretical value of $\Delta S_0/v_r^2$ from Equation 19. It is evident from Figure 9 that the result obtained will be highly dependent on the value of Z chosen. Figure 10 has been calculated by putting $Z = 5$, $x \rightarrow \infty$, and it will be seen that $\beta V_0/RT$ is independent of v_r , over a very wide range, and equal to 0.16. Changing the value assigned to Z affects the value of $\beta V_0/RT$ (0.09 for $Z = 4$, 0.21 for $Z = 6$) without altering its constancy. Clearly, the free energy data over a wide concentration range are very accurately reproduced by Equation 28 with $Z = 5$ and $\beta V_0/RT = 0.16$. In Figure 8 (curve I), the calculated and observed values of $-\Delta G_0/TV_r^2$ are indistinguishable except in the region of dilute solutions, where the calculated curve (IA) lies considerably above the experimental one, and has a markedly different shape. This discrepancy will be encountered in another form in the next section (page 170), in the departure of the reduced osmotic pressure π/c from linear dependence on c . In Figure 12 (page 171) curve IA gives the theoretical osmotic pressures calculated from the above values of Z and $\beta V_0/RT$.

An alternative way of testing Equation 28, devised by Huggins (25), may be presented in the following slightly modified form. A function Φ is defined by the equation:

$$\Phi = \frac{1}{v_r} \left(\frac{\Delta G_0}{RT} - \ln v_0 \right) - \left(1 - \frac{1}{x} \right) \quad (30)$$

Using the simplest form for the entropy of dilution (Eq. 12, page 158) it follows that:

$$\Phi = \mu v_r \quad (31)$$

TABLE III
VALUES OF μ AND $\beta V_0/RT$ FOR VARIOUS SYSTEMS

System	Range of v_r	μ	$\frac{\beta V_0}{RT}$	Ref. No.
Natural rubber				
-benzene	0-1	0.43	..	(21)
-carbon tetrachloride	0.14 -0.24	0.28	0.08	(41)
-cymene	0.20 -0.38	0.33	0.12	(41)
-chloroform	0.10 -0.20	0.37	0.17	(41)
-dichloroethylene	0.13 -0.24	0.43	0.23	(41)
-thiophene	0.15 -0.29	0.45	0.25	(41)
-ether	0.31 -0.46	0.55	0.33	(41)
-toluene	0.002-0.010	0.43	0.23	(2)
-carbon disulfide	0.2 -0.6	0.49	0.26	(50)
Gutta-percha				
-carbon tetrachloride	0.002-0.008	0.28	0.08	(40)
-toluene	0.001-0.008	0.36	0.16	(40)
Balata-toluene	0.001-0.006	0.36	0.16	(40)
Hydrorubber-toluene	0.002-0.01	0.45	0.25	(40)

where $\mu = \beta V_0/RT$. Huggins has shown that a wide selection of data for polymer-liquid systems are accurately represented by Equation 31; and in Table III, some of his values of μ for rubber-liquid systems are listed, with the concentration ranges from which they were obtained.

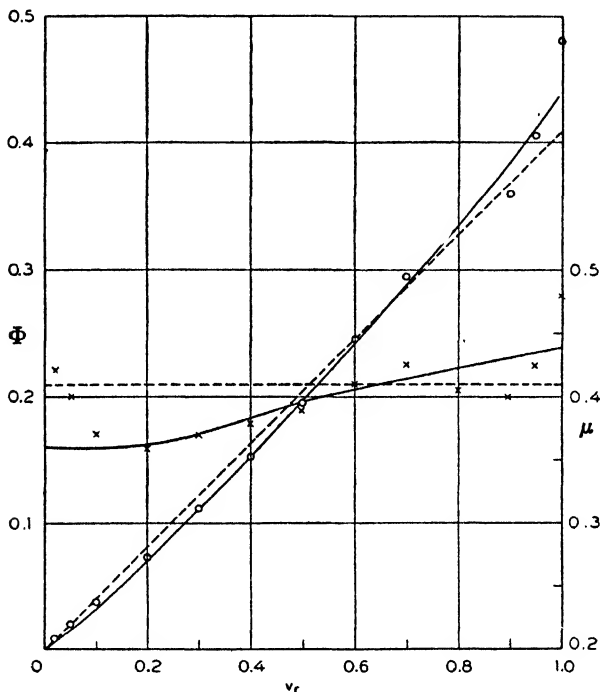


Fig. 11.—Values of Φ (circles) and μ (crosses) for the system natural rubber-benzene. Curves calculated from Equation 32, with $Z = 5$ and $\beta V_0/RT = 0.16$ for unbroken curves and $Z = \infty$ and $\beta V_0/RT = 0.41$ for broken curves.

This remarkably simple result requires further investigation. If Equation 19 is used in place of 12, it is easily shown that Equation 31 must be replaced by:

$$\mu = \frac{\Phi}{v_r} = \frac{\beta V_0}{RT} - \frac{Z}{2v_r^2} \ln \left\{ 1 - \frac{2v_r}{Z} \left(1 - \frac{1}{x} \right) \right\} - \frac{1}{v_r} \left(1 - \frac{1}{x} \right) \quad (32)$$

It follows that μ should be neither independent of v_r , nor equal to $\beta V_0/RT$. In Figure 11, Φ and μ are plotted against v_r , values of ΔG_0 being taken from the smoothed data of Gee and Treloar. The unbroken curves are calcu-

lated for $Z = 5$ and $\beta V_0/RT = 0.16$, and the broken from $Z = \infty$ and $\beta V_0/RT = 0.41$. While the former gives the better fit, it is evident that this method of plotting is somewhat insensitive, and could scarcely be employed to deduce Z and $\beta V_0/RT$ from μ . The values of $\beta V_0/RT$ listed in Table III have been calculated by the author from Equation 32 by assuming $Z = 5$.*

Figure 10 contains, in addition to the benzene data, plots of $\beta V_0/RT \sim v$, calculated from the free energy curves of Figure 8, taking $Z = 5$ and $x \rightarrow \infty$ in all cases. The points shown were read off from the smoothed curves, and are therefore not strictly experimental points; they are included in order to show the discrepancies between $\beta V_0/RT$ from vapor pressure and swelling pressure data. This disagreement, revealed as discontinuities in some of the curves (toluene, carbon tetrachloride), arises of course from experimental errors; in particular, direct vapor pressure measurements become very inaccurate in the region $v_r = 0.3$ to 0.5 . The observed constancy of $\beta V_0/RT$ is surprisingly good, while the negative values found for carbon tetrachloride and chloroform are consistent with the calorimetric data of Table I, although the order of the two liquids is reversed.

Table IV compares values of β read from Figure 10 with those calculated from Equation 27, taking $\sqrt{E_r/\bar{V}_r} = 7.98$ (cal. per cc.)^{1/2} for natural rubber (see page 186). The agreement found is only very approximate, but is probably as good as the considerations advanced on pages 163-164 would lead one to expect.

TABLE IV
COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF β

Liquid	$\sqrt{E_s/\bar{V}_s}$, (cal./cc.) ^{1/2}	β_{obs} , cal./cc.	$\beta_{\text{calc}} =$ $(\sqrt{E_r/\bar{V}_r} - \sqrt{E_s/\bar{V}_s})^2$
Benzene	9.18	1.0 ₆	1.44
Toluene	9.02	~0.6	1.08
Carbon disulfide	10.05	2.5	4.3
Acetone	9.77	~9	3.2
Ether	7.60	2.4	0.14

It will be evident that a full comparison of theory and experiment is as yet hardly possible, and in particular much more accurate data are needed for the heats of dilution of rubber-liquid systems. Equation 28 undoubtedly reproduces the form of the free energy-composition curve with con-

* This value of Z appears physically reasonable, but is to be regarded as very tentative; much more precise data would be needed to calculate it with certainty.

siderable accuracy over a wide concentration range, but it is not yet proved that the division of free energy into heat and entropy terms is so completely satisfactory. It is indeed probable that, where the heat of mixing is large, we obtain states of nonrandom mixing, in which both the entropy and heat of mixing have values lower than theoretical, although the free energy is in close accord with calculation.

The behavior of dilute solutions has not yet been satisfactorily accounted for, and it is somewhat surprising to find the theory least successful in this region. A possible clue is furnished by the viscosities of rubber solutions in different solvents, a full discussion of which lies outside the scope of this chapter. The explanation offered for the varying viscosities of a rubber in a range of solvents is based on the different degrees of coiling of the molecule. Variations of this kind will affect both the heat and entropy of mixing, and it is possible that they are not adequately accounted for by the present theory.

The general agreement between theory and experiment is sufficiently good to enable the theory to be used with considerable confidence in discussing the problems which arise in the interaction of rubbers with liquids.

V. Applications of Thermodynamics to Specific Problems

1. *Molecular Weight of Rubbers from Osmotic Data*

Osmotic pressure measurements have been widely used to obtain the molecular weight of rubbers. The principal difficulty in doing so is that rubber solutions do not in general obey van't Hoff's law:

$$\Pi = \frac{c}{M} RT \quad (33)$$

The method generally adopted has been to extrapolate Π/c to infinite dilution, and assume that:

$$\lim_{c \rightarrow 0} (\Pi/c) = RT/M \quad (34)$$

This procedure remained without theoretical basis until the statistical theory of polymer solutions was worked out. By writing c for the concentration of the solution (g. per cc.) and ρ_r for the density of the rubber, Equation 29 may be combined with Equation 2 to give:

$$\frac{\Pi}{c} = \frac{RT}{M} + \frac{RT}{\rho_r^2 V_0} \left(\frac{1}{2} - \frac{1}{Z} - \frac{\beta V_0}{RT} \right) c \quad (35)$$

from which Equation 34 follows at once.

The experimental difficulty in applying Equation 34 is to carry out the extrapolation to infinite dilution with the necessary accuracy. A number of extrapolation formulae have been proposed, of which the earliest, due to Ostwald (40), was:

$$\Pi = \frac{RT}{M} c + bc^n \quad (36)$$

where b and n were constants and the term bc^n was regarded as a swelling pressure. We have seen that there is no thermodynamic distinction between osmotic pressure and swelling pressure, so that this interpretation of the second term is unsound, but it is to be noted that if $n = 2$, Ostwald's equation becomes formally identical with Equation 35. It has been widely used in this form, especially by Meyer and coworkers.

Reference must be made to another method of extrapolation introduced by Sackur (45) and applied to rubber by Meyer and Mark (35). The osmotic anomaly was attributed to a solvation of the particles and van't Hoff's equation was therefore replaced by:

$$\Pi = \frac{RT}{M} \frac{c}{1 - cs} \quad (37)$$

Schulz (46) has adopted this interpretation and has related the solvation, s , to the osmotic pressure by the equation, $\Pi s^r = k$ to obtain finally:

$$\Pi = \frac{cRT}{M \{1 - c(k/\pi)^{1/r}\}} \quad (38)$$

It is clear from the foregoing thermodynamic analysis that there is no basis for this treatment, but it has been very widely used both by Schulz and by Staudinger and his coworkers (51). It leads to different (usually higher) molecular weights than are obtained by Meyer's method.

Experimental results do not wholly confirm Meyer's procedure since the most accurate osmotic data, namely those for solutions of natural rubber in benzene (21) and of polyisobutylene in cyclohexane (10), show that Π/c is not a linear function of c . The existence of this doubt regarding the correct method of extrapolating the osmotic data to infinite dilution greatly enhances the difficulty of calculating the true molecular weight; and, indeed, the author has concluded that it is scarcely possible to obtain the molecular weight of a high-molecular natural rubber by extrapolating the osmotic data for benzene solutions. The difficulty will be apparent

from Figure 12, and cannot be resolved by measurements at higher dilution unless the present experimental accuracy can be improved. The author has suggested that in view of this difficulty it is better to make osmotic measurements in a solvent with a high heat of dilution, so that the slope of the $\Pi/c \sim c$ curve is reduced. In the case of natural rubber he has shown (15) that by using a mixed solvent containing 15 parts of methyl alcohol by volume and 85 parts of benzene, the reduced osmotic pressure is

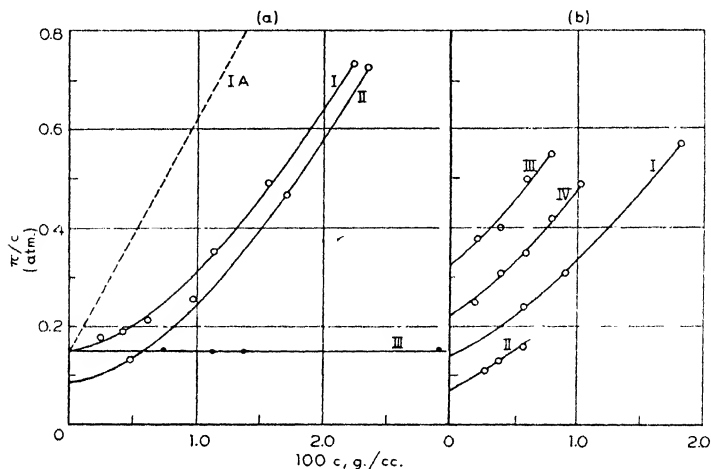


Fig. 12.—Osmotic pressure data. *a*, Natural rubber: curves I and II, benzene (21); III, benzene plus 15% methanol (15); IA, theoretical curve for benzene ($Z = 5$, $\beta V_0/RT = 0.16$). *b*, Toluene solution: curve I, lightly milled crêpe (34); II, crude natural rubber purified by alumina (51); III, emulsion polymer of butadiene (51); IV, sodium polymer B85 of butadiene (51).

practically independent of the concentration at 25° C. up to a rubber concentration of 2.5%, as shown in Figure 12. Flory (9) has argued that it is not permissible to assume this value to represent any better estimate of the value at infinite dilution than the figure obtained by extrapolating the benzene data. The author, however, is of the opinion that the use of this mixed solvent gives the most reliable estimate at present available of the osmotic molecular weight of natural rubber. This view is supported by the data of Flory for polyisobutylene (Fig. 14), which show the constant values of Π/c found for benzene solutions to agree well with $(\Pi/c)_{c=0}$ obtained by extrapolating the figures for cyclohexane solutions.

In comparing the results obtained by different workers, it is important to notice that they have employed different methods of extrapolation

so that their molecular weights are not strictly comparable. In Figures 12 to 14, some of the actual experimental observations are replotted and extrapolated according to a self-consistent scheme, *i. e.*, it has been assumed that the $\Pi/c \sim c$ plot shows a slight curvature, and that plots for rubbers of different molecular weight are nearly parallel. This is in agreement with the observations of Flory for polyisobutylene in cyclohexane (Fig. 14), but not in agreement with the observations of Gee and Treloar for rubber in benzene. The latter workers found the slope of the $\Pi/c \sim c$ plot to be smaller for the lowest molecular weight fractions they examined

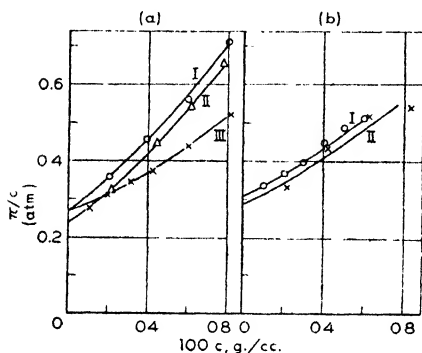


Fig. 13.—Osmotic pressure data (51). *a*, Gutta-percha: curves I and II, carbon tetrachloride; III, toluene. *b*, Balata in toluene.

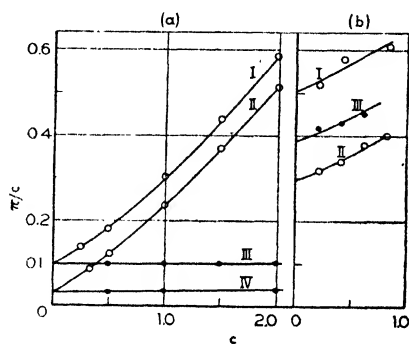


Fig. 14—Osmotic pressure data. *a*, Polyisobutylene (10): curves I and II, cyclohexane; III and IV, benzene. *b*, Toluene solutions of: I and II, hydro-rubber; III, hydrogutta.

than for total rubber. Subsequent (unpublished) experiments made by the author with still lower molecular weight rubbers failed to confirm this trend; and the procedure now adopted seems to be in best agreement with the whole body of experimental data.*

In Table V, the molecular weights obtained by this new extrapolation are compared with those given by the original workers, and it will be seen that the method of extrapolation is capable of producing a considerable degree of uncertainty.

The only other absolute determinations of molecular weight with which

* The discrepancy may arise from the fact that the lowest molecular rubber examined by Gee and Treloar was a thermal degradation product. Subsequent (unpublished) work has shown that such products possess more or less branched structures, and are therefore not strictly comparable with a fraction of natural rubber hydrocarbon of the same mean molecular weight.

TABLE V
OSMOTIC MOLECULAR WEIGHTS OF RUBBER

Rubber	Solvent	Fig. No.	Curve	10 ⁻³ M	
				New	Original
Natural rubber	Benzene (+15% methanol)	12a	I and III	165	165
	Benzene	12a	II	290	290
	Toluene	12b	I	180	270
	Toluene	12b	II	350	350
Butadiene emulsion polymer	Toluene	12b	III	76	78
Butadiene sodium polymer	Toluene	12b	IV	108	133
Gutta-percha	Carbon tetrachloride	13a	I and III	89	112
	Toluene				
	Carbon tetrachloride				
Balata	Toluene	13b	I	80	88
	Toluene	13b	II	86	99
	Cyclohexane	14a	I and III	245	245
Benzene					
Polyisobutylene	Cyclohexane	14a	II and IV	820	820
	Benzene				
	Benzene				
Hydrorubber	Toluene	14b	I	49	59
	Toluene	14b	II	84	103
Hydrogutta	Toluene	14b	III	63	78

these figures can be compared are based on ultracentrifuge measurements. Some figures have been recorded by Lansing and Kraemer (31) for two samples of sol rubber. No osmotic data are available for these same rubbers, but viscosity data were recorded, and comparison with the viscosities of rubbers whose osmotic molecular weight had been determined indicates that the ultracentrifuge molecular weights are higher by a factor of approximately two than the osmotic molecular weights of a similar rubber. No satisfactory explanation of this anomaly has yet been suggested, but it may arise simply from heterogeneity of the rubbers employed. It is clear that a direct comparison between the osmotic and ultracentrifuge methods is highly desirable.

MICELLAR THEORY OF RUBBER STRUCTURE

A note may be added at this point concerning an alternate theory of the structure of natural rubber which has been widely held. Pummerer and coworkers (43) have suggested that the very high molecular weights found for rubber in benzene solution are not true molecular weights, but represent rather the average size of a micelle made up of relatively large numbers of rubber molecules. As the author has shown (16), this theory was based essentially on a false interpretation of the behavior of natural rubber

in camphor solution. In the first place, it was stated that natural rubber dissolves in camphor to give mobile solutions of high concentration: this has now been shown to be due entirely to an irreversible degradation of the rubber which can be avoided by dissolving the rubber in camphor *in vacuo*, when solutions of high viscosity are obtained. In the second place, the low molecular weights obtained by the Rast method were due to a failure to correct for the departure of these solutions from ideal behavior; their true interpretation depends on the recognition of the very large entropy of mixing of rubber with camphor.

2. Solubility of Rubbers in Different Liquids

A rubber will be completely miscible with a liquid if the free energy of dilution is negative at all concentrations. If it is assumed that the heat of dilution of any rubber by any liquid may be represented by an equation of the form (51), then it is easy to find a critical value below which $\beta V_0/T$ must lie in order that the liquid may be miscible in all proportions with the rubber. Figure 9 (page 161) shows that $\Delta S_0/v_r^2$ reaches a minimum value of 0.63 cal. per mole per degree C. (for $Z = 5$, $x = 5000$); if $\beta V_0/T$ is less than this quantity, ΔG_0 will always be negative. We can go somewhat further than this, by assuming β to be given by Equation 27 and adopting the values obtained in a subsequent section for the cohesive energy densities of the various rubbers. It is then possible to calculate $\beta V_0/T$ for any combination of rubber plus liquid, and thus to predict whether or not these two will be completely miscible.

If $\beta V_0/T > 0.63$, a two-phase equilibrium should be obtained over a part of the concentration range. The composition of the two phases may be derived by writing the conditions for equilibrium between the two phases in the form:

$$\left. \begin{aligned} \Delta G'_0 &= \Delta G''_0 \\ \Delta G'_r &= \Delta G''_r \end{aligned} \right\} \quad (39)$$

On substituting the value given by Equation 28 for the free energies of dilution and solution, two simultaneous equations are obtained whose solution gives the compositions of the two phases in equilibrium. The equations must be solved graphically, and the principal features have been worked out by Flory (9) and by Gee (17). Flory finds that for any value of βV_0 there exists a critical temperature above which the rubber and liquid are miscible in all proportions. The temperature and concentration at the critical point are given by:

$$T_{\text{crit}} = \frac{2 \beta V_0 x}{R(1 + \sqrt{x})^2}$$

$$v_{r, \text{crit}} = \frac{1}{1 + \sqrt{x}}$$
(40)

At any temperature appreciably below the critical the dilute phase consists essentially of pure liquid. The author has shown that these conclusions are dependent to some extent upon the exact form assumed for the heat of mixing, but qualitatively they are confirmed. The temperature coefficient of solubility is so large for a rubber of high molecular weight that a critical temperature should exist for any liquid above which the liquid and rubber are completely miscible, and below which no appreciable dispersion of the rubber occurs. The rubber phase may, however, be highly swollen by the liquid and may contain no more than 5% of rubber. Similar critical phenomena are to be expected if the solvent power of a liquid is reduced by adding a nonsolvent.

The problem of the solubility of polymers has been treated in a rather different way by Brønsted (3) and Schulz (47). Brønsted related the distribution of a polymer between two phases to the difference of potential energy between them. Assuming this difference of energy to be proportional to the molecular weight of the polymer, he wrote for the concentrations C' and C'' of a polymer in the two phases:

$$\log \frac{C'}{C''} = \frac{\lambda M}{RT}$$
(41)

where λ is constant for a series of polymers in a particular liquid. This equation was further developed by Schulz and applied to the case of a mixture of two liquids by representing λ as a linear function of the liquid composition. If one of the liquids is a solvent and the other a nonsolvent, it follows that the proportion, γ , of the latter in the critical mixture which will just dissolve a polymer of molecular weight M is given by:

$$\gamma = A + B/M$$
(42)

where A and B are constants. This equation has been widely applied and shown to fit the data for a number of polymers (18). Although this method is thus qualitatively successful, it must be pointed out that the derivation of Brønsted's original equation, which forms the basis of all subsequent development, is incorrect. As has been shown in the first section of this chapter, the principal difference between polymers and low-molecular materials lies in the entropy of mixing, and not in the heat term.

The author has investigated the relationship between the Brønsted-Schulz theory and the correct thermodynamic formulation of the problem and has shown (18) that, with certain approximations, the solution of Equations 39 may be reduced approximately to a form closely analogous to Brønsted's equation (Eq. 41):

$$\ln \frac{v_r'}{v_r''} \simeq M \left(a - \frac{b}{RT} \right) \quad (43)$$

where $a = (1 - v_0'')/M_0$ and $b = (\beta V_0/M_0) [1 - (v_0'')^2]$. The phase designated by prime is taken to be the dilute one, and the derivation involves the approximation $v_0' \simeq 1$.

In discussing the application of these theoretical considerations to practical solubility problems, it is necessary to bear in mind that certain important assumptions have been made. The rubber has been assumed homogeneous: this will never be the case, although a more or less close approximation may be achieved by careful fractionation. When a rubber containing a range of molecular weights is treated with a liquid, at a temperature in the neighborhood of the critical solution temperature, there is a tendency for the rubber to divide itself between the liquid and rubber phases so that the material of lower molecular weight is preferentially dissolved. This is the basis of one method of fractionation and will be considered in more detail in pages 190-191; here we need only note that its effect will be to reduce greatly the apparent temperature coefficient of solubility, and to blur the sharpness of the critical solution phenomena. The most complete confirmation of this point is found in Brønsted's work on the solubility of polystyrene (4).

Another way in which an actual rubber may differ from the theoretical ideal is in the presence of extraneous material. In the case of natural rubber there is abundant evidence (see pages 191-192) that the protein content exercises a profound influence on its solubility. Rubbers may also undergo change by oxidation or other chemical reactions. The manipulation of purified natural rubber and many of its derivatives is greatly hindered by an irreversible loss of solubility. Rubbers which have been obtained in solution frequently become insoluble on removal of the solvent, even though care is taken to exclude oxygen: no satisfactory explanation of this behavior has yet been given.

These considerations make it difficult to test the solvent power of a liquid for a rubber adequately by simply bringing the two in contact: the results are frequently highly dependent on the history of the rubber specimen and on the degree of agitation employed. For example, if

natural rubber is extracted with hexane, without agitation, only a portion (variable) is removed, and the residue, which contains the bulk of the protein, is very difficult to disperse in benzene. Total natural rubber generally dissolves readily in benzene, although Kemp and Peters (30) have reported that a considerable residue (of high nitrogen content) remains behind if agitation is avoided.

A quantitative comparison of the solvent powers of a series of liquids for a rubber may be obtained by dissolving the rubber as completely as possible under the most favorable conditions, and then determining the proportion of a nonsolvent required to cause precipitation. Fairly systematic studies of the solubilities of polybutene (8) and chlorinated natural rubber (44) have been made in this way. Some of the figures, with the less complete data for natural rubber (52), are compared in Table VI with $\beta V_0/T$ values calculated from the estimated cohesive energy densities of the rubbers and liquids.

TABLE VI
SOLVENT POWER FROM PRECIPITABILITY

Liquid	$\sqrt{\frac{E_0}{V_0}}$ (cal./cc.) ^{1/2}	Polybutene		Chlorinated rubber		Natural rubber	
		$\beta V_0/T$, cal./mole per ° C.	<i>P</i>	$\beta V_0/T$, cal./mole per ° C.	<i>P</i>	$\beta V_0/T$, cal./mole per ° C.	<i>P</i>
Hexane	7.4	0.04	22.9	1.25	Insol.
Heptane	7.5	0.02	26.4	1.25	Insol.
Cyclohexane	8.2	0.01	53
Decalin	8.3	0.03	47
Tetralin	8.4	0.07	38
Dipropyl ketone	8.4	0.23	222
Carbon tetrachloride	8.6	0.08	23
Xylene	8.6	0.33	21.7	0.10	38
Toluene	9.0	0.60	20.3	0.00	50
Ethyl acetate	9.1	0.00	249
Benzene	9.2	0.67	14.6	0.00	49	0.43	9

In calculating β from Equation 27, the following values for $\sqrt{E_r/V_r}$ have been assumed: polybutene, 7.7; chlorinated rubber, 9.1; natural rubber, 8.0. The first two are estimates, based on the chemical structures of these rubbers. *P* represents the number of cubic centimeters of precipitant required to produce opalescence in 100 cc. of rubber solution, the precipitants used being: polybutene, 2-ethylbutanol; chlorinated rubber, "lactol spirits;" natural rubber, acetone.

According to the theory, *P* should reach a maximum value at $\beta V_0/T = 0$, while a liquid for which $\beta V_0/T > 0.63$ should not be a solvent. These predictions are very roughly borne out by Table VI, but the extremely great solvent power of dipropyl ketone and ethyl acetate for chlorinated

rubber is anomalous. In fact, this high activity is common to all the ketones and esters studied, and must be attributed to some specific interaction between the carbonyl group and the chlorinated rubber. It is well known that such interactions exist in simple liquids, and are especially reflected in the evolution of heat on mixing chloroform with acetone, ethyl acetate, etc.

One further solubility problem requires consideration at this point, by reason of its close connection with the above method of determining solvent power. While it is true that the addition of, say, methanol to a benzene solution of rubber ultimately causes precipitation, yet small additions result in an *enhanced* solvent power. This is strikingly shown by the data of Kemp and Peters (30) on the extraction of natural rubber by hexane. Small additions of alcohols or acetone greatly increase the proportion of rubber extracted, while larger additions of course cause precipitation. Furthermore, the order of effectiveness in promoting solution is very nearly the same (methanol > ethanol > butanol > acetone) as in causing final precipitation. The effect has been ascribed to the solvation by the alcohol of the polar portions of the rubber-protein complex or perhaps of oxygenated groupings in the rubber. In the author's opinion, the phenomenon is probably more fundamental, since it appears in a particularly striking form in the work of Brønsted on polystyrene. This material, although insoluble in either acetone or *n*-propyl laurate, dissolves in mixtures of the two, and can be precipitated by addition of either liquid in excess. No complete analysis of the problem has been given, but it is probably noteworthy that the pairs of liquids which show the effect most strongly are those whose deviation from Raoult's law will be largest. The partial vapor pressures of benzene and methyl alcohols above a mixture are almost equal to those of the pure compounds (32), so that the solvent power of the mixture may well approximate more closely that of the two components added together than their mean. This is of course only a very crude picture, but no thermodynamic study of a ternary rubber-liquid₁-liquid₂ system has yet been published.*

* This is no longer true. A semiquantitative analysis (20a) of the effects of mixed liquids shows that a mixture will have solvent properties intermediate between those of its components only when the heat of mixing of the liquids is small compared with the heat of mixing of either with the rubber. If the heat of mixing of the liquids is large, the mixture shows enhanced solvent properties. One consequence of this is that the method of comparing solvent powers outlined above will only be valid if the non-solvent is carefully chosen so as to avoid the production of mixtures of enhanced solvent power. A less complete analysis along similar lines has been applied by Scott and Magat (49a) to the problem of fractionation.

Summarizing, we may say that the thermodynamic theory of rubber solutions describes satisfactorily the essential features of the experimental work on the solubility of rubbers in liquids, but requires much further development before the details can be filled in.

3. *Limited Swelling of Rubbers in Liquids*

The phenomenon of limited swelling may be regarded as a special case of the problem of solubility, in which the rubber content of the dilute phase is negligibly small. Swelling is a normal accompaniment of solution, but we shall restrict our consideration here to rubbers which are wholly insoluble, *i. e.*, in general to vulcanized rubbers. Experimentally, swelling may be observed either by means of the increase in volume or the increase in weight, and a number of experimental techniques have been devised. A review of them has been given by Proske (42) but most measurements of swelling have employed a relatively crude experimental technique; this is doubtless adequate for many purposes. For rubbers which are reasonably coherent and solid in the swollen state, the simplest method is to weigh the swollen rubber after wiping the surface rapidly with filter paper to remove adhering liquid. This method gives quite consistent results, provided that the rubber specimen under examination does not contain materials soluble in the swelling agent. Such materials are in fact frequently present in compounded rubbers, and they distribute themselves between the rubber and the liquid, so that the measured swelling depends on the relative volumes of rubber and liquid employed. This difficulty may of course be overcome by extracting the rubber with a large excess of liquid and then drying, before making the swelling measurement. A very large body of data for natural rubber is recorded in the literature, but its unsystematic nature makes much of it almost valueless as a basis for the scientific study of swelling. It is evident that the system rubber-liquid should reach a definite equilibrium state in which swelling would become constant, but in practice it is usually observed that natural rubber swells rapidly at first, and then more slowly, with no well-defined limit. Scott (49) showed that it was possible to divide the process of swelling into two fairly definite portions, an initial rapid swelling, followed by a slow uptake of liquid occurring at an approximately constant rate. This secondary process—termed the “increment” by Scott—has a very much larger temperature coefficient than the initial swelling, and was ascribed by Scott to an irreversible chemical breakdown of the rubber. He therefore proposed that the true swelling should be derived from the experimental figure by subtracting the increment, a suggestion which has gained

general acceptance. The author has confirmed the essential correctness of this procedure by showing (13) that if the swelling is carried out *in vacuo* no increment is observed. A number of attempts have been made to correlate the swelling powers of different liquids for rubber with some physical or chemical property of the liquids. It was early recognized that natural rubber is much more highly swollen by hydrocarbons than by polar liquids such as esters and alcohols. A quantitative relationship between the swelling, Q (cc. of liquid per cc. of swollen rubber), and the dielectric constant, ϵ , of the liquid was proposed by Ostwald (39):

$$Q = k \epsilon^{2.16} \quad (44)$$

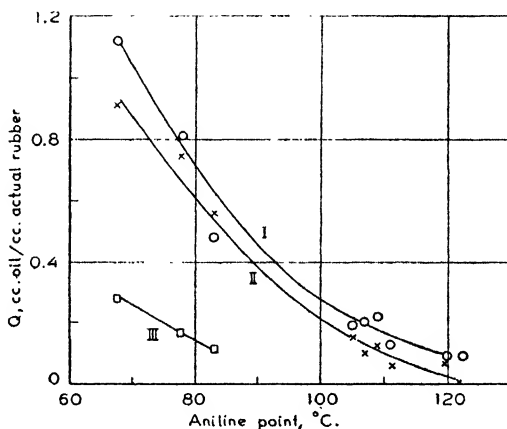


Fig. 15.—Swelling powers of mineral oils for: I, Neoprene G; II, Neoprene E; III, Perbunan; recalculated on the basis of actual rubber content of the compounds, after correcting the swelling for "increment" by extrapolation to zero time.

The accumulation of more precise data showed that this equation was invalid. More recently, Carman, Powers and Robinson (5) have shown that the swelling powers of a series of mineral oils are closely related to their aniline points.* This relationship holds for a series of rubbers, data for each rubber falling on a separate curve, as shown in Figure 15.

The most systematic attempt to relate the swelling power of liquids for natural rubber with their chemical constitution was made by Whitby, Evans and Pasternack (53), who found that the swelling power of a homologous series of liquids increases as the series is ascended. Polar groups in

* The aniline point of an oil is the temperature at which it is just miscible with a given proportion, 50% in this work, of aniline.

general tend to diminish the swelling, OH and CN being particularly effective. Chlorination usually increases the swelling power; and it is generally observed that aromatic liquids are much more powerful swelling agents than aliphatic liquids containing the same polar group.

We have now to consider whether a quantitative theory of swelling can be worked out on the basis of the thermodynamic treatment outlined on pages 157–164. The first difficulty in doing so is that the entropy calculation given there does not apply quantitatively to vulcanized rubbers. The presence of cross links in the rubber structure decreases the number of possible configurations of the molecule, so that the entropy of swelling of vulcanized rubber must evidently be less than that of raw rubber, but there is at present no estimate of the extent of the difference.* One would not expect to find any significant difference in the entropy of swelling for low solvent contents; this is confirmed by the fact that the swelling of raw and vulcanized rubbers in a poor swelling agent is the same (43). (The swelling of the vulcanized material must of course be referred to its rubber content.) Starting from this observation, the author has proposed (19) an empirical method of deriving an approximate curve for the entropy of swelling of vulcanized rubber. The thermodynamic condition for the maximum swelling of a vulcanized rubber is $\Delta G_0 = 0$. Consequently, if it is assumed that the heat of swelling of the rubber by the best swelling agent which can be found is zero, it follows that the entropy of swelling is zero at the concentration given by the maximum swelling in this particular liquid. If now the theoretical entropy for linear rubbers is plotted in the form $\Delta S_0/v_r^2 \sim v_r$, an approximate curve for the entropy of swelling of this particular vulcanized rubber may be sketched, as in the broken curve of Figure 9 (page 161). The maximum swelling of this rubber in any other liquid may now be estimated by drawing on the same figure a horizontal line representing $\Delta H_0/Tv_r^2 = \beta V_0/T$. At the point at which this cuts the entropy curve we have $\Delta G_0 = 0$, and the corresponding abscissa gives the composition of the swollen rubber at equilibrium. The next step is to relate the heat of swelling to the cohesive energy densities

* In a paper published since this chapter was written, Flory (10a) has shown that, if the rubber is completely cross linked into a network in which the molecular weight between junction points is M_c , the entropy of swelling is reduced (compared with that of noncross-linked rubber) by:

$$\delta\Delta S_0 = \frac{R}{M_c} \rho_r V_0 v_r^{1/3}$$

This leads to an entropy curve differing only very slightly from the broken curve of Figure 9.

of the rubber and the liquid, as in Equations 26 and 27. According to Equation 27, the rubber should swell to its maximum extent in a liquid whose cohesive energy density is equal to that of the rubber, and to a smaller extent in liquids whose cohesive energy densities are either smaller or larger. It follows, therefore, that if the swelling of a given rubber in a series of liquids is plotted as a function of the cohesive energy density of the liquids, a curve should be obtained showing a maximum, whose position

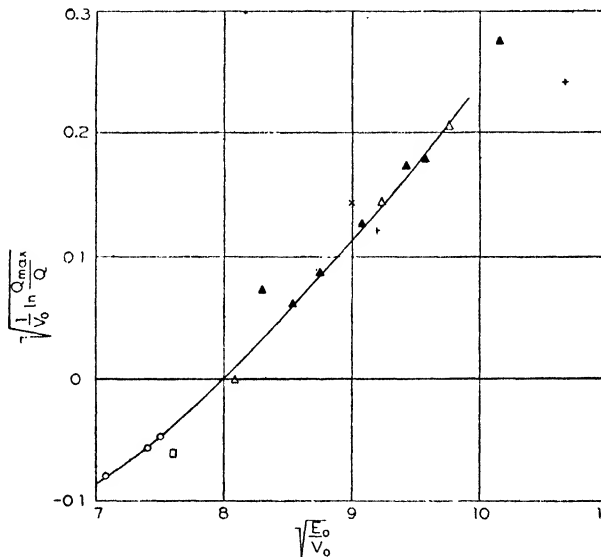


Fig. 16.—Determination of cohesive energy density of natural rubber from swelling data. The symbols in Figures 16 to 23 are: O, hydrocarbon; ▲, ester; Δ, ketone; □, ether; ×, aldehyde; +, nitrile; ●, acid; ○, alcohol; ◇, nitro compound.

may be used to estimate the cohesive energy density of the rubber. More precisely, the swelling should be a function of:

$$\sqrt{V_0} \left(\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}} \right) = y$$

say, and the author has shown that this is indeed the case for a considerable range of liquids. Before this plot can be made it is necessary to estimate the cohesive energy density of the rubber. This may be done by making use of the observation that the swelling, Q , can be represented as a function of y by a curve closely resembling the Gauss function:

$$Q = Q_{\max} e^{-\alpha y^2}$$

In order to represent the data exactly, α must be treated as variable. Substituting for y and rearranging gives:

$$\sqrt{\frac{F_0}{V_0}} = \sqrt{\frac{E_r}{V_r}} = \sqrt{\frac{1}{\alpha V_0} \ln \frac{Q_{\max}}{Q}} \quad (45)$$

Hence, if Q_{\max} is estimated by a rough plot of Q vs. $\sqrt{E_0/V_0}$, $\sqrt{E_r/V_r}$ may be estimated by plotting $\sqrt{\frac{1}{\alpha V_0} \ln \frac{Q_{\max}}{Q}}$ as a function of $\sqrt{E_0/V_0}$. A typical plot is shown in Figure 16. This procedure was applied by the author to the swelling of a series of natural and synthetic rubber compounds in a

TABLE VII
LIQUIDS USED IN SWELLING MEASUREMENTS

Liquid	E_0 , cal./mole	V_0 , cc./mole	$\sqrt{E_0/V_0}$, cal./cc.
<i>n</i> -Pentane	5,750	115.2	7.07
<i>n</i> -Hexane	7,130	130.3	7.40
<i>n</i> -Heptane	8,240	146.4	7.50
Ethyl ether	6,000	103.8	7.60
<i>iso</i> -Butyl <i>n</i> -butyrate ^a	10,080	166.4	7.78
<i>n</i> -Butyl <i>n</i> -butyrate ^a	10,750	165.7	8.06
<i>n</i> -Butyl acetate	9,560	131.7	8.53
<i>n</i> -Propyl acetate	8,810	115.1	8.75
Ethyl acetate	8,060	97.8	9.08
Ethyl formate	7,110	80.0	9.43
Methyl acetate	7,310	79.7	9.58
Methyl formate	6,360	61.6	10.16
Diisopropyl ketone	9,250	14.7	8.08
Ethyl methyl ketone	7,600	89.5	9.22
Acetone	7,000	73.3	9.77
Butyraldehyde	7,600	88.2	9.00
<i>n</i> -Capronitrile	10,120	119.9	9.19
Propionitrile	8,000	70.2	10.68
Acetonitrile	7,420	52.5	11.89

^a E_0 estimated from values for other esters since no suitable vapor pressure data were available.

range of aliphatic liquids (20). Details of the liquids and of the compounds used are given in Tables VII to IX; the swelling data are plotted in Figures 17 to 22.

TABLE VIII
NATURAL RUBBER COMPOUNDS USED IN SWELLING MEASUREMENTS

Material ^a	Parts by weight in compound				
	I	II	III	IV	V
Smoked sheet	100	100	100	100	100
Sulfur	3.5	3	3	3	3
Zinc oxide	6	5	5	100	18
Stearic acid	0.5	3	3	2.5	1.5
Mercaptobenzothiazole	0.5	1	1	...	1
Carbon black	...	45	100
Nonox S	...	1.5	1.5	1	1
Pine tar	...	1	2	...	3.5
Tetramethylthiuram disulfide	0.1	1	...
Magnesium carbonate	50	42
Mineral oil	5	...
Magnesium oxide	4
Red oxide	14
Lithopone	64
Paraffin Wax	1.5
TOTAL	110.5	159.5	215.6	262.5	253.5

^a All compounds were vulcanized for 30 minutes at 40 pounds' steam.

TABLE IX
SYNTHETIC RUBBER COMPOUNDS USED IN SWELLING MEASUREMENTS

Material	Rubber No. (see Table X)						
	VI	VII	IX	X	XI	XII	XIII
Rubber (synthetic)	100	100	100	100	100	100	100
Di- <i>o</i> -tolylguanidine	0.5	1
Magnesium oxide	4	10
Carbon black	...	35	60	60	60	50	55
Whiting	...	100
Nonox S	2	2
Stearic acid	0.25	0.25	0.5	1	0.5	1	1
Zinc oxide	1	5	10	5	10	5	5
Diphenylguanidine	0.1	...	0.1
Dibenzothiazyl disulfide	0.35	1	0.35	1	1
Dibutyl phthalate	20	...	40	...
AgeRite powder	1
Sulfur	1.5	...	2	2
Tar	5
TOTAL	107.8	253.3	171	189.5	171	199	169
Time of vulcanization, min.	30	30	50	15	50	45	45
Steam pressure, lb./sq. in.	40	40	50	30	50	40	40

Figure 17 gives the results for five different compounds of natural rubber, and it will be observed that similar curves are obtained in all cases, all having their maxima at the same point. It follows that the compound-

ing ingredients used do not affect the essential nature of the swelling. Reinforcing fillers appear to reduce swelling by holding together the rubber

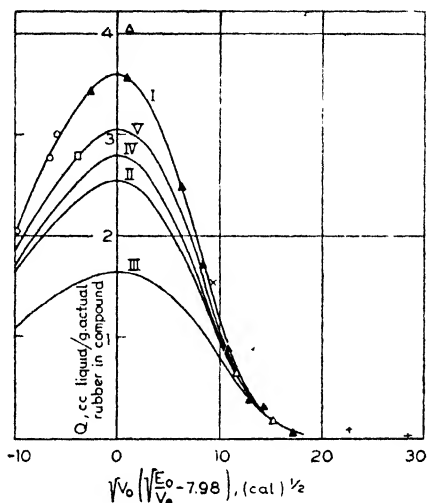


Fig. 17.—Swelling of natural rubber compounds. I-V, points are for I only. Curves in Figures 17 to 22 are numbered according to the number of the compound in Tables VIII and IX.

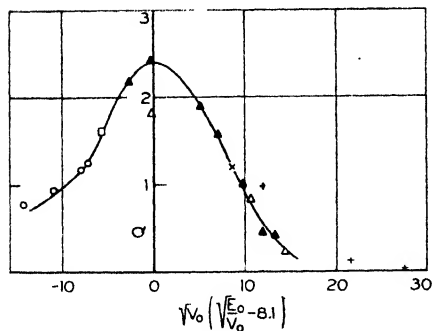


Fig. 18.—Swelling of Buna S (XIII).

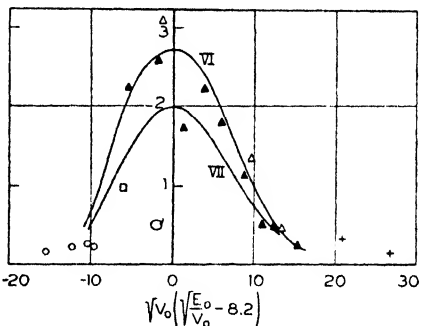


Fig. 19.—Swelling of Neoprene GN (VI and VII). Points are for VI.

structure, and thus diminishing the maximum swelling, without significantly effecting the swelling in poor swelling agents. The cohesive energy densities of the rubbers estimated from these data are in Table X.

The interpretation of these values in the case of copolymers requires some care. We are, in effect, assuming the molecule to have a uniform

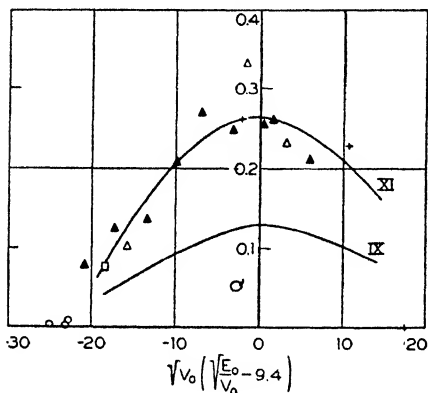


Fig. 20.—Swelling of Thiokol F (IX) and FA (XI). Points are for XI.

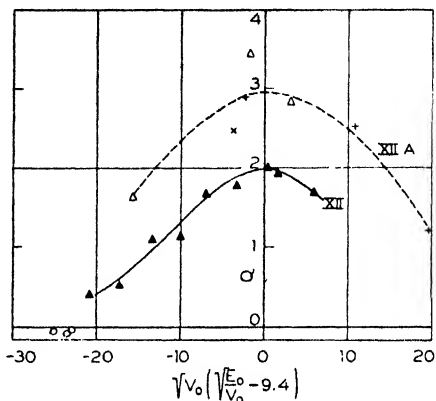


Fig. 21.—Swelling of Buna N (XII). Curve XII is for esters, XIIA for ketones and nitriles.

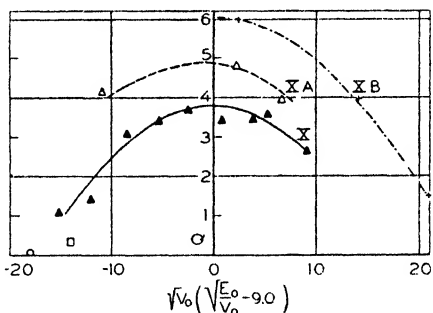


Fig. 22.—Swelling of Thiokol RD (X). Curve X is for esters, XA for ketones and XB for nitriles.

TABLE X
COHESIVE ENERGY DENSITIES OF RUBBERS

Rubber	Numbers	E_T/V_r , cal./cc.
Natural	I to V	63.7
Buna S	XIII	65.5
Neoprene GN	VI and VII	67
Thiokol RD	X	81
Thiokol F	IX	88
Thiokol FA	XI	88
Buna N	XII	88

force field around it, an assumption which is evidently not true for molecules possessing polar and nonpolar portions. The difficulty is particularly serious for copolymers, in which the polar groups are rather widely separated by hydrocarbon chains, and it is evidently a somewhat crude approximation to treat the molecular field as uniform.

It is to be observed that, while liquids of different chemical structure all give points on the same curve in the case of natural rubber, this is no longer the case for some of the synthetics, especially Thiokol RD. Another limitation of the theory is evident from Figure 23, in which the

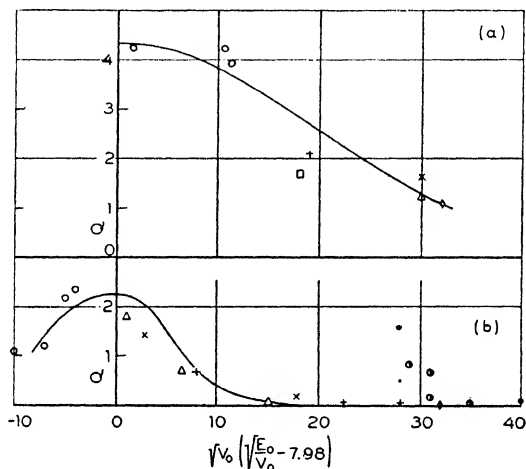


Fig. 23.—Swelling of vulcanized natural rubber (44): *a*, in aromatic liquids; *b*, in aliphatic liquids.

swelling data of Whitby *et al.* have been plotted so as to bring out the difference between aliphatic and aromatic liquids. Not only do the two classes of liquids fall on different curves, but certain liquids, notably alcohols and acids, fall completely off the curve. Many of these discrepancies are to be attributed to the incomplete validity of the equation used to determine the heat of mixing. As we have noted previously, this equation is of only approximate validity for mixtures of liquids, and in particular it neglects entirely the effect of specific interactions between polar groups in the two molecules. Thus, for example, it is well known that the heat of solution of alcohols in hydrocarbons is quite small (26), the explanation being that the alcohol dissolves in the hydrocarbon in an associated form. It is not therefore surprising to find that the swelling power of alcohols is

greater than would be expected from their cohesive energy densities. Again, chlorinated liquids, especially chloroform, mix with hydrocarbons with a very small heat absorption (26) (or even a heat evolution), so that Whitby's observation, that chlorinated liquids have a high swelling power for rubber, is readily understood. It is doubtless along lines such as these that the observed departures from the simple theory of swelling are to be understood. It is clear, therefore, that the theory cannot in its present form give a complete quantitative account of swelling, but it does at least provide a background for the understanding of the essential features of the phenomenon.

4. Solubility of Solids in Rubbers

The solubility of solids in rubbers is a problem of some importance in the understanding of the mechanism of vulcanization, since the question as to

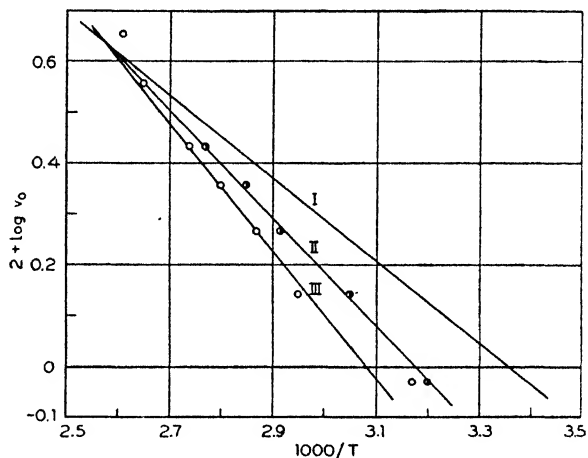


Fig. 24.—Solubility of sulfur in rubber: I, theoretical; II, natural rubber (27); III, Buna S (54).

whether the various ingredients are dissolved in the rubber evidently determines whether or not they may be involved in a homogeneous vulcanization reaction. Measurements of solubility have been made only for sulfur, in natural rubber (27) and in Buna S (54). Solubility in the two rubbers is approximately the same (Fig. 24), and is sufficiently large for the whole of the sulfur normally present in a vulcanizate to be in solution at the vulcanizing temperature. Since supersaturation readily occurs

to the extent of some 2%, it is only in the case of very large sulfur contents that there is any probability of uncombined sulfur crystallizing out again on cooling, in the form of a "bloom." The solubility of sulfur in rubber may be readily calculated by an extension of the methods applied to liquids. We may begin by considering the solubility of liquid sulfur at the melting point, T_f . The cohesive energy density of liquid sulfur has been estimated by Hildebrand (22) in two ways: from the vapor pressure, a value of 137 cal. per cc. was obtained, while the solubility behavior of sulfur in a range of liquids gives values which average 163 cal. per cc. The equilibrium composition of a rubber-sulfur solution is given by putting $\Delta G_0 = 0$ in Equation 28. Taking the experimental value for the solubility (10 g. of sulfur per 100 g. of either rubber), we calculate $v_0 = 0.045$ at $T = 390^\circ \text{K.}$, whence $\beta V_0 = 1620$ cal. per mole. β should now be given by Equation 27, while V_0 must be interpreted as the molar volume of a sulfur molecule, S_8 . For natural rubber $\sqrt{\bar{E}_r/\bar{V}_r} = 8.0$ (cal. per cc.)^{1/2}; and, putting $\beta V_0 = 1620$, we find for the cohesive energy density of sulfur a value of 141 cal. per cc., in excellent agreement with Hildebrand's estimate. If we carry out the same calculation using William's data for Buna S, the value found is 144 cal. per cc.

In order to calculate the solubility of sulfur below its melting point, we must take into account the heat and entropy of fusion. If L_f is the latent heat of fusion of sulfur (assumed to be 1700 cal. per mole, independent of T), the entropy of fusion is L_f/T_f . Hence the condition for equilibrium between solid sulfur at temperature T and rubber is (putting $Z = 5$, $x \rightarrow \infty$, in Equation 19):

$$L_f + \beta V_0 v_r^2 = T \left[R \left\{ \ln \frac{1}{v_0} + 2.5 \ln \left(1 - \frac{v_r}{2.5} \right) \right\} + \frac{L_f}{T_f} \right] \quad (46)$$

This equation is readily solved for T by assuming values of v_r , and gives the curve shown in Figure 24, which includes also the experimental results for natural rubber and for Buna S. It will be seen that the temperature coefficient of solubility observed experimentally is somewhat larger than that calculated in this way, but the agreement is fairly satisfactory. The same method of calculation could, of course, be applied to antioxidants, accelerators, etc., but there are at present no data by which the conclusions can be tested. It may, however, be noted that the x-ray studies of Clark, LeTourneau and Ball (7) show the presence of crystalline accelerators in rubbers at room temperatures, which fixes an upper limit of 0.5% for the solubility at room temperature of the particular accelerators they studied.

5. Fractionation of Rubbers

The physical properties of rubbers are determined in part by their chemical nature, in part by their average molecular weight and in part by the distribution of molecular sizes. The last factor has received little attention hitherto, but a number of attempts have been made to separate rubbers into a series of more homogeneous fractions. The methods adopted fall broadly into two classes: (1) those based on the more rapid diffusion into a solvent of the lower molecular components; and (2) the equilibrium distribution of inhomogeneous rubbers between sol and gel phases by the use of a liquid which is on the border line between solvent and non-solvent. A discussion of the mechanism of the first method is outside the scope of this chapter, but in principle, at any rate, the efficacy of the second should be capable of quantitative analysis by an extension of the methods developed above. The problem is much more complex than any we have previously discussed. One complicating factor is the fact, already noted, that the temperature coefficient of solubility of a high-molecular rubber is so large that in general a liquid chosen at random is either completely miscible with rubber at all convenient working temperatures, or does not disperse it at all. In order to achieve fractionation it is therefore necessary to employ mixtures of solvent and nonsolvent, and it is evident from Schulz's empirical equation (Eq. 42), that it should be possible to achieve fractionation by progressively changing the composition of such a mixture. A thermodynamic analysis of the problem requires us to treat the system as quaternary, even if we make the simplification of supposing only two rubbers of different molecular weight to be present. It has been observed experimentally that the solvent compositions of the two phases are in general quite different (4), so that it is not permissible to treat the solvent mixture as a single liquid. The analysis of such a system has not yet been carried out. Schulz (48) has extended his treatment of the solubility of a single rubber by the modification of Brønsted's equation to the form:

$$\ln \frac{c'_i}{\alpha c_i^n} = - \frac{\lambda M_i}{RT} \quad (47)$$

where α is an empirical constant, introduced to allow for the possibility that different mixtures of solvent and nonsolvent may show different fractionating powers. Schulz gave an arithmetical solution to this equation, employing arbitrary values of the constants, from which he concluded that the efficiency of a fractionation could be greatly improved by working with dilute solutions. A similar conclusion was reached by the author (17)

based on an empirical attempt to extend Flory's entropy equation, in order to introduce the entropy of mixing of rubbers of different molecular weight. Neither of these derivations is in any sense rigorous, but the practical conclusion is amply borne out by experiment (13).

Probably the best practical application of these principles to a fractionation is given by the work of Flory on polyisobutylene (10). Polyisobutylene was dissolved in benzene to give a 1% solution; acetone was added until precipitation began; the mixture was then warmed until it became homogeneous and cooled slowly with stirring until separation began, when it was thermostated in order to allow an equilibrium separation to occur. After removing the supernatant liquid, the precipitate was re-dissolved in benzene plus acetone, of the same ratio, but the total concentration was reduced to *ca.* 0.1%. The polymer was then reprecipitated in the same way, removed and dried. Further fractions were obtained by combining the supernatant liquors, concentrating to make the solution 1% and repeating the process. No data were reported from which a molecular distribution function could be constructed.

Fractionation of natural rubber is complicated by the presence of non-rubber constituents which have a profound effect on its solubility. The earliest method of separation was based on the observation that if rubber is extracted with an indifferent solvent such as ether or petroleum ether, only a portion dissolves. This portion was termed "sol" rubber and the residue "gel," the two being for some time regarded as approximately homogeneous, distinct fractions of rubber. Kemp and Peters (30) showed that the amount of sol which could be extracted was very dependent on the care with which oxygen was excluded during the extraction process, and concluded that really fresh rubber would be insoluble in the absence of air. Sol rubber was in fact regarded as an oxidation product of gel. This view cannot be supported, since the thermodynamic study of the system rubber hydrocarbon-benzene (21) leads to the conclusion that a rubber of any molecular weight should be completely miscible with benzene. It is observed that the gel fraction contains the bulk of the protein content of the original rubber, and in any attempt to fractionate rubber the least soluble fractions always contain most of the protein.

A fractionation of total rubber is not therefore simply a separation of rubbers differing only in molecular weight; and care is required in interpreting the results of the various attempts which have been made to fractionate rubber. In the author's opinion, which is supported by many unpublished results, the best available method consists in a preliminary separation, to remove oxygenated and nitrogenous material, followed by a

series of precipitations along the lines used by Flory in his work on polyisobutylene. The work of Midgley, Henne and Renoll (36) cannot be considered to conform to the above description, since the solutions used were too concentrated, while low fractions were continually returned to the material being fractionated.

The most systematic attempts to fractionate rubber have employed diffusion methods, but in two very different ways. Kemp and Peters (28) extracted crêpe with hexane, renewing the whole of the supernatant liquid at intervals. They found that the viscosity molecular weight of successive fractions increased progressively, there being no indication of the separation of a sharply defined band of molecular weights. The range of molecular weights, recalculated on the basis of the author's standardization of the viscosity method (15) was from 185,000 to 490,000. The final extract was 52.4% of the total rubber, and Kemp and Peters expressed the opinion that the "gel" residue must be of still higher molecular weight. That this is not necessarily the case was shown by some osmotic pressure measurements on sol and gel rubbers reported by the author (15). The sol, comprising 40% of the original acetone extracted crêpe, had a molecular weight of 300,000. The gel residue was dissolved in benzene plus 15% methyl alcohol, and found to have a molecular weight of 210,000; its intrinsic viscosity was also less than that of the sol. A possible objection to these measurements, which have not yet been confirmed, is that a true molecular dispersion of the gel may not have been achieved.

A different diffusion method was worked out by Bloomfield and Farmer (1), its aim being to achieve separation by an equilibrium distribution of rubbers of different molecular weights between two phases, rather than to rely on the lower molecular fraction diffusing out more *rapidly*. The rubber, after purification to remove nitrogenous and acetone-soluble material as completely as possible, was extracted with mixtures of petroleum ether and acetone of increasing hydrocarbon content. Successive extractions were carried out with a given mixture until diffusion practically ceased; a richer mixture was then employed. In this way crêpe rubber of mean molecular weight (viscosity) 344,000 was split into the fractions given in Table XI. The lowest fraction contained about 1% oxygen; the insoluble residue was of high protein content (3.3% nitrogen, *ca.* 6% oxygen). The middle fractions were pure hydrocarbon, within the limits of analytical accuracy, and could not readily be further fractionated by this diffusion method. Subsequent (unpublished) work has shown them to contain a wide molecular weight range, and to be capable of fractionation by a method similar to that of Flory. Kemp and Peters (30) have shown that, by the use of a

wider range of hexane-acetone mixtures, a range of low-molecular materials may be extracted from crêpe or latex film, approximately 2.5% of material of molecular weight (recalculated as above) $< 100,000$ being obtained.

In the author's opinion, these diffusion processes are of value chiefly for the preliminary purification of rubber, in order to obtain a suitable starting material for fractionation by a precipitation method. If a true fractionation is to be achieved by the latter it is imperative that dilute solutions be employed, and it would appear that gradual precipitation by cooling has important advantages over the rapid addition of a precipitant.

TABLE XI
FRACTIONS FROM CRÊPE RUBBER OF MEAN MOLECULAR WEIGHT 344,000

Petroleum ether in extractant, %	Per cent of total rubber extracted	Molecular weight
48 to 52	1.5	30,000 to 60,000
52 to 60	15.0	216,000
50 to 62.5	69.7	324,000
64 to 85	12.3	Not determined
Insoluble	1.8

The thermostating of the two-phase system after precipitation in order to allow time for equilibrium to be achieved is a very important factor in determining the success of the work.

No molecular distribution curve can be drawn for natural rubber, since none of the existing data can be regarded as adequate for this purpose. The general trend of the evidence suggests a very wide distribution, and the large quantities of a single fraction obtained by some workers are almost certainly to be attributed to faulty experimental technique.

It will be seen from this brief review that the subject of fractionation is at present in a most unsatisfactory state, both theoretically and experimentally. The problems involved do not appear insuperable, and considerable advances may therefore be confidently anticipated.

6. General Conclusions

In each of the problems considered in this section, we have been able to explain the experimental data in a qualitative or semiquantitative manner. In no single case is complete quantitative agreement found, and it is evident therefore that a great deal of work remains to be done in this field. The present statistical calculations of the entropy and free energy of mix-

ing of rubbers and liquids require refining, and in particular the region of dilute solutions must be reinvestigated. On the experimental side, there is a great need for more extensive and precise thermodynamic data, especially on the heats of mixing. The general review of the field which we have made must, however, be considered not unsatisfactory, for it must be borne in mind that the mixing of low-molecular liquids is by no means fully understood as yet.

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SIGNIFICANCE OF VISCOSITY MEASUREMENTS ON DILUTE SOLUTIONS OF HIGH POLYMERS

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	PAGE
I. Introduction	197
II. General Characteristics of Viscous Flow.....	199
III. Experimental Results of Viscosity Measurements.....	207
IV. Determination of Molecular Weights of High Polymers.....	216
1. End-Group Determinations.....	218
2. Cryoscopic Determination.....	218
3. Osmotic Pressure.....	219
4. Ultracentrifugal Studies.....	224
5. Light Scattering by High-Polymer Solutions.....	226
V. Relation between Solution Viscosity and Molecular Weight.....	228
1. Linear Relationships.....	228
2. Nonlinear Relationships.....	233
3. Discussion of Results.....	239
VI. Theoretical Treatment of Viscosity.....	239
1. Dependence of Intrinsic Viscosity on Particle Shape.....	242
2. Dependence of Viscosity on Swelling.....	244
Bibliography.....	249

I. Introduction

A study of natural and synthetic high polymers has become of very great importance to modern industry. It is necessary to know the molecular structure of materials of this class in order that we may use them to advantage. High polymers which are prepared in the laboratory must be characterized so that we can record accurately the result of a particular synthesis and thereby correlate results and suggest methods for the improvement of the product.

The structural features which are of most importance are the types of groups present, their arrangement in the molecule and the size of the molecular unit. The groups which are combined to form these high-polymer structures are usually known from the monomers used in the preparation

or may be determined by chemical analysis, infrared studies and other methods. A considerable amount of information may be obtained on the arrangement of these groups by means of x-ray diffraction analysis. The size of the molecular units is of considerable importance in determining many physical properties and in the study of the mechanism of the reactions used to produce high polymers. For determining the molecular size of high polymers, many methods are being used including osmotic pressure, sedimentation in the ultracentrifuge, determination of end groups, and measurement of dilute solution viscosities. It is the purpose of this chapter to survey the results of the viscosity method and to point out the value of viscosity measurements in the study of the chemistry of high polymers.

In 1930 Staudinger (81) and his collaborators reported extensive measurements on the solution viscosities of several homologous series of hydrocarbon derivatives. They showed that the fractional increase in the viscosity over that of the solvent per unit concentration of dissolved solute was proportional to the molecular size of the dissolved substance. Staudinger proposed the following equation:

$$\frac{\eta_{sp}}{C_{gm}} = \left(\frac{\eta - \eta_0}{\eta_0} \right) / C_{gm} = K_m M$$

$$C_{gm} \rightarrow 0$$

where K_m is a characteristic constant for each homologous series, η and η_0 are the viscosities of solution and pure solvent, C_{gm} is the concentration in base moles* per liter and M is the molecular weight of the polymer. Staudinger attempted to justify this equation in his treatise on the high-molecular organic compounds by considering that a linear polymer in general occupied a sphere having a diameter equal to the length of the polymer chain. This derivation was never considered satisfactory and numerous other attempts have been made to explain this phenomenon.

Staudinger later proposed that the specific viscosity of a solution of high polymer containing one chain equivalent weight per liter could be used to measure the molecular weight according to the equation:

$$\eta_{sp} = K_{aqu} M$$

where a chain equivalent weight (M_{ch}) of the polymer is defined as follows:

$$M_{ch} = M/n = M_0/n_0$$

* One base mole or *grundmol* as used by Staudinger (M_0) is a weight of polymer in grams equal to the molecular weight of the monomer used to prepare it or of the repeating unit in the polymer. Thus, for rubber, $C_{gm} = 1$ for a solution containing 68 grams per liter.

where n is the number of atoms in the molecular chain (excluding side groups) and n_0 is the number of atoms in the monomer which become part of chain. In this case K_{aqu} was supposed to be a universal constant which could be applied to many homologous series, and had a value of about 0.95×10^{-4} .

Many workers have used this general idea of solution viscosity as a measure of molecular weight and have found that the relationships are by no means as simple as those originally proposed. While it has not been possible so far to make the measurement of solution viscosity an absolute method, it is still of very great importance in the study of compounds of high molecular weight. The reasons for this are the following:

(1) For any given type of high polymer, the solution viscosity increases continuously with the molecular weight and hence may be used as a relative measure of molecular weight.

(2) Solution viscosities may be determined rapidly and with an accuracy which is greater than that for most other methods.

(3) Certain qualitative predictions may be made as to the general form of these molecules in solution.

The results obtained by viscosity measurements on solutions of proteins and some other highly polar polymers have been interpreted in terms of an axial ratio or shape factor for the molecule. A review of some of these studies has been given by Lauffer (60), who feels that the idea of an elongated particle is a better explanation of the viscosity of these solutions than the older concept of a solvated molecule. There is considerable reason to believe that this is correct in the case of these classes of high polymers. However, the results to be discussed will not include those on proteins but will be restricted principally to the study of elastomers and other compounds of high molecular weight which have relatively weak intramolecular forces. It is believed that such materials are not solvated in the sense that the solvent is bound to the polymer molecule but rather that the molecular chain winds at random through the solvent molecules, resulting in a molecular particle which is very similar to a microscopic portion of swollen gel.

II. General Characteristics of Viscous Flow

Before considering the results of the measurements of viscosity on dilute solutions of high polymers, it will be well to review the general nature of viscous phenomena, the origin of viscosity, and the experimental methods available, in order to estimate the significance of the data obtained by various investigators.

Liquids exhibit a resistance to flow known as viscosity. This is the

property which regulates motion of adjacent portions of the liquid and can be considered as a type of internal friction. The coefficient of viscosity may be defined as the shearing force per unit area required to maintain a velocity gradient at right angles to the force of 1 cm. per sec. per cm. between two parallel surfaces. This may be expressed by the following equation:

$$\eta = \sigma / (du/dy)$$

where η is the coefficient of viscosity of the liquid, σ is the shearing stress or force per unit area, u is the velocity in the direction of flow and y is the distance in the direction normal to the planes of shear in the liquid.

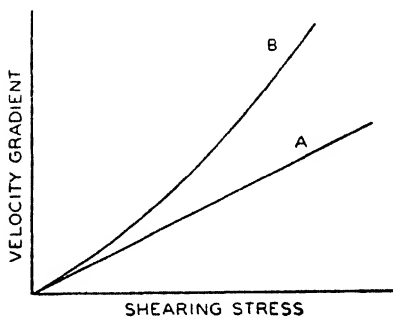


Fig. 1.—Velocity gradient as a function of shearing stress for (A) Newtonian liquid and (B) non-Newtonian liquid.

In the most simple liquids of low molecular weight, the velocity gradient is a linear function of the shearing stress, as shown in Figure 1. This means that the viscosity is independent of the rate of shear in the liquid. More complex substances of high molecular weight and colloidal suspensions usually do not exhibit this simple behavior. The general type of relationship in this case is also illustrated in Figure 1. From the definition of viscosity, it is seen that this means that

the viscosity of the liquid or suspension decreases with increasing shearing stress applied to the liquid. Liquids which show this linear relationship are in general known as Newtonian liquids, while those which show a nonlinear relationship between shearing stress and velocity gradient are known as non-Newtonian liquids.

In the case of very concentrated solutions of substances of high molecular weight or concentrated colloidal suspensions, it is often found that the viscosity is not only a function of the shearing stress but may also vary according to the previous history of the motion within the liquid. Thus, even though the shearing stress is kept constant, the viscosity often decreases with the length of time that the liquid has been in motion. This property is known as thixotropy, and is probably associated with the breaking up of arrangements within the liquid which give rise to a minimum potential energy.

This effect of velocity gradient on the viscosity of high-polymer solutions has been studied by Staudinger and others. In general, the differences

may be quite large if the viscosity of the solution is several times that of the pure solvent, but for more dilute solutions in which the relative viscosity is less than 1.5 there is probably not much change in viscosity produced by the variations in shearing stress obtained in the instruments usually used for the determination of viscosity. Mead and Fuoss (63) have corrected their viscosities to zero rate of shear in their study of polyvinyl

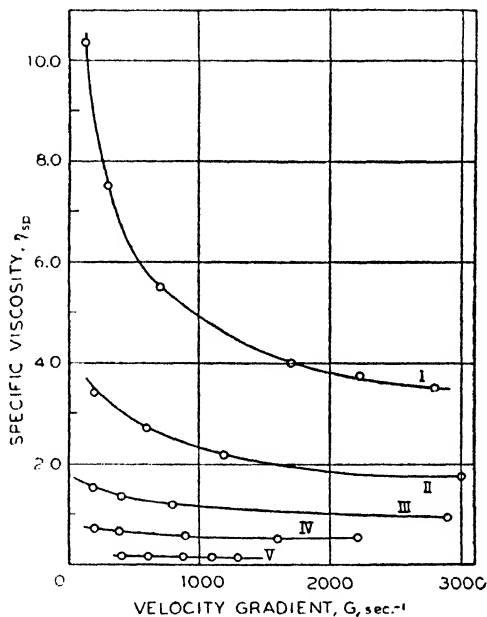


Fig. 2.—Variation of specific viscosity with velocity gradient and concentration for polystyrene of molecular weight 600,000 in tetralin at 20° C. (81). Curve I, 0.40%; II, 0.20%; III, 0.10%; IV, 0.05%; V, 0.01%.

chloride in various solvents. Baker, Fuller and Heiss (4) investigated the effect of capillary size on the viscosity of ω -hydroxyundecanoic acid self-polymer solutions. They show that the viscosities vary with capillary size for the more concentrated solutions (2–4%) but that for dilute solutions the viscosities do not vary with the capillary sizes studied.

A quantity which has been found useful in the study of high-polymer solutions and which is known as the specific viscosity (η_{sp}) may be defined by the following equation:

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

where η is the viscosity of the solution and η_0 is the viscosity of the pure solvent (same temperature velocity gradient, etc.).

The curves shown in Figure 2 illustrate the influence of velocity gradient on the specific viscosity of polystyrene solutions of various concentrations. It should be noted, however, that the concentration of the solutions alone is not the determining factor in this reduction of viscosity by increasing velocity gradient, but rather the relative or specific viscosity of the solution, and this may vary over very wide limits for equal concentrations of polymers of different molecular weights.

In the case of simple liquids, Eyring (20) has presented a theory which explains much of the experimental data. He has assumed that a liquid contains holes which are somewhat smaller than the molecular size and that the number of holes increases with increasing temperature. It is this effect which is primarily responsible for the large decrease in the density of liquids at elevated temperatures. The liquid may thus be treated as a system of molecules, part of which are in the solid state, while those molecules in the neighborhood of the holes are in the gaseous state. The effect of shearing stress on the liquid is to reduce the activation energy necessary for a molecule to jump from one position into an adjacent hole if the jump is in the direction of the force and to increase the activation energy if the jump is in the reverse direction. This activation energy is related to the change in internal energy on vaporization of the liquid. Eyring has shown that the heat of activation for a viscous flow which is obtained from the temperature coefficient of viscosity is about one-fourth to one-third of the energy of vaporization (ΔE_{vap}) for most simple liquids. The viscosity of mixtures of simple liquids is given by the logarithmic equation:

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

where x_1 and x_2 are the mole fractions. This follows from Eyring's treatment, since the activation free energy for such mixtures would be expected to be an average value based on the mole fractions of the components.

In the case of suspensions of colloidal particles, the increase in viscosity over that of the continuous phase originates by a mechanism different from that which applies in the case of simple solutions. If the suspension is free of electric charge and other complicating phenomena, the viscosity may be attributed to the distortion of the lines of flow in the continuous phase around the suspended particles. Einstein (17) has shown that, if the suspensions are not very concentrated, the specific viscosity is independent of the size of the particles and depends only on the volume fraction

(ϕ) of the suspended material, provided it is in the form of rigid spheres. He has expressed this in the form of the following equation:

$$\eta_{sp} = 2.5\phi \quad (1)$$

For higher concentrations this relationship is no longer linear but has been expressed as a power series expansion as follows:

$$\eta_{sp} = a_1\phi + a_2\phi^2 + a_3\phi^3 + \dots$$

A considerable amount of experimental data has shown that the first coefficient, namely 2.5, is correct. The value of the second coefficient depends on a much more complex analysis of the problem and its magnitude is not known with as great a degree of certainty. However, Guth and Simha (33), as well as Guth and Gold (32), have obtained the value 14.1 for this coefficient (a_2). Experimental values on suspensions of known size do not indicate such a large value for a_2 in most instances. The value of this coefficient is of great importance in the explanation of the change in intrinsic viscosity with the concentration of high-polymer solutions.

One interesting, and perhaps the most accurate, method of treating this complex problem is that of Eilers (15, 16). He has derived an empirical equation for the relation between relative viscosity and volume fraction after considering the best data on bitumen and paraffin oil suspensions for which the particle size is known and effects of charge are not important. Many of these data were obtained by Bredée and de Booy (9, 10). Eilers' equation is:

$$\eta_r = \left[1 + \frac{2.5\phi}{2(1 - (\phi/a))} \right]^2 \quad (2)$$

where a for suspensions of uniform size is 0.74, the volume fraction of close-packed spheres. For nonuniform suspensions, he finds a may be as large as 0.78. In either case, η_r becomes infinite where $\phi = a$. Eilers' equation for uniform particle size in the form of a power series expansion is:

$$\eta_{sp} = 2.5\phi + 4.94\phi^2 + 8.78\phi^3 + \dots \quad (3)$$

There have been several different methods of explaining the viscosity of high-polymer solutions. In the case of proteins, a considerable amount of success has resulted by considering that the molecule in solvent has about the same density as in the solid state but that it is in the form of an elongated ellipsoid or rodlike particle. Lauffer has surveyed this field of interpretation of viscosity of protein and other highly polar polymer solutions.

This requires a modification of the Einstein equation which takes into account the flow around ellipsoidal particles rather than spherical particles.

For nonspherical particles Simha (77) gives the following relationships in terms of axial ratio:

For rods:

$$\eta_{sp}/\phi = \frac{f^2}{15(\log 2f - 3/2)} + \frac{f^2}{5(\log 2f - 1/2)} + \frac{14}{15} \quad (4a)$$

For disks:

$$\eta_{sp}/\phi = \frac{16}{15} \frac{f}{\tan^{-1} f} \quad (4b)$$

In this treatment Brownian motion is considered predominant. Experimental measurements on rodlike particles of known axial ratio are in agreement with the first of these equations.

In the case of elastomers and other high polymers of low polarity this treatment has not been very successful, since it results in a very high axial ratio and does not seem to be compatible with other facts. The various theories of viscosity of elastomer solutions will be taken up in a later section (pages 239-242).

Many methods have been employed for the determination of the viscosity of dilute polymer solutions. The one most frequently used is based on the resistance to flow when a liquid passes through a capillary tube. If the length of the tube is many times the diameter of the bore, the viscosity of a Newtonian liquid is given approximately by the equation of Poiseuille:

$$\eta = \frac{\pi a^4 P}{8 l V} t$$

where a is the radius of the capillary, l is the length of the capillary, V is the volume of liquid passing through the capillary in time t and P is the driving pressure (dynes per sq. cm.).

Since $\pi a^2 P$ is the total force acting on the liquid in the capillary, the pressure to be used in this equation may be calculated from the difference in hydrostatic pressure acting at the two ends of the tube and the gravitational force acting per unit cross section on the liquid in the length of the capillary. Most of the measurements on high-polymer solutions have been made using modified Ostwald viscometers in which the liquid flows from an upper bulb to a lower one under its own hydrostatic pressure.

The Fenske modification of this viscometer requires less precision in the adjustment of the capillary to the vertical position. An improved viscom-

eter described by Ubbelohde (87) eliminates errors due to surface tension and is very satisfactory for precision high-polymer work. This instrument makes use of the principle of suspended level at the bottom of the capillary and is also not as sensitive to deviations from the exact vertical position as is the Ostwald viscometer.

In some cases studies have been made using additional external pressure to vary the rate of shear. The viscometer designed by Bingham (7) probably is one of the most accurate for this type of work. It has taken into account end effects and changes in pressure head during the determination. A complete discussion of many of the problems involved in the determination of viscosity is given by Bingham (8).

There are two main sources of error in a capillary-tube type of viscometer. The first arises from the fact that the shearing stress exerted on the liquid is not uniform but varies with the distance from the center of the capillary according to the equation:

$$\sigma = Pr/2l$$

For very dilute polymer solutions which behave as Newtonian liquids, this effect is probably not important. However, at higher concentrations, where the viscosity varies with the shearing stress, the result obtained is an average value which depends on the dimensions of the instrument and the relation between viscosity and shearing stress. The second source of error is due to the fact that not all of the potential energy of the liquid is converted to thermal energy by viscous friction but some reappears as kinetic energy of the liquid leaving the capillary. It is therefore generally necessary to include a kinetic energy correction in the Poiseuille equation (8, 84):

$$\eta = \frac{\pi a^4 P}{8(l + \lambda)V} t - \frac{m\rho V}{8\pi(l + \lambda)} \cdot \frac{1}{t} \quad (5)$$

where λ is a small end correction of the magnitude equal to a few diameters, ρ is the density of the liquid and m is a small constant, usually about 1.12.

By proper design of the viscometer, this correction may be made small, but in general for precision work it is necessary to determine its value. The kinetic energy correction is of more importance when working with dilute solutions than with concentrated solutions. With the Ostwald or Ubbelohde viscometer this equation is usually reduced to the simplified form:

$$\eta = A\rho t - \frac{B\rho}{t}$$

where A and B are constants of the instrument.

The viscometer is calibrated by employing two or more liquids of accurately known viscosity or water at several temperatures. It is also possible to determine the kinetic energy correction using the results on a liquid of accurately known viscosity at one temperature and the approximate dimensions of the instrument.

In the determination of specific viscosities it is not necessary to apply the kinetic energy correction to solvent and solution data individually. If η'_{sp} is the approximate uncorrected specific viscosity defined by:

$$\eta'_{sp} = (t - t_0)/t_0$$

where t and t_0 are the flow times of solution and solvent, the true specific viscosity will be given very nearly by:

$$\eta_{sp} = \eta'_{sp}(1 + \Delta)$$

where:

$$\Delta = \frac{2 + \eta'_{sp}}{1 + \eta'_{sp}} \left(\frac{B}{At_0^2} \right)$$

This correction, Δ , does not vary greatly with η'_{sp} , and hence the same correction may be used for a fairly wide range of values for η'_{sp} .

Flory (24) has used an equivalent method of calculating the relative viscosity:

$$\eta_r = \left(t - \frac{B}{At} \right) / \left(t_0 - \frac{B}{At_0} \right)$$

A second type of instrument which is used for the determination of viscosity is the rotating cylinder or the Couette type of viscometer. This has the advantage of uniform velocity gradient if the clearance, δ , is small compared with the radius, a . Under these conditions if the end correction is neglected:

$$\eta = \frac{T\delta}{2\pi a^3 l \omega} \quad \text{and} \quad G = \frac{1}{\eta} \frac{T}{2\pi a^2 l} = \frac{a\omega}{\delta}$$

where T is the torque, l is the length of the cylinder, ω is the angular velocity and G is the velocity gradient.

Since the end correction cannot usually be neglected, rings or air pockets are used to eliminate the shearing stresses at the bottom surfaces of the cylinder. Another method (70) uses a conical bottom on the cylinder with an angle between the rotor and stator of the proper magnitude to give the same shearing stress at the bottom as is found at the sides of the cylinder.

This type of instrument has not proved very useful for the investigation of very dilute solution viscosities, since the frictional effects and precision with which the parts must move do not allow as great an accuracy in the measurement of viscosity as with the capillary tube viscometer. The rotating cylinder viscometer, however, is the best to use for the investigation of more concentrated solutions which are not Newtonian liquids.

The third method used in viscosity work is that of the determination of the velocity of a ball falling through the liquid when it has reached a uniform velocity. This is based on Stokes' law relating the viscosity to the frictional force, f , which acts on a sphere of radius r moving through a viscous liquid with velocity u :

$$f = 6\pi r\eta u \quad (6)$$

When the velocity becomes uniform, the frictional force, f , just balances the gravitational force and:

$$\eta = \frac{2}{9} \frac{gr^2(\rho_b - \rho_0)}{u}$$

where ρ_b and ρ_0 are the density of ball and liquid, respectively.

However, here, as with the capillary viscometer, the velocity gradient varies with the distance from the ball. It is also necessary to use very small balls with liquids of low viscosity or else to have the density of the sphere near that of the liquid. In the latter case, the results are very sensitive to small changes in density between the solvent and solution and also to changes in the density due to temperature differences.

III. Experimental Results of Viscosity Measurements

When a substance of high molecular weight is dissolved in a solvent of low molecular weight, the viscosity of the solution, η , is greater than that of the pure solvent, η_0 . The increase in viscosity expressed as a fraction of the viscosity of the solvent is known as the specific viscosity, η_{sp} , of the solution, thus:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

where η_r , the relative viscosity, equals η/η_0 .

The magnitude of this increase depends on the concentration of polymer. The increase per unit concentration may be termed the "reduced" viscosity, η_{sp}/c . This is the quantity which Staudinger originally proposed as being proportional to the molecular weight of the solute. Various work-

ers have used different concentration units, which has led to some confusion. Staudinger has employed the "base mole" per liter of solution, C_{gm} , as his unit of concentration (see footnote, page 198). This assumes *a priori* a knowledge of the structure of the polymer. In the United States the most frequent concentration unit is grams per 100 cubic centimeters. However, workers have expressed concentration as grams per liter, volume fraction and base moles per liter. The unit, c , which will be used here in

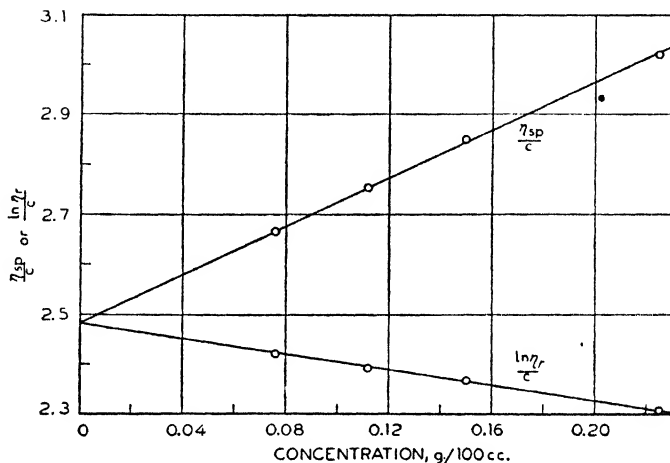


Fig. 3.—Reduced viscosity of polystyrene-S-2 in benzene at 30.0° C.
 $[\eta] = 2.482$, $k' = 0.379$, $\beta = 0.127$.

discussing viscosity, unless otherwise specified, will be g. per 100 cc. of solution.

The reduced viscosity cannot be used as a measure of molecular weight unless the concentration at which the determination is made is specified, since this quantity varies with the concentration, as shown in Figure 3.

Staudinger (81) recognized this and defined his proportionality constant with molecular weight K_m in terms of the limit approached by the reduced viscosity at infinite dilution. Thus:

$$\left(\frac{\eta_{sp}}{C_{gm}}\right)_0 = K_m M \quad (7)$$

where:

$$\left(\frac{\eta_{sp}}{C_{gm}}\right)_0 = \frac{\eta_{sp}}{C_{gm}} \quad (8)$$

$\lim_{c \rightarrow 0}$

A second method used by Staudinger of expressing the relation between viscosity and molecular weight is:

$$\left(\frac{\log_{10} \eta_r}{C_{gm}} \right)_0 = K_{cm} M \quad (9)$$

It was pointed out by Hess and Sakurela (35) that the logarithmic form varies less with concentration than the reduced viscosity. They also showed, as did Kraemer and Van Natta (56), that if natural logarithms (\ln) are used these two forms approach the same value at infinite dilution, thus:

$$\lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$$

This may be seen from Figure 3. If the values at zero concentration are used:

$$K_m = 2.3 K_{cm}$$

However, if the values obtained at any other concentration are used, this will not be true.

Kraemer (52) recognized the value of extrapolation to infinite dilution and defined a new term based on g. per 100 cc. of solution. This is the intrinsic viscosity, $[\eta]$, and is equal to

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} \quad (9a)$$

It is to be hoped that the term "intrinsic viscosity" may be restricted to Kraemer's definition even though there are some arguments for the usefulness of other expressions. Because the logarithmic form does not vary much with concentration in most cases, many workers have expressed intrinsic viscosity in this form by the result obtained at one low concentration, where $\eta_r < 0.5$.

If a series of polymers of increasing molecular weight are studied, the relationship between reduced viscosity and concentration is represented by a series of straight lines of increasing slope, a , provided η_r is not too great. The equation of these lines is given by:

$$\eta_{sp}/c = [\eta] + ac$$

Schulz and Blaschke (73) have shown that the slopes are related to $(\eta_{sp}/c)_0$ by:

$$\eta_{sp}/c = (\eta_{sp}/c)_0 [1 + K_\eta \eta_{sp}]$$

For polymethylmethacrylate in chloroform, $K_\eta = 0.30$. This equation was put in the more convenient form of a power series by Mead and Fuoss (63). Mark and coworkers (2) now use this form to express data:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (10)$$

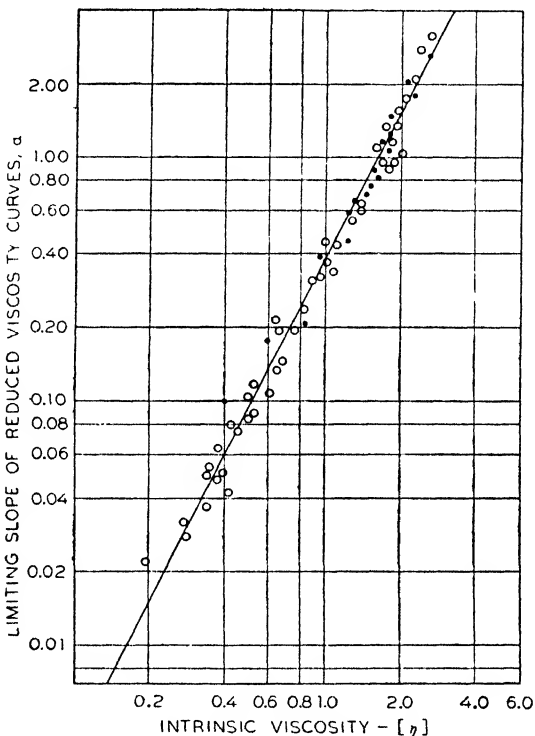


Fig. 4.—Relation between a and $[\eta]$ for polystyrene samples and fractions in toluene (o) and benzene (●). Equation of line: $\log a = \log 0.375 + 2.0 \log [\eta]$ or $a = 0.375 [\eta]^2$.

k' in this equation is equal to the first approximation to K_η . The value of k' for many high polymers in good solvents appears to be about 0.38. This is illustrated in Figure 4 by data collected by Tingey (85) on polystyrene in benzene and toluene solutions.

Since the relation between $\log a$ and $\log [\eta]$ is linear with a slope of 2.0, it follows that:

$$a = k'[\eta]^2$$

Mead and Fuoss (63) use the logarithmic form and obtain for polyvinyl chloride in the best solvent, cyclohexanone:

$$\frac{\ln \eta_r}{c} = [\eta] - \beta[\eta]^2 c \quad (11)$$

They find $\beta = +0.12$. However, it can be shown mathematically that:

$$\beta = 0.50 - k'$$

It should be noted that k' and β are dimensionless and therefore independent of the concentration units used. Hence, the value Mead and Fuoss obtain for k' is also 0.38.

Huggins (42) has derived a relationship of the form of Equation 10 by considering that Stokes' law applies to the individual atoms in the polymer and that the viscosity which should be used is a fraction of the solution viscosity, not the solvent viscosity.

It should be emphasized that, while k' has a value of about 0.38 for many linear polymers in good solvents, its value may be different if the polymer is branched, the solvent poor, or for other reasons.

In a great many cases, data have been reported without extrapolation of $(\ln \eta_r)/c$ to infinite dilution. It has been argued that, if the concentration is sufficiently low, the value obtained does not differ greatly from the true intrinsic viscosity. This is usually correct since β is small in most cases. It is important, however, that the value of k' (or β) be determined because it represents an additional constant which may be used to characterize the polymer or to interpret polymer-solvent relationships.

If the volume fraction or weight per unit volume of solution is used to express concentration, the intrinsic viscosity of a hydrocarbon polymer is usually about the same in good solvents of widely differing densities, such as benzene and carbon tetrachloride. It is not true, however, that the intrinsic viscosity in general is independent of the solvent. A good solvent for a polymer may be defined as a solvent which shows no heat of mixing with the polymer. Most good solvents give about the same intrinsic viscosity and the values are higher than for other solvents. Poor solvents for a polymer are, in general, compounds having much higher or much lower cohesive energy density than the high molecular weight substance. These give lower intrinsic viscosities and the decrease depends on how great the difference is between the solute and the solvent. Alfrey, Bartovics and Mark (1) have shown that, as the solvent is made poorer by the addition of a nonsolvent, the specific viscosity decreases to a limiting value at which precipitation begins. This limiting value of η_{sp} appears to be independent

of the nature of the initial good solvent and of the type of nonsolvent used to precipitate the polymer. However, in considering such results on mixed solvents, it is well to bear in mind the possibility that separation probably occurs due to the fact that the mixture surrounding the polymer particle is rich in the better solvent. Such an effect has been reported in some early work by Tompkins (86), who studied the differences in composition within swollen rubber gels and the surrounding medium. It is well known that, when the precipitate has separated from a fractionation by mixed solvents, the composition of the solvent mixture in the dispersed phase differs from that in the continuous phase.

There is a considerable amount of data in the literature on the effect of pure solvents on the intrinsic viscosity. Mead and Fuoss have studied the effect of various solvents on the viscosity of polyvinyl chloride solutions. Although the intrinsic viscosities range from as high as 2.00 in cyclohexanone to 0.57 in mesityl oxide, the values of k' are all between 0.35 to 0.41. Evans and Young (19) have made an extensive study of the effect of solvent on the relative viscosity of polymer solutions. Kemp and Peters (51) have reported the effect of various solvents on the reduced viscosity of polyisobutylene fractions in solution, as shown in Table I. Their values, however, were not extrapolated to infinite dilution.

TABLE I
EFFECT OF SOLVENT ON $\frac{\log_{10} \eta_r}{C_{gm}}$ WITH POLYISOBUTYLENE SOLUTIONS (51)

Molecular weight	Solvent			
	<i>n</i> -Hexane	Cyclohexane	Carbon tetrachloride	Benzene
168	0.026	0.009
392	0.054	0.036
504	0.064	0.049
1,080	0.145	0.185	...	0.126
1,700	0.226	...	0.267	0.193
4,100	0.547	0.715	...	0.427
6,300	0.840	1.130	...	0.620
30,000	3.95	5.23	4.74	2.14
50,000	6.65	9.42	8.00	3.20
100,000	13.6	19.6	...	Insoluble

It has been pointed out by Gee (30) that the intrinsic viscosity parallels the swelling behavior of the cross-linked polymer in the same solvents. It is shown in another chapter of this book (page 145) that the swelling behavior of high polymers may be explained on the basis of their cohesive energy density. The cohesive energy density (CED) of a substance is the

energy required to separate the molecules contained in one cubic centimeter of the liquid to a distance sufficiently great that there are no longer any forces acting between the molecules. It may be defined, therefore, in terms of the molal heat of vaporization, ΔH , and the molal volume, V , by the following equation:

$$\text{CED} = \frac{\Delta H - RT}{V} = \alpha^2 \quad (12)$$

It has been shown by Scatchard (71) and Hildebrand (36) that the heat of mixing for many liquids may be calculated from their cohesive energy densities. The quantity which actually enters these equations is the square root of the cohesive energy density, which may be termed the "interaction constant" of the substance, α . The partial molal heat of dilution $\Delta\bar{H}_1$ is then given by the following equation:

$$\Delta\bar{H}_1 = K V_1 (\alpha - \alpha_0)^2 V_2^2 \quad (13)$$

where V_2 is the volume fraction of the polymer, V_1 is the molal volume of solvent, α and α_0 are the interaction constants of polymer and solvent and K is a small coefficient of order of magnitude unity.

Figure 5 shows the relation to be expected between swelling, and intrinsic viscosity, and the value of the interaction constant of the solvent. A maximum is obtained in both of these quantities for that solvent which has an interaction constant equal to that of the polymer. Table II lists a few interaction constants of common solvents. While these general ideas appear to give a satisfactory explanation for the solvent behavior in many cases, there appear to be some solvents which fall out of line. It would seem that these anomalous effects are related to lack of symmetry of the force field about these solvent molecules, since the greatest deviations usually occur with unsymmetrical molecules containing polar substituents. Thus, chloroform and low molecular weight esters and ketones often fail to give the results expected from their cohesive energy densities.

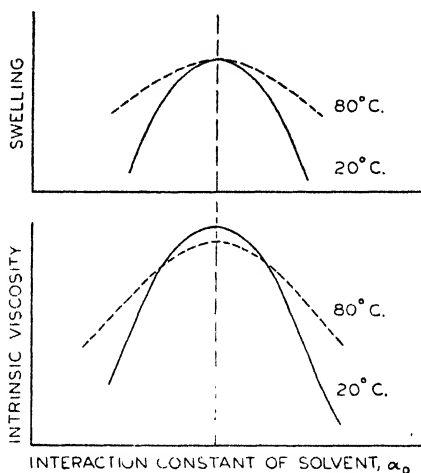


Fig. 5.—Similarity in behavior of the swelling of a cross-linked polymer and the intrinsic viscosity of the same polymer without cross links.

TABLE II
INTERACTION CONSTANTS, α_0 , OF SOLVENTS

Solvent	α_0	Solvent	α_0
<i>n</i> -Propane	5.8	Benzene	9.1
<i>n</i> -Butane	6.6	Dioxane	10.0
<i>n</i> -Hexane	7.0	<i>n</i> -Butanol	11.4
Cyclohexane	7.8	Ethanol	12.7
Carbon tetrachloride	8.5	Methanol	14.3
Toluene	8.9	Water	23.4

The general effect of temperature on intrinsic viscosity is similar to the effect on swelling. This is also shown in Figure 5. There seems to be one difference however. When using the best solvent, there is almost no effect of temperature on the extent of swelling; but the intrinsic viscosity decreases slightly with increasing temperature.

Our present model for this type of polymer molecule in solution is that of a highly kinked or curled chain which on the average occupies a roughly spherical volume much larger than the true volume of the polymer molecule. The remainder of this apparent "swollen" volume, ϕ , of the molecule is occupied by solvent molecules. These are not attached to the polymer molecule by secondary valence forces as in the older solvation theories. The volume, ϕ , depends on the number of atoms in the polymer chain, the length of the primary valence bond between atoms, the angles between bonds and the freedom of rotation about these bonds. If rotation is not completely free about these bonds, the apparent swollen volume will be increased if the extended form has a slightly lower potential energy. Increasing the temperature will make the distribution in rotational positions more random and hence decrease the volume, ϕ . This change in volume might be expected to be much greater in the case of a linear polymer molecule than it is in the case of a rather highly cross-linked network. For poor solvents the effect of increasing temperature is qualitatively the same, that is, both the swelling and intrinsic viscosities are increased.

There is one further important relationship concerning the intrinsic viscosity of polymer mixtures which should be considered before taking up the determination of molecular weight. These substances of high molecular weight may be separated into various fractions having different intrinsic viscosities by two general methods: the first consists in extracting the polymer by means of a series of poor solvents which show increasing ability to dissolve the material. This method has been used by Kemp and Peters (48), Sebrell (75) and others. It is a convenient method of separation because the solvent may be refluxed, and thus the volume of solvent

does not become excessively large. The separations obtained by this means are usually not very sharp and the number of fractions is limited. The second method of fractionation is that of precipitation of the polymer dissolved in a good solvent by a nonsolvent, a method which has been used by Schulz (72), Spurlin (80), Harris (79), Flory (24) and Mark and coworkers (2, 6). It has been shown by Flory and by Harris that a single fractionation is not usually sufficient to give a sample having a narrow range of molecular weights. If the intrinsic viscosity is determined on the whole polymer, $[\eta]_T$, and on a series of fractions obtained from this sample, it has been found experimentally that the following relationship holds:

$$[\eta]_T = \sum_1^n [\eta]_i x_i \quad (14)$$

where x_i is the weight fraction of the fraction having an intrinsic viscosity $[\eta]_i$.

An example of this is shown in Table III, in which are listed the intrinsic viscosities obtained by H. C. Tingey of this laboratory on purified natural rubber fractions and in which the calculated value of the intrinsic viscosity of the whole polymer is compared with the experimental value. The relationship found may be seen from the following equations, in which $\eta_0, \eta_1 \dots \eta_i \dots \eta_n$ are the viscosities of the solvent (η_0) and of solutions containing all fractions up to and including the i^{th} fraction. $c_1, c_2 \dots c_i \dots c_n$ are the concentration of the respective fractions. c_T is the total concentration of all fractions. $x_1, x_2 \dots x_n$ are the weight fractions of the fractions in the whole polymer. The derivation is based on the fact that the relative viscosity of a component at concentration c_i is the same when referred to a dilute solution containing other components as it is when referred to pure solvent. Therefore:

$$\ln \frac{\eta_1}{\eta_0} = [\eta]_1 c_1 = c_T [\eta]_1 x_1$$

$$\ln \frac{\eta_2}{\eta_1} = [\eta]_2 c_2 = c_T [\eta]_2 x_2, \text{ etc.}$$

$$\therefore \sum_1^n \ln \frac{\eta_i}{\eta_{i-1}} = c_T \sum_1^n [\eta]_i x_i$$

$$\text{but } \sum_1^n \ln \frac{\eta_i}{\eta_{i-1}} = \ln \frac{\eta_T}{\eta_0} = c_T \sum_1^n [\eta]_i x_i \quad \text{since } \eta_n = \eta_T$$

$$\text{hence } [\eta]_T = \frac{\ln (\eta_T/\eta_0)}{c_T} = \sum_1^n [\eta]_i x_i$$

It was this relationship between the intrinsic viscosities of fractions and the whole polymer that led Lansing and Kraemer (59) to point out that, if the Staudinger viscosity law holds, then the intrinsic viscosity measures the weight average molecular weight, since, if:

$$[\eta]_i = KM_i$$

$$[\eta]_T = K \sum M_i x_i = KM_w \quad (15)$$

TABLE III

INTRINSIC VISCOSITIES OF NATURAL RUBBER FRACTIONS AND WHOLE RUBBER (85)
Viscosities in Benzene at 30° C.

Sample No., <i>i</i>	Intrinsic viscosity, $[\eta]_i$	Fraction of whole rubber, x_i	Contribution to $[\eta]_T$, $[\eta]_i \cdot x_i$
7	0.69	0.0946	0.065
6	0.900	0.0474	0.042
5	0.985	0.0321	0.031
4	1.194	0.1991	0.238
3	2.33	0.1508	0.359
2	2.60	0.1712	0.445
1	4.39	0.3048	1.338

Polymer accounted for = 1.000.

Sum of contributions = $\sum [\eta]_i \cdot x_i = 2.518$.

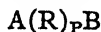
Experimental viscosity of whole rubber = $[\eta]_T = 2.519$.

IV. Determination of Molecular Weights of High Polymers

It is not possible from our present theoretical knowledge to determine the molecular weight of a high polymer from viscosity measurements alone. Staudinger originally hoped that this would be possible. However, a large collection of experimental data has failed to reveal any simple relationship which holds for a wide variety of substances. It is necessary, therefore, to determine the molecular weight–intrinsic viscosity curve for each polymer–solvent system. Once this has been done, the intrinsic viscosity in the same solvent offers a convenient method of finding the molecular weight of new samples of this same polymer. It is, therefore, desirable to review briefly the absolute methods of determining the molecular weights of these materials.

Strictly speaking, molecular weight is a property of a pure substance. Most high polymers, with the exception of the proteins, are not pure substances, but are a mixture of hundreds or thousands of pure substances which are members of the same homologous series.

If the polymer is linear, its chemical formula may be represented by



where P varies from one to infinity (or at least to some very large number). A and B are end groups. We can therefore only speak of the average molecular weight of a polymer. The value of the average consequently depends on what type of average is considered or obtained by the particular experimental method used. There are four important average molecular weights encountered in high-polymer work. These are: number average \bar{M}_n ; weight average, \bar{M}_w ; Z average, \bar{M}_z ; and viscosity average, \bar{M}_η . The first three of these averages are defined by the following relations:

$$\bar{M}_n = \frac{\sum_1^{\infty} M_i n_i}{\sum_1^{\infty} n_i} = \frac{1}{\sum (x_i/M_i)} \quad (16)$$

$$\bar{M}_w = \frac{\sum M_i x_i}{\sum x_i} = \sum M_i x_i \quad (17)$$

$$\bar{M}_z = \frac{\sum M_i^2 x_i}{\sum M_i x_i} \quad (18)$$

in which the weight fraction, x_i , of molecular weight, M_i , is related to the number of moles per gram of polymer, n_i , by:

$$x_i = M_i n_i$$

$$\text{and } \sum x_i = 1$$

The definition of viscosity average molecular weight is more complex and depends on the experimental observation (which will be discussed in the next section) that for fractionated material:

$$[\eta]_i = K M_i^a$$

Hence, according to equation (14):

$$\begin{aligned} [\eta]_r &= K \sum M_i^a x_i = K \bar{M}_\eta^a \\ \text{or } \bar{M}_\eta &= [\sum M_i^a x_i]^{1/a} \end{aligned} \quad (19)$$

The viscosity average molecular weight was first suggested by Flory (24). If the exponent, a , is equal to unity, it becomes identical with the weight average molecular weight.

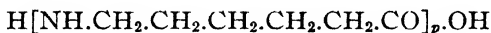
Since different experimental methods do not give the same type of average, it is usually better when determining the relation between intrinsic viscosity and molecular weight to use well-fractionated material of

narrow molecular weight range, because only under these conditions are the various averages nearly equal.

1. End-Group Determinations

Methods for the evaluation of molecular weights by end groups are based on either: (a) the determination of an element or group which is present only on one or both ends of the molecule; or (b) differences in the ratios between two of the elements in the polymer due to the end groups.

Thus, Matthes (62) has determined the degree of polymerization in the ϵ -aminocaproic acid polymers:



by the determination of the number of primary amino groups using the Van Slyke method. If p is the per cent of primary amino nitrogen, then the degree of polymerization, P , is:

$$P = \left(\frac{1400}{p} - 18 \right) / 113$$

This general method is one of the most direct and accurate evaluations of molecular weights possible, provided the degree of polymerization is not too great. It was used by Kraemer and Van Natta (56) for poly- ω -hydroxydecanoic acid polymers in one of the earliest complete investigations of a nonprotein high polymer. Baker, Fuller and Heiss (4) employ end group titration for their work on ω -hydroxyundecanoic acid self polyesters. Much of Staudinger's early work on homologous series is based on this direct chemical method.

Since these methods fundamentally determine the number of moles of polymer, the molecular weight obtained is the number average, \bar{M}_n .

2. Cryoscopic Determination

This method also determines \bar{M}_n . Freezing point depressions have been used by Staudinger (81) and Kemp and Peters (48, 50, 51). It has been difficult to use cryoscopic methods for molecular weights much greater than 5000. By using multiple-junction thermocouples and an accurately designed calorimeter, this method can probably be extended to much higher molecular weights. It should be borne in mind, however, that it will be necessary to extrapolate to infinite dilution since the depression, ΔT , from the freezing point of the solvent, T_f , measures the solvent activity, a_1 , by:

$$-\ln a_1 = \frac{\Delta H_F}{RT_F^2} \Delta T \quad (20)$$

If Raoult's law holds, $a_1 = N_1$, the mole fraction of solvent. For fairly dilute solutions, this leads to the equation:

$$\left(\frac{\Delta h_F}{T_F}\right) \frac{\Delta T}{C_w} = \frac{RT_F}{M_2} \quad (21)$$

where Δh_F is the heat of fusion per gram of solvent and is thus independent of its molecular weight. M_2 is the molecular weight of the solute and C_w is the concentration as weight fraction. However, it is well known that Raoult's law does not hold for high molecular weight polymers, except at extremely low concentrations, and hence the activity of the solvent can no longer be taken as equal to its mole fraction. A correction must, therefore, be applied to the right-hand side of Equation 21, just as will be shown in the next section on osmotic pressure, so that:

$$\left(\frac{\Delta h_F}{T_F}\right) \frac{\Delta T}{C_w} = \frac{RT_F}{M_2} + b' C_w \quad (22)$$

The constant b is very nearly independent of the molecular weight but depends on the solvent used.

3. Osmotic Pressure

The measurement of the osmotic pressures of dilute polymer solutions has been used extensively for the determination of molecular weights. It is more sensitive than cryoscopic, end group or other methods of determining number average molecular weights. It also has the advantage of not being affected by impurities of low molecular weight since these pass through the membrane. The osmometers usually consist of two metal blocks into the faces of which shallow cylindrical grooves have been cut. The edges of these grooves serve as supports for the membrane. The osmotic pressures are usually read from the difference in height of the solvent and solution in two capillaries connected through channels leading to the grooves on the two sides of the membrane. Osmometers of improved design have been described by Flory (24) and by Fuoss and Mead (29). Other osmometers have been used for high-polymer work by Herzog and Spurlin (34), Schulz (72) and Meyer, Wolff and Boissonnas (67).

The membranes are usually nitrocellulose, denitrated nitrocellulose (69) or cellophane. Various methods of swelling to obtain the proper permeability have been described.

The cellophane membranes are usually swollen in ammonium or sodium hydroxide or zinc chloride solution. The swelling may then be retained by soaking in a 50% solution of triethylene glycol in water and then in the solvent to be used. Another method is that of treating with a series of solvents, such as alcohol, 50-50 alcohol-benzene, and finally in benzene.

Another type of osmometer which has been used by this laboratory is one constructed entirely of glass (Fig. 6). It has the advantages that it is much cheaper to construct than the metal block type and that a large number may be kept in a small thermostat until equilibrium is reached. Leakage and stopcock grease are eliminated by using a mercury seal on the ground glass joint. Because of the small area of the membrane, this type of osmometer has the disadvantage of requiring two to four days, rather than a few hours, to reach equilibrium. The membrane, after being soaked in triethylene glycol, is cemented to the lower end of the osmometer with polyvinyl alcohol solution, dried in air and baked for about 20 minutes at 100° C. The glycol is then removed by soaking in the solvent to be used. Carefully matched capillaries of about 0.4 mm. diameter should be used.

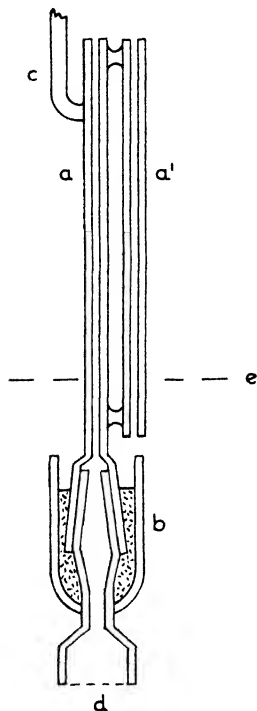


Fig. 6.—Glass osmometer (U. S. Rubber Co. design): *a* and *a'*, matched capillaries; *b*, mercury-sealed joint; *c*, support rod; *d*, membrane; *e*, solvent level.

The osmotic pressures measured in high-polymer work are usually less than 100 mm. of solvent and often less than 10 mm. Because of large deviations from Raoult's law, it is necessary to make measurements at concentrations of less than one gram per hundred cubic centimeters of solvent. It is, therefore, essential that an accuracy of a few tenths of a millimeter of solvent be attained. The osmotic pressure determination in

itself is not particularly sensitive to changes in temperature since the solution and solvent are separated by a very thin membrane (0.001–0.003 in.) and hence are always at very nearly the same temperature. It is, however, necessary to prevent temperature fluctuations, the reason being that the volume of liquid in the osmometer is much greater than that in the capillaries which gives rise to a large thermometer effect. If the capillaries are

larger, much longer times are required to reach equilibrium (or for dynamic readings). If small capillaries are used, they must be carefully matched or proper corrections for capillary rise applied.

Jullander and Svedberg (46a) have recently described an osmotic balance by means of which the difference in pressure is obtained by weighing rather than measuring a height. The solution half of the osmometer is hung from a balance arm and is suspended in the solvent. A much larger capillary is used which makes the time required to reach equilibrium longer. However, they claim an increase in accuracy over other methods by a factor of ten. For this reason, osmotic pressures may be measured at much lower concentrations.

The results of osmotic pressure (π) determinations are usually shown by plotting π/c against c . An example of this is given in Figure 7, taken from the very careful investigation of polyisobutylene by Flory (24). If the van't Hoff equation:

$$\pi = c_0 \frac{RT}{M_2}$$

held, the value of π/c would be a constant and independent of concentration. This is quite definitely not the case for high-polymer solutions in this concentration range. The values increase rapidly with concentration and usually show a linear or slightly curved relationship for polymers dissolved in a good solvent ($\Delta\bar{H}_1 \approx 0$).

A linear relationship has been deduced by Flory (23), Huggins (41) and Miller (68); and, in general, experimental investigations on high-polymer solutions seem to support this deduction. From thermodynamics, it is shown that the partial molal free energy of dilution, $\Delta\bar{F}_1$, is related to the osmotic pressure and partial molal volume of the solvent, \bar{V}_1 , by:

$$\pi\bar{V}_1 = -\Delta\bar{F}_1 = T\Delta\bar{S}_1 - \Delta\bar{H}_1$$

Huggins' expression (44) derived by statistical mechanics for the partial molal entropy of dilution, $\Delta\bar{S}_1$, is

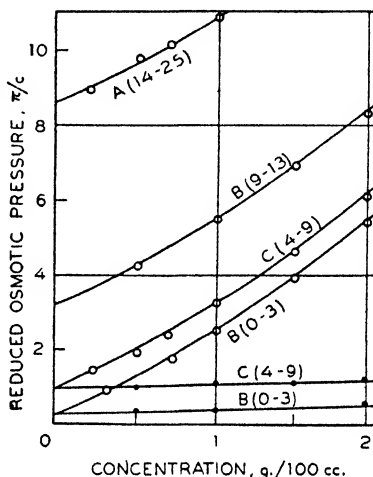


Fig. 7.—Reduced osmotic pressures of polyisobutylene fractions in cyclohexane (o) and benzene (●) solutions (24).

$$\begin{aligned} \Delta S_1/R &= - \left[\ln (1 - V_2) + \left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) V_2 + \frac{1}{Z'} V_2^2 + \frac{4}{3Z'^2} V_2^3 + \dots \right] \\ &= \frac{\bar{V}_1}{\bar{V}_2} V_2 + \left(\frac{1}{2} - \frac{1}{Z'}\right) V_2^2 + \dots \end{aligned} \quad (23)$$

where V_2 is the volume fraction of solute, Z' is the effective average coordination number of the solvent molecules and solute submolecules (~ 5 to 10) and \bar{V}_2 is the partial molal volume of solute. Scatchard (71) and Hildebrand (36) have shown:

$$\Delta \bar{H}_1 = K_{1,2} \bar{V}_1 \bar{V}_2^2$$

where $K_{1,2}$ depends on the interaction constants of solvent and solute. If we convert volume fraction to g. per cc. (c_0):

$$\begin{aligned} \frac{\pi}{c_0} &= RT \left[\frac{1}{M_2} + \frac{1}{d_2^2 \bar{V}_1} \left(\frac{1}{2} - \frac{1}{Z'} - \frac{K_{1,2}}{RT} \right) c_0 + \dots \right] \\ &= RT \left[\frac{1}{M_2} + bc_0 + \dots \right] \end{aligned} \quad (24)$$

This theoretical expression is of the general form of the data expressing the relation between π/c_0 and c_0 for high-polymer solutions. However, the coefficient of c_0 in the right-hand member of Equation (24) gives too large a slope for the best solvents, where $K_{1,2}$ might be expected to have a value close to zero. In order to settle this point, more accurate data are needed on the temperature coefficient of osmotic pressure, from which $\Delta \bar{H}_1$ may be calculated.

In the absence of these data, Huggins prefers to treat this coefficient as an empirical constant, μ_1 and expresses the relationship in the form:

$$\frac{\pi}{c_0} = RT \left[\frac{1}{M_2} + \frac{1}{d_2^2 \bar{V}_1} \left(\frac{1}{2} - \mu_1 \right) c_0 + \dots \right] \quad (25)$$

He has shown that the constant, μ_1 , is of great value in correlating data for a given polymer-solvent system and in explaining the solubility of high polymers. The values of μ_1 for rubber in various solvents are given in Table IV.

One other interpretation of the increase in π/c with concentration should be mentioned which is based on the introduction of a van der Waals' type factor in the van't Hoff equation. This has been discussed by Mark (61, 65) and an extension of the treatment has been used by Schulz (72). The basis

TABLE IV
HUGGINS' VALUES OF μ_1 FOR RUBBER IN VARIOUS SOLVENTS (43, 44)

Solvent	μ_1
Benzene + 10% ethanol.....	0.26
Carbon tetrachloride.....	0.28
Cymene.....	0.33
Tetrachloroethane.....	0.36
Chloroform.....	0.37
Toluene.....	0.43
Benzene.....	0.43
Chlorobenzene.....	0.44
Carbon disulfide.....	0.49
Amyl acetate.....	0.49
Benzene + 15% methanol.....	0.50
Ether.....	0.55
Ethylene chloride.....	0.62 (?)

for these relationships is the belief that, although the actual concentration of polymer may be small, the free volume is greatly reduced due to the "swelling" of the polymer molecules in solution. This necessitates the introduction of a swelling factor, s , giving the equation:

$$\begin{aligned} \frac{\pi}{c_0} &= \frac{RT}{M} \left(\frac{1}{1 - s c_0} \right) \\ &= RT \left(\frac{1}{M_2} + \frac{s}{M_2} c_0 + \frac{s^2}{M_2} c_0^2 + \dots \right) \end{aligned} \quad (26)$$

Since this equation is similar to Equation (24), it will be seen that for very dilute solutions the swelling factor, s_0 , must be proportional to the molecular weight if b is to be a constant. The data in Table XI (page 235) illustrate the dependence found by Schulz of s on molecular weight and concentration. The decrease in s with concentration is similar to that obtained by Eilers in his treatment of viscosity.

In fact, the basic reason for the value of the coefficient of c_0 found by Flory (23) and Huggins (41) appears to be the reduction in the number of available locations for polymer segments with increasing concentration. Since they are also treating the polymer chain as wandering at random through the solution, this reduction in the number of available locations is very similar to a decrease in the swelling factor.

Schulz relates the swelling factor, s , to the osmotic pressure, π , by:

$$\pi s^\nu = k \quad (27)$$

The value of the exponent ν is about 2. This equation corresponds to infinite swelling when the concentration and osmotic pressure approach

zero. A treatment similar to that of Eilers (16), which gives a limiting swelling factor, s_0 , at infinite dilution results in the relationship:

$$\pi s^2 = \frac{RT}{M} (s_0 - s) \quad (28)$$

This is equivalent to the Schulz equation when $s \ll s_0$.

4. Ultracentrifugal Studies

While the ultracentrifuge has been applied extensively to the study of proteins, the results on elastomers and other high polymers of low polarity are rather meager. There are several important reasons for this. Proteins are often purified until they are monodisperse or at most contain material of only a few discrete molecular weights, while the elastomers, condensation polymers and addition polymers contain a wide range of molecular weights and even well-fractionated material is far from monodisperse. Also, the sedimentation constant for the latter class of materials does not vary as much with molecular weight as it does for those proteins which show low intrinsic viscosities. Many of the present ultracentrifugal techniques have been developed for aqueous solutions and hence are not applicable to elastomers or hydrocarbon polymers.

There are two general methods employed for the determination of molecular weights by the ultracentrifuge. The equilibrium method is based on establishing that distribution of solute in the cell in a centrifugal field such that at every point the increase in the partial molal free energy due to concentration differences along the cell is equal to the decrease in free energy due to the position of the solute molecule in the potential field. For conditions in which the laws of ideal solutions are obeyed, the average molecular weight, \bar{M}_{wx} , varies along the cell and depends on the experimental method used to determine the concentration. If the concentration is determined directly as by light absorption (53, 55):

$$\bar{M}_{wx} = \frac{RT}{(1 - V\rho)\omega^2 x} \frac{d \ln c}{dx} \quad (29)$$

where V is the partial specific volume of solute, ρ is the density of the solvent, ω is the angular velocity and x is the distance from the axis of rotation. The average molecular weight of the whole sample in the cell is a weight average given by:

$$\bar{M}_w = \frac{\int_{x_0}^{x_n} \bar{M}_{wx} c_x dx}{\int_{x_0}^{x_n} c_x dx} \quad (30)$$

If the quantity which is determined experimentally is the concentration gradient or refractive index gradient by the *Schlieren* or line displacement method, the average molecular weight is the Z average, \bar{M}_z (59).

For polymer solutions which show nonideal behavior, Equation 29 must be changed, since the term $RT(d \ln c/dx)$ arises from substituting c for a_2 , the activity of the solute.

Signer and Gross (76) have made an investigation of polystyrene and polymethylmethacrylate by the ultracentrifugal method. They discuss the effect on the results of these deviations from ideal solution laws.

The second ultracentrifugal method is that of sedimentation velocity. In order to calculate molecular weights, it is necessary to make an independent determination of the frictional factor by measurement of the diffusion coefficient, D . This method generally gives values between \bar{M}_n and \bar{M}_w , depending on the distribution function used (31a, 46). For fractionated material, the molecular weight is given by:

$$M = \frac{RTS}{D(1 - V\rho)} \quad (31)$$

where

$$S = \frac{dx/dt}{\omega^2 x}$$

and dx/dt equals the velocity of displacement of the boundary.

Kraemer and Lansing (54) have extended the investigation of ω -hydroxydecanoic acid by ultracentrifugal analysis with the results shown in Table V.

TABLE V

MOLECULAR WEIGHT OF A FRACTIONATED ω -HYDROXYDECANOIC ACID POLYMER (54)

Method	Molecular weight
End-group titration.....	25,200
Sedimentation equilibrium.....	27,000
Diffusion coefficient alone.....	2,400,000 ^a
Sedimentation velocity alone.....	7,600 ^a
Diffusion plus sedimentation velocity.....	52,000 ^b
Viscosity.....	31,000

^a Assuming that the frictional coefficient is that of a sphere having a volume equal to the molecular volume of the solid polymer.

^b The reason for this high value is believed to be that the frictional coefficient at the concentrations studied was not the same for sedimentation and diffusion.

Ultracentrifugal studies of rubber and polychloroprene have also been reported by Kraemer (55). These results are compared in Table VI with the intrinsic viscosities. The values of the degree of polymerization (D.P.)

divided by the intrinsic viscosity correspond to values of $K_{C.M.}$ defined by Kemp and Peters (48) with a constant factor which is given by:

$$K_{C.M.} \text{ (Kemp and Peters)} = 23 \frac{D.P.}{[\eta]_V V_1}$$

TABLE VI
MOLECULAR WEIGHT OF RUBBER AND POLYCHLOROPRENE BY ULTRACENTRIFUGAL ANALYSIS (55)

Sample	Solvent	Mol. wt.	D.P.	$[\eta]_V$	D.P./ $[\eta]_V$	$K_{C.M.}$ (K & P)
Sol rubber A	Ether	400,000	5900	1.68	3500
	Benzene	2.36	(2500) ^a	5.7×10^4
Sol rubber B	Ether	435,000	6400	1.86	3400
	Benzene	3.40	(1900) ^a	4.3×10^4
Low-viscosity rubber	Ether	69,000	1020	0.31	3300
	Chloroform	63,500	940	0.46	2000	4.6×10^4
Polychloroprene	<i>n</i> -Butyl chloride	180,000	2000	0.99	2000
	Benzene	1.33	(1500) ^a
	<i>n</i> -Butyl chloride	333,000	3750	1.78	2100
	Benzene	2.38	(1600) ^a
	Chloroform	103,000	1170	0.70	1700

^a The values in parentheses are calculated on the assumption that the molecular weight is the same in both solvents.

Kemp and Peters find the value for their $K_{C.M.}$ in good solvents to be 0.75×10^4 . This was determined from data on portions of rubber of very low molecular weight. If the results of both investigators are approximately correct, this leads to the result that, in the case of rubber, the molecular weight increases more rapidly than the first power of the intrinsic viscosity.

5. Light Scattering by High-Polymer Solutions

A new method for the determination of molecular weights of high polymers in solution which shows considerable promise is that of the determination of the intensity of scattered light when a beam of unpolarized light passes through the solution.

Debye (13) has recently pointed out that, if the particles are less than one-tenth the wave length of light in diameter, the total amount of light scattered is related to the molecular weight of the solute in such a way that the intensity of scattered light at 90° to the direction of the beam may be used for the measurements. Thus, if a beam of light of initial intensity I_0 passes through l cm. of a solution of high polymer (concentration, c_0 ,

g. per cc.), its transmitted intensity will be reduced to I . If all the light is lost by scattering, *i. e.*, no absorption or fluorescence:

$$\ln \frac{I_0}{I} = (T_1 + T_2)l = Tl$$

where T_1 is the scattering coefficient of the solvent and T_2 is the scattering coefficient of the solute.

For substances of very high molecular weight in concentrations of about 1%, T_2 is much greater than T_1 . In general, however, the difference (ΔI) between I_0 and I is very small if the light path is of the order of one centimeter in length.

Since the fraction of light scattered is small, it is difficult to determine accurately by measurement of the transmitted intensity of these solutions. The intensity of scattered light, I_s , at some angle, usually 90° , is more easily and more accurately determined. For a given apparatus, there will be a linear relationship between ΔI and I_s :

$$\Delta I = kI_s$$

The value of the constant k may be determined by using solutions of high turbidity on which the fraction of light transmitted may be measured accurately, provided the angular distribution of scattered intensities is the same in both cases.

Doty, Zimm and Mark (14) have recently published data on polystyrene from which molecular weights have been calculated (Table VII). Earlier data by Gehman and Field (31) for which no molecular weights were calculated have been treated by Debye.

TABLE VII
MOLECULAR WEIGHTS FROM LIGHT SCATTERING AND OSMOTIC PRESSURE
OF POLYSTYRENE FRACTIONS (14)

Osmotic molecular weight	Turbidity molecular weight	Solvent
100,000	88,500	Toluene
127,000	137,000	Toluene
200,000	285,000	Toluene
100,000	95,000	Methyl ethyl ketone
200,000	250,000	Methyl ethyl ketone

The relationship between the scattering coefficient and the molecular weight for fractionated material is given by:

$$\frac{c_0}{T_2} = \frac{3\lambda^4 N_0}{32\pi^2 n_0^2 (\partial n / \partial c_0)^2} \left[\frac{1}{M_2} + \frac{2b}{RT} c_0 + \dots \right] \quad (32)$$

$$= \frac{1}{II} \left[\frac{1}{M_2} + \frac{2b}{RT} + \dots \right] \quad (33)$$

where c_0 is the concentration in g. per cc., N_0 is 6.02×10^{23} , λ is the wave length of light in cm., n_0 is the refractive index of the solvent, n is the refractive index of the solution and b is the slope constant in osmotic pressure equation. Thus, also in this method, it is necessary to extrapolate the values of c/T to infinite dilution. The reciprocal of this extrapolated value may be called the intrinsic scattering power of the polymer in the solvent used:

$$[T] = (T_2/c_0)_0 \quad (34)$$

$\lim_{c_0 \rightarrow 0}$

Thus, for fractionated material:

$$[T] = IIM$$

which is similar to the Staudinger viscosity equation, but it is to be hoped that it will prove to be more rigorously true. For material having a distribution of molecular weights, the value obtained by this method is the weight average, \bar{M}_w .

Zimm and Doty (88) have also pointed out that the slope of c_0/T_2 against the concentration will be greater for unfractionated material than for fractionated polymer. If the value of b is known, the moments of the distribution curve might be calculated from the experimental slopes at various concentrations.

V. Relation between Solution Viscosity and Molecular Weight

The relation between solution viscosity and molecular weight is at the present time by no means a settled question. The results as expressed by the various workers in this field may be divided into two general classes: (1) linear and (2) nonlinear relation between reduced viscosity and molecular weight.

1. Linear Relationships

The relation between the limiting reduced viscosity and molecular weight as originally proposed by Staudinger (81) was:

$$[\eta_{sp}/C_L]_0 = K_m P + y \quad (35)$$

The concentration (C_L) used here is in grams per liter. The fact that an

additive constant, γ , is required for polymers of low molecular weight is obvious, since in the polymer:

$$A(R)_pB$$

the first few additions of structural units R to end groups A and B will make rather large changes in the polarity and solvent interactions. After this, however, the changes in viscosity will depend primarily on the degree of polymerization, P. For very high molecular weights, the effect of γ is unimportant.

The degree of polymerization is used in Equation 35 because it was believed that the length of the chain rather than the molecular weight determines the viscosity. Thus, for the polyolefins, the length is proportional to P, while the molecular weight depends on the kind of side groups present as well. In order to try to express the results of viscosity measurements on different polymers in units which might have about the same proportionality constant with the molecular weight, Staudinger makes use of concentrations in base moles, which, neglecting the constant factor, gives:

$$[\eta_{sp}/C_{gm}]_0 = K_m M \quad (36)$$

Other workers have used various modifications of this treatment and hence in the following discussions of the results which show a linear relationship with molecular weight, the particular equation used will be given.

The Polyoxyethylene Glycols.—Fordyce and Hibbert (28) have studied these compounds in two solvents at three different temperatures. The polymers were prepared so as to contain only species of one molecular weight. Specific viscosities at only one concentration were determined. The results appear to be given by:

$$\eta_{sp} = \beta + K'_m M$$

TABLE VIII
VISCOSITY CONSTANTS FOR POLYOXYETHYLENE GLYCOLS (28)

Solvent	Temperature, C.	$K'_m \times 10^4$	β
Carbon tetrachloride	20	0.57	0.187
	30	0.48	0.159
	40	0.34	0.121
Dioxane	20	0.62	0.128
	30	0.56	0.119
	40	0.53	0.095

at a concentration equal to 4.4% by weight. The values of the constants are given in Table VIII. The maximum molecular weight of their polymers was about 8000.

ω -Hydroxydecanoic Acid Polymers.—These polymers were investigated in 1932 by Kraemer and Van Natta (56). They used fractionated material and determined the molecular weights by titration and by the ultracentrifuge. They have extrapolated reduced viscosities to infinite dilution and expressed their results as intrinsic viscosity. For molecular weights between 780 and 17,000, their results are expressed by:

$$[\eta] = 0.065 + 0.585 \times 10^{-4} M$$

Viscosity measurements were made at 25° C. in *sym*-tetrachloroethane. For molecular weights greater than 17,000, the intrinsic viscosities were greater than are given by this equation; *i. e.*, the relationship became nonlinear.

ω -Hydroxyundecanoic Acid Polymers.—The viscosity-molecular weight relationship for these fractionated polymers has been given by Baker, Fuller and Heiss (4). The molecular weights were obtained from end group titrations and range from 200 to 12,600. The determination of viscosity was in chloroform solution at 25° C. at a concentration of 0.4 g per 100 cc. For the logarithmic form the results are within 2% of the true intrinsic viscosity. Their results are:

$$\eta_{sp}/c = 0.42 \times 10^{-4} M_w - 0.03$$

$$\text{or } \frac{\ln \eta_r}{c} = 0.31 \times 10^{-4} M_w + 0.07$$

In a later paper (5) they show that, at infinite dilution, both forms give the same value for the intrinsic viscosity. By preparation of known mixtures, they have also shown that the weight average rather than the number average is measured by these viscosity determinations.

Polydecamethylene Adipate.—The results on this polyester have been determined by Flory and Stickney (27). The polymers were not fractionated but Flory (22) has given a complete treatment of their molecular weight distribution; hence their weight average molecular weight could be calculated from M_w , which was obtained from end group analysis. For molecular weights (M_w) up to 30,000, they find:

$$\left[\frac{\ln \eta_r}{C_{gm}} \right]_0 = K_m M_w + y'$$

Their results are given in Table IX.

TABLE IX

LIMITING REDUCED VISCOSITIES OF POLYDECAMETHYLENE ADIPATE SOLUTIONS (27)

Solvent	Temperature, C.	$K_m \times 10^4$	η'
Diethyl succinate	79	0.197	0.067
Chlorobenzene	25	0.335	0.094
	79	0.294	0.051

Polyvinyl Chloride.—Mead and Fuoss (29, 63) have determined, by dynamic osmotic pressure measurements, the molecular weights of four samples of polyvinyl chloride. The samples had fairly narrow molecular weight distributions. One refractionated sample which gave an osmotic molecular weight of 100,000 was checked by sedimentation and diffusion measurements. The ultracentrifugal value was 102,000. These results agree with the Staudinger equation and give a K_m value of 0.7×10^{-4} in cyclohexanone at 25° C.

Polymethyl Methacrylate.—The results of the investigation of methyl methacrylate polymers by Staudinger and Warth (83) were used by Houwink as one of the examples of viscosity data which shows a nonlinear relationship with molecular weight.

Recently, a more careful study of this polymer was made by Schulz and Dinglinger (74). A total of eighteen fractions was obtained from seven samples prepared under various conditions. The intrinsic viscosities were measured in chloroform at 20° C. Osmotic pressures were determined in acetone at 27° C. Schulz and Dinglinger express their results as:

$$[\eta_{sp}/C_L]_0 = K_m P + B$$

with $K_m = 0.47 \times 10^{-4}$ and $B = 95 \times 10^{-4}$. However, they show that excellent agreement with the experimental results is obtained from:

$$[\eta] = KM^a$$

with $K = 3.3 \times 10^{-5}$ and $a = 0.85$.

Schulz and Dinglinger also give a thorough treatment of the type of result to be expected on unfractionated material, assuming the molecular weight distribution function is known.

Other Polymers.—The polymers described in the preceding sections for which the relationship between intrinsic viscosity and molecular weight is strictly linear have been of only moderately high molecular weight and somewhat polar in nature with the possible exception of polyvinyl chloride.

Many of the early investigations of Staudinger, where the maximum molecular weights were only a few thousand, also gave the limiting reduced viscosity proportional to the molecular weight. However, attempts by many workers to extend the law to truly high-molecular substances usually resulted in a K_m value which decreased with molecular weight. Staudinger has assumed that his viscosity law holds strictly for linear polymers and that these decreases in the proportionality constant are due to branching in the compounds of high molecular weight.

Meyer (64) attacked the validity of the Staudinger relation:

$$[\eta_{sp}/C_{gm}]_0 = K_m M$$

and has shown that in most cases the value of K_m decreases even though there is no reason to believe that the molecules are branched. Meyer's summary of the data in the literature is given in Table X. It is seen from this table that only in some cases is the intrinsic viscosity a linear function of the molecular weight. This is not true for all polymers. Branching should not be used as an excuse for the failure of the law unless it can be proved that the polymers are branched. This should not be interpreted as meaning that branching has no effect. Branched molecules certainly should give different solution viscosities than linear molecules of the same molecular weight.

TABLE X
DECREASE IN K_m VALUES WITH INCREASING MOLECULAR WEIGHT (64)

Polymer	Molecular weight	$K_m \times 10^4$	Solvent
Polystyrene	438	7.0	Benzene
	193,000	1.25	Benzene
Polyvinyl chloride	60,000	1.05	Tetrahydrofuran
	150,000	0.54	Tetrahydrofuran
Polyvinyl acetate	75,000	0.52	Acetone
	640,000	0.25	Acetone
Polyvinyl alcohol	40,000	0.68	Water
	108,000	0.43	Water
Cellulose acetate	678	16.6	<i>m</i> -Cresol
	272,000	3.6	<i>m</i> -Cresol
Polyprane	422	3.8	Benzene
	100,000	1.1	Benzene
Polymethyl acrylate	74,500	0.45	Acetone
	321,000	0.31	Acetone
Polymethyl methacrylate	25,000	0.056 ^a	
	260,000	0.019 ^a	
Sebacic hexanediol polymer	1,500	0.063 ^a	
	20,700	0.034 ^a	

^a Concentrations in g. per 100 cc.; solvent not given.

2. *Nonlinear Relationships*

Mark (61a), on the basis of theoretical considerations and measurements on cellulose acetate, proposed that:

$$[\eta] = KM^a \quad (37)$$

Houwink (37) has shown that $a = 0.6$ in this equation for several polymers. He has stated that this is in agreement with Kuhn's (57, 58) theoretical treatment which predicts values of a , for randomly coiled molecules, as low as 0.5.

Several recent careful investigations given below have shown that the value of a in some cases is definitely not 1.0 as proposed by Staudinger. The value of the exponent depends on the polymer structure, solvent interaction, and possibly on branching. Those cases in which a linear relationship is found appear to be special cases in which the exponent in Equation (37) happens to be near unity.

Polyisobutylene.—The most complete and accurate investigation of the relation between solution viscosity and osmotic molecular weight of any high polymer is Flory's study of polyisobutylene (24). Twenty-three sharp fractions of polyisobutylene having molecular weights of between 5600 and 1,300,000 were employed.

Four samples of this polymer were prepared using different catalysts and different temperatures of preparation. These were fractionated from a 1% solution and the fractions reprecipitated from a solution of about 0.2% concentration. This second fractionation is essential if material of narrow molecular weight range is to be obtained. This is especially true of the first portions to be precipitated, as this high molecular weight material carries down a considerable amount of the polymer having a lower degree of polymerization. No evidence was found for differences in fractions of the same molecular weight from these four preparations. This and the absence of gel formation at high yields are taken as evidence for absence of branching in polyisobutylene.

Flory did not extrapolate his viscosity data to infinite dilution nor has he reported the slope constant k' or β . However, all the determinations, which were made in diisobutylene at 20° C., were at polymer concentrations such that the relative viscosities were between 1.15 and 1.4. Values of $(\ln \eta_r)/c$ calculated in this range are within 2% of the true intrinsic viscosity.

This paper also gives an excellent treatment of the effect of solvent on the osmotic pressures. In cyclohexane, a good solvent, the π/c values

increase rapidly with concentration, while in benzene, a poor solvent for polyisobutylene, there is very little change. However, the data in both solvents extrapolate to the same value of $(\pi/c)_0$ at infinite dilution.

The results of Flory's determinations are shown in Figure 8 and may be expressed by the relation:

$$[\eta] = KM^a$$

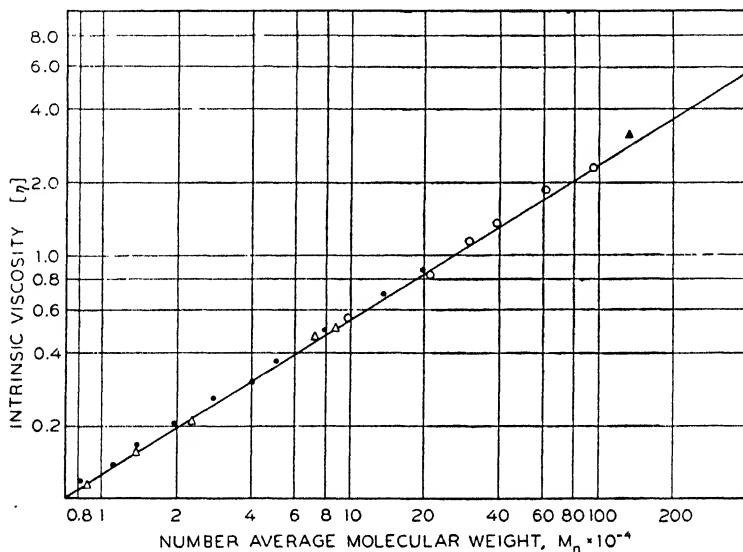


Fig. 8.—Intrinsic viscosity vs. molecular weight for polyisobutylene fractions (24): ●, polymer A; ▲, polymer B; ○, polymer C; △, polymer D.

where $K = 3.60 \times 10^{-4}$ and $a = 0.64$. The molecular weights of fractionated polyisobutylene may be calculated from the intrinsic viscosities in diisobutylene at 20° C. from the equivalent expression:

$$\log M = 5.378 + 1.56 \log [\eta]$$

Staudinger has reported the viscosity on one sample of polyisobutylene having a cryoscopic molecular weight of 1490 which is not in bad agreement with the results of Flory. The calculation of a Staudinger "constant" from this one measurement is certainly not warranted.

Kemp and Peters (51) have reported a constant based on samples which were not sharply fractionated and had cryoscopic molecular weights between 200 and 1000. Samples of higher molecular weight were also re-

ported but the results were discarded as they did not follow the laws of ideal solutions.

Polystyrene.—This polymer has been the subject of more study than any other. Schulz (72) has shown that fractions of the same molecular weight have lower intrinsic viscosities if the polymerization is carried out at higher temperatures, as may be seen from a few of his results illustrated in Table XI. This effect has been interpreted as being due to branching and in this case the explanation may very well be correct. However, the polymers prepared at low temperatures show decreasing K_m values with increasing molecular weight of the fractions, indicating that the Staudinger equation probably does not hold accurately.

TABLE XI
OSMOTIC PRESSURE OF POLYSTYRENE IN TOLUENE (72)^a

Fraction	Identification	$c_0 \times 10^3$	$p \times 10^3$	p/c_0	s	sc_0
III	Prepared at 20° C., $(p/c_0)_0 = 0.059$, $M = 420,000$, $[\eta] = 4.4$	5	0.52	0.104	86	0.43
		9.9	1.4	0.141	59	0.58
		19.6	5.6	0.285	40.5	0.79
		29	12.0	0.415	29.5	0.86
III	Prepared at 20° C., $(p/c_0)_0 = 0.130$, $M = 189,000$, $[\eta] = 2.3$	5	1.03	0.20	74	0.38
		9.9	2.50	0.25	49	0.48
		14.8	4.75	0.31	40	0.59
		19.6	7.8	0.40	34	0.67
		29	16.0	0.55	26	0.75
II	Prepared at 135° C., $(p/c_0)_0 = 0.109$, $M = 225,000$, $[\eta] = 0.99$	2.5	0.35	0.14	98	0.24
		5	0.90	0.18	79	0.39
		9.9	2.28	0.23	53	0.52
		19.6	7.0	0.36	35	0.69
		29	15.2	0.52	27	0.78
III	Prepared at 200° C. (under N ₂), $(p/c_0)_0 = 0.36$, $M = 68,800$, $[\eta] = 0.54$	2	0.87	0.43	87	0.17
		5	2.46	0.49	54	0.27
		9.9	5.65	0.57	37	0.37
		19.6	15.1	0.77	27	0.54

^a c_0 = concentration in g. per cc., p = osmotic pressure in atm.

Alfrey, Bartovics and Mark (2) have succeeded in explaining much of the discrepancy in the values for polystyrene. They have fractionated polymers made at 60°, 120° and 180° C. by the catalyzed reaction. Table XII gives their summary of these results. They have reported the constants K and a in the equation:

$$[\eta]_V = \left[\frac{\eta_{sp}}{V_2} \right]_0 = KM^a$$

where V_2 is the volume fraction of the polymer. This table also lists the slope constants for viscosity, k' (Eq. 10, page 210), and for reduced osmotic

pressure, μ (Eq. 25, page 222). Viscosities were measured in toluene at 30° and 40° C.

From the data in Table XII it may be seen that a increases from 0.7 to 1.1 with increasing temperature of polymerization. Thus, some samples of polystyrene might have a value of $a = 1.0$ and appear to prove the Staudinger equation. It remains to be seen whether or not chain branching is the explanation of this change in the exponent. Due to what has been called the "space filling" factor, the effective size of a branched molecule may be expected to increase more rapidly with molecular weight than a linear molecule. However, for small branched molecules, the density of material in this apparent volume will be greater than for a linear molecule, thus leading to smaller values for K .

TABLE XII
VISCOSITY AND OSMOTIC PRESSURE CONSTANTS FOR POLYSTYRENE (2)

Polymerization temperature, °C.	M_2	$[\eta]_V$	Constants
60	2,050,000	355	$k' = 0.42$
	1,580,000	295	$\mu = 0.48$
	890,000	200	$K = 1.6 \times 10^{-2}$
	550,000	140	$a = 0.70$
120	340,000	155	$k' = 0.33$
	240,000	118	$\mu = 0.45$
	167,000	86	$K = 0.66 \times 10^{-2}$
	108,000	62	$a = 0.80$
180	169,000	73	$k' = 0.21$
	145,000	59	$\mu = 0.43$
	132,000	53	$K = 0.04 \times 10^{-2}$
	110,000	45	$a = 1.10$

Cellulose Acetate.—Several articles have been written on the solution viscosity of cellulose acetate. The results of Bartovics and Mark (6) are on very narrowly fractionated material and constitute one of the best studies of this polymer. Viscosity measurements were made in acetone at 30° and 40° C. These authors also use volume fraction intrinsic viscosity, $[\eta]_V$. In these units they obtain the following constants: $K = 1.04 \times 10^{-2}$; $a = 0.67$; $k' = 0.70$; and $\mu = 0.43$. In a mixture of acetone and methyl alcohol the intrinsic viscosity is lower, k' is lower (0.60) and μ is larger (0.46). Molecular weights were obtained from osmotic pressures by both the static and the dynamic methods. The molecular weight range was from 25,000 to 126,000.

ϵ -Aminocaproic Acid Polymers.—Although this polymer is much more polar than the elastomers and related materials, the results obtained with it by Matthes (62) serve to call attention to a problem in solution

viscosity which requires further study. Matthes has determined the molecular weight of these polymers (which do not appear to have been fractionated) by end group analysis. Intrinsic viscosities were determined in concentrated and 40% sulfuric acid and are given in Table XIII together with the characteristic constants for the calculation of molecular weights.

The points of interest in these results are that a nonlinear expression is found in both cases and the exponent is smaller for the solvent showing the lower intrinsic viscosities. Since both the polymer and solvents are quite polar, there are, undoubtedly, large heat effects in both solvents which make it difficult to say with any certainty that the concentrated acid is a "good" solvent. However, it is the only data known to the author where extrapolated intrinsic viscosities have been obtained in two solvents which show different exponents. More complete data should be obtained on elastomers in several solvents to determine more accurately the change in this exponent between good and poor solvents.

TABLE XIII

RELATION BETWEEN INTRINSIC VISCOSITY AND DEGREE OF POLYMERIZATION FOR ϵ -AMINOCAPROIC ACID POLYMERS IN CONCENTRATED AND 40% SULFURIC ACID (62)

Polymerization degree, P	Intrinsic viscosity, $[\eta]$	
	Concd. H_2SO_4	40% H_2SO_4
3.53	0.062	0.049
4.43	0.070	0.051
5.40	0.104	0.074
8.29	0.102	0.080
7.56	0.102	0.078
10.2	0.145	0.101
16.5	0.165	0.105
14.6	0.189	0.104
21.0	0.239	0.136
38.9	0.306	0.164
40.4	0.333	0.179
43.5	0.337	0.181
Characteristic constants	Concd. H_2SO_4	40% H_2SO_4
k'	0.25	0.42
K	1.2×10^{-3}	2.4×10^{-3}
a	0.668	0.510

Rubber.—Although natural *Hevea* rubber has been the most important elastomer, the results of viscosity and molecular weight studies have been in very poor agreement because in no case reported in the literature has the purified rubber hydrocarbon been separated into a large number of fractions of narrow molecular weight distribution. In many cases low

molecular weight rubbers have been prepared by mill breakdown or oxidation. This procedure, undoubtedly, changes the structure somewhat and may give rise to intramolecular cross links which are more responsible for the lower viscosity than actual reduction in molecular weight, as is indicated by some of the results of Caspari (11). An example of this general treatment of rubber is seen from the results of Staudinger and Fischer (82) in Table XIV.

TABLE XIV
RELATION BETWEEN $[\eta]$ AND OSMOTIC MOLECULAR WEIGHT FOR RUBBER
IN TOLUENE AT 20° C. (82)

Product	$[\eta]$	M_n
<i>Purified rubber:</i>		
(1) Alkali treated (Pummerer)	1.26	92,000
(2) Aluminum-oxide treated	9.00	352,000
(3) Ether-soluble rubber		
(a) Easily soluble fraction	3.89	231,000
(b) Difficultly soluble fraction	4.60	170,000
<i>Masticated rubber:</i>		
(1) Sample I		
(a) Easily soluble fraction	1.10	82,000
(b) Difficultly soluble fraction	1.68	143,000
(2) Sample II		
(a) Easily soluble fraction	1.29	71,000
(b) Difficultly soluble fraction	0.91	68,000
<i>Oxidized rubber (KMnO₄):</i>		
(1) Sample I		
(a) Easily soluble fraction	1.38	102,000
(2) Sample II		
(a) Easily soluble fraction	1.08	88,000
(b) Difficultly soluble fraction	1.48	116,000

Kemp and Peters (48, 49), on the basis of a few samples of very low molecular weight, roughly fractionated, give:

$$M = \frac{\log \eta_r}{C_{gm}} \times 0.75 \times 10^4$$

which is equivalent (in benzene at 25° C.) to:

$$[\eta] = 4.5 \times 10^{-5} M$$

Gee (30) has given a careful analysis of the results on rubber (in benzene) and believes that they can best be expressed by a linear relation:

$$[\eta] = 1.6 \times 10^{-5} M$$

Gee's data represent only a few fractionated samples; hence the writer believes that, if a linear relationship holds, more weight should be put on the ultracentrifugal results of Kraemer (55) and the osmotic data of Meyer

and Wertheim (66). At the present time, for rubber in benzene or toluene, it can only be said that, approximately:

$$[\eta] = M \times 10^{-5}$$

Because of the poor quality of the published data on the intrinsic viscosity of rubber solutions, it is not possible to say whether or not the Staudinger equation or the nonlinear form holds, but the results on other hydrocarbon polymers suggest that the linear Staudinger form does not apply here.

3. Discussion of Results

Since viscosity measures an entirely different sort of molecular weight (M_v) from that obtained by end groups or osmotic pressures (M_n), it is evident that a given type of polymer may give widely different viscosity results for the same number average molecular weight, depending on the molecular weight distribution in the sample. If, however, sharply fractionated material is used, all types of average molecular weights are essentially the same. Only under these conditions may a definite answer be obtained concerning the relationship between viscosity and molecular weight, if the molecular weight distribution is not known. Unfortunately, much of the data in the literature has been on unfractionated or poorly fractionated material.

The problem of determining whether the generalized Staudinger equation:

$$[\eta] = KM + y$$

or the nonlinear form:

$$[\eta] = KM^a$$

is the correct expression for the observed data is not as simple as it might appear. Both forms contain two arbitrary constants. Hence, unless a wide range of molecular weights is studied and the experimental error is small, it may be impossible to decide which expression is correct. The application of statistical methods to the data should give more assurance of the proper form.

Flory's results, however, cover the necessary conditions so that, at least in the case of polyisobutylene, there seems to be no doubt that the nonlinear expression is correct.

VI. Theoretical Treatment of Viscosity

As was pointed out earlier, it is not possible from viscosity measurements alone to determine the molecular weight of a high polymer. By this we

mean that there is no completely adequate theoretical treatment of the subject, and even those theories which have been fairly successful require additional information such as bond angles, interatomic distances, chain structure and other data often difficult to obtain.

This is in contrast to the so-called thermodynamic methods by which it is possible to count the number of solute particles and hence determine its molecular weight. This may be done without additional knowledge of the solute. The equations used are strictly not the result of thermodynamics alone but are derived from this science plus certain other experimental relations which are used to define molecular weight. The first of these is the gas law:

$$pv = \frac{w}{M} RT \quad (38)$$

This law has been found to hold for all pure gaseous substances if measurements are made at sufficiently low pressures. M is a characteristic constant for each substance and is called its molecular weight.

If two such substances, whose molecular weights have been thus defined, are examined in the liquid state, it has been proved experimentally that:

$$p_A = p_A^0 \frac{w_A/M_A}{w_A/M_A + w_B/M_B} = p_A^0 N_A \quad (39)$$

provided that $w_B/M_B \ll w_A/M_A$, where p_A is the partial vapor pressure of A , p_A^0 is the vapor pressure of pure A and N_A is the mole fraction of A . This equation is known as Raoult's law and may be considered as a secondary definition of molecular weight (M_B) of a substance (B) which cannot be studied in the gaseous state.

Deviations from these laws at higher concentrations may often be derived by the methods of statistical mechanics. This has been done for high-polymer solutions by Flory, Huggins and others.

Viscosity measurements cannot easily be interpreted in terms of these fundamental definitions of molecular weight. It appears that the viscosity of dilute polymer solutions measures the size and shape of the particles in solution. If the molecules of a high polymer in solution were spheres having a volume equal to the molecular volume ($M_B/d_2^3 N_0$), then the intrinsic viscosity should be given by:

$$[\eta] = 0.025/d_2^3 \quad (39a)$$

since, according to the Einstein equation, the limiting viscosity depends

only on the volume fraction of the disperse phase. In order even to consider using the Einstein equation, however, the particles must be very large compared with the solvent molecules. However, this condition should be met fairly well even for the minimum volume of a molecule of polymer whose molecule weight is 10^4 or greater.

The intrinsic viscosities of high-polymer solutions do not agree with Equation 39a in two important ways:

(1) The intrinsic viscosities are greater than 0.025 by several orders of magnitude (the density of the polymer, d_2 , is usually about unity).

(2) Intrinsic viscosities do vary with the molecular weight of the solute.

If the general picture of a particle which distorts the streamlines of the solvent medium is to be maintained, the observed differences may be explained in two ways. The first is that the particle contains only polymer but that it is not spherical; an elongated particle, either an ellipsoid or rod, is usually assumed. The second explanation is that the particle is roughly spherical but that it contains solvent as well as polymer. Sackur originally suggested this with the idea that the solvent was bound to the solute by solvation forces. At the present time it is assumed, at least for hydrocarbon polymers and solvents, that the chain molecule wanders at random through the solvent. This gives a molecular particle which may have a volume several hundred times that of the molecular volume of the polymer molecule. The solvent flows around this just as it would flow around a large "gel" fragment, from highly swollen and lightly vulcanized rubber.

A third mechanism given by Huggins (38-40) is based on a molecular picture similar to the second except that the polymer chain is supposed to have so little restriction on the motion of the solvent molecules enmeshed in it that the solvent flows through the tangled mass. According to Huggins, the velocity gradient causes the molecule to rotate around an axis which is perpendicular to the plane containing the direction of shear and the direction of maximum velocity gradient. In spite of such rotation, however, each atom is in general, by this theory, not moving with the same velocity as the liquid immediately surrounding it. After calculating this relative velocity, Huggins assumes Stokes' law to find the work done by the atom on the liquid; and, after suitable summation and averaging, the increase in viscosity is obtained. Although Huggins' mathematical analysis of this model is excellent, the theory appears to have one weak point, namely, the assumption that Stokes' law holds for the force acting on the individual atoms. This treatment gives:

$$\frac{\eta_{sp}}{C_L} = \frac{6\pi N_0 a \bar{F}_{xz}}{1000 n \left(1 - \frac{6\pi N_0 a \bar{F}_{xz}}{1000 n} C_L \right)} \quad (40)$$

in which N_0 is Avogadro's number, a is the radius of a chain atom and n is the number of atoms in the chain. If Brownian motion is large or the velocity gradient, g , small, the value of \bar{F}_{xz} may be expressed as a function of the bond lengths, l and angles, θ . For large n , with a rigid but randomly kinked molecule, this results in:

$$[\eta_{sp}/C_L]_0 = 2.94 \times 10^{20} B_\infty l^2 a n \quad (41)$$

where:

$$B_\infty = \frac{1 + \cos \theta}{1 - \cos \theta} \quad (42)$$

Huggins' treatment, therefore, results in a linear relation between molecular weight and intrinsic viscosity, since the number of atoms in the chain, n , is directly proportional to the molecular weight. In their more general form, Huggins' equations also predict a small additive constant in the equation for reduced viscosity.

In a later paper, Huggins points out that, if the viscosity of the solution, η , had been used in his equations rather than that of the solvent, η_0 , this would give:

$$\eta_{sp}/c = [\eta_{sp}/C]_0 + [\eta_{sp}/C]_0^2 c$$

This is equivalent to Equation 10 (page 210) with $k' = 1$. Lower values of k' are said to be explained if a modified Stokes' law is used, *viz.*:

$$\text{Force} = 6\pi k' \eta a u$$

where k' is a factor representing the reduction in the force due to the presence of polymer molecules.

1. Dependence of Intrinsic Viscosity on Particle Shape

When a colloidal solution of polymer molecules having a spherical or ellipsoidal shape is sheared, the particles rotate in the continuous solvent phase. In the case of spheres, the streamlines are distorted around a sphere so that they are closer together in a plane normal to the direction of shear than they would be if the particle were not present. This means that the rate of shear is greater and hence the over-all viscosity is increased due to the increase in the amount of work which must be done. If the

particle has the same volume but is ellipsoidal in shape, the extra energy required is somewhat less if the major axis is in the direction of shear and much greater if this axis is in the direction of maximum velocity gradient. If the particle is large enough that the angular velocity function for its rotation is given by hydrodynamic forces alone, it is found that the particle spends most of its time with its major axis in the direction of flow, *i. e.*, there is a sharp maximum in the angular probability function at $\phi = 0$. The net effect, however, since it spends some of its time in the direction which gives a very high contribution to increased viscosity, is to increase the viscosity somewhat over that given by spheres. This result is expressed by the equation of Eizenschitz (18):

$$\frac{\eta_{sp}}{\phi} = \frac{1.15 f}{\pi \ln (2 f)} \quad (43)$$

where f is the axial ratio of the ellipsoid.

On the other hand, if Brownian motion is large (small particles or high temperatures), the particle no longer spends most of its time with its axis in the direction of least resistance but has an almost equal probability of being in any direction. More precisely, the angular probability function has a slight maximum at $\phi = 45^\circ$ if the rotary diffusion constant, θ , is large compared with the velocity gradient, G . In this case, the increase in viscosity over that of spheres is much greater and, according to Eizenschitz, is about proportional to the square of the axial ratio rather than the first power:

$$\frac{\eta_{sp}}{\phi} = \frac{f^2}{15 \ln (2 f) - \frac{45}{2}} \quad (44)$$

A more recent equation of Simha (Eq. 4, page 204) is in better agreement with some of the experimental data on particles of known axial ratio.

TABLE XV
AXIAL RATIO AND LENGTH OF POLYSTYRENE MOLECULES

M	$[\eta]_V$	l/d	d	l	l_{max}
519	4.00	3.3	7.7	25	12.5
2,460	7.64	6.4	10.4	67	60
5,225	11.84	9.0	12.0	108	125
7,600	14.78	10.6	12.8	136	182
13,000	23.70	14.6	13.7	200	312
30,000	28.15	16.5	17.5	289	720
80,000	58.70	26.3	20.7	544	1922
270,000	250.00	61.0	23.4	1427	6490

Simha (78) has applied this analysis of viscosity to the data of Signer and Gross on polystyrene. These results are given in Table XV in terms of volume fraction intrinsic viscosity. The values of the maximum extended length, l_{\max} , were calculated using a length of 2.5 Å. per styrene unit. The results in Table XV may be generalized according to Simha by: $l/d = 0.12 M^{1/2}$; $l = 0.34 M^{1/2}$; $d = 2.9 M^{1/2}$.

2. Dependence of Viscosity on Swelling

The idea of a highly elongated molecule has considerable merit in explaining the results of flow double refraction and depolarization of scattered light in concentrated solutions. In dilute solutions, however, the molecular lengths appear to be much too high for the randomly kinked molecule, even though this "effective length" is somewhat greater than the average distance between the ends of the chain. Furthermore, in making the calculations of length and axial ratio, it is assumed that the ellipsoid contains only polymer. Lightly cross-linked polymers are capable of swelling to several hundred times their original volume.

A very satisfactory treatment of this case is that of Flory and Rehner (25, 26), who find from statistical mechanics that the molecular weight between cross links is given by:

$$M_c = -\rho V_1 V_2^{1/3} / [K V_2^2 / 2 + \ln(1 - V_2) + V_2] \quad (45)$$

The constant K depends on the heat of mixing and is zero or very small if polymer and solvent have the same cohesive energy density. If the swelling is large, the volume swelling factor, S (volume of swollen polymer per cubic centimeter of unswollen polymer), is given by:

$$S = \frac{1}{V_2} = \left[\frac{M_c(1 - K)}{2 M_1} \right]^{3/4} \quad (46)$$

It is, therefore, to be expected that a linear molecule will also entrap a volume of solvent much larger than its true molecular volume. Since such swelling must certainly take place, the magnitude of the axial ratio required to explain the results will be greatly reduced and may not differ much from unity. For the purpose of the following discussion, it will be assumed that $f \approx 1.0$, but this is by no means certain.

Fikentscher and Mark (21) used the idea of a "swollen" molecule very early in high-polymer development. Mark (61) has discussed this effect in an article on the form of high polymers in solution. Kuhn (57) considered the effect of shear on the stretching of such a particle. Alfrey,

Bartovics and Mark (1) believe that the effect of a poor solvent in reducing the intrinsic viscosity is in the reduction of the swelling volume. This is similar to the effect of the heat term, K , in the Flory–Rehner equation for cross-linked gels. Gee (30) believes that the rigid ellipsoid model is so far from our concept of a rubber molecule in solution that it does not seem profitable to discuss it further. He implies that intrinsic viscosity bears the same relationship to cohesive energy densities as does macroscopic swelling.

If a swelling factor, S_0 , is associated with a molecular particle at infinite dilution, the intrinsic viscosity is given by:

$$[\eta]_{V_1} = 2.5 S_0 \tag{47}$$

Or if the expression of Eilers (16) is used for η_{sp}/c at higher concentrations and S is the swelling factor at that concentration:

$$\eta_{sp}/V_2 = 2.5 S + 4.94 S^2 V_2 + \dots \tag{48}$$

$$= (2.5 S) + 0.79(2.5 S)^2 V_2 + \dots \tag{49}$$

If the swelling factor at infinite dilutions, S_0 , increases with the molecular weight and is sufficiently large, Equation 47 offers a reasonable explanation of the large values of the intrinsic viscosity of high polymers. Equation 49, however, predicts a larger value of k' than is found for most linear polymers in a good solvent if the swelling factor, S , is independent of concentration and equals S_0 . Eilers has shown that this equation fits the data for the highly cross-linked formaldehyde resins with a constant but small swelling factor, as is shown in Table XVI.

For linear polymers Eilers finds that there is a linear relation between S and the apparent hydrodynamic volume fraction, SV_2 . One example of

TABLE XVI
SWELLING FACTOR FOR THREE-DIMENSIONAL POLYMERS (16)

Concentration range, g./100 cc.	Polymerization time, min.	Specific gravity	Range of η_r	Swelling factor, S
I. Phenol-formaldehyde resins, 1 to 40	20	1.105	1.049 to 3.408	1.02 ± 0.01
	60	1.156	1.059 to 5.328	1.33 ± 0.04
	90	1.172	1.072 to 4.290	1.63 ± 0.03
II. Cresol-formaldehyde resins, 1 to 40	90 ^a	1.144	1.064 to 6.538	1.40 ± 0.04
	100 ^b	1.145	1.026 to 4.042	1.11 ± 0.02
	360 ^c	1.138	1.048 to 3.778	1.08 ± 0.02

^a Tricresol-formaldehyde. ^b *p*-Cresol-formaldehyde. ^c *o*-Cresol-formaldehyde.

this is given in Figure 9 which uses the solution viscosity data on cellulose acetate in *m*-cresol. This result is expressed by:

$$S = \frac{bS_0}{b + (S_0 - 1)V_2} \quad (50)$$

where b is the value of the apparent volume fraction for which $S = 1$. Table XVII shows the values Eilers has calculated for several linear polymers. The values of S_0 vary greatly with the molecular weight but the values of b are fairly constant and generally lie between 0.7 and 1.0. It would be expected that we should find $b = 1.0$ since some swelling would be

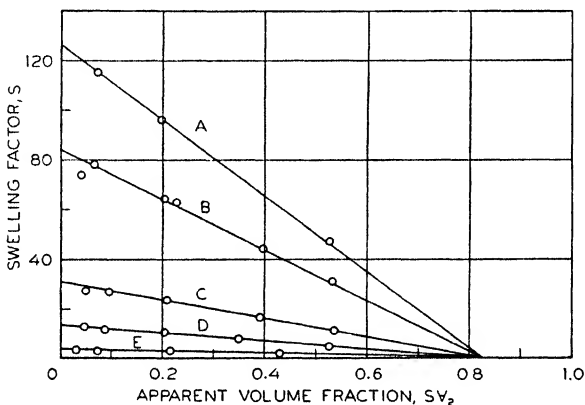


Fig. 9.—Relationship between swelling factor, S , and concentration of cellulose acetate (16). Molecular weights are: Curve A, 130,000; B, 84,000; C, 23,600; D, 11,200; E, 3150.

expected even with small amounts of solvent. The reason for this discrepancy appears to be that extrapolation to zero velocity gradient should be made in calculating the values of S . If this is done, we find that for $S \gg 1.0$:

$$S \approx \frac{S_0}{1 + S_0 V_2} \approx S_0 - S_0^2 V_2 + \dots \quad (51)$$

If this value of S is used in Equation 49, it is found that:

$$\eta_{sp}/V_2 = 2.50 S_0 + \left(0.79 - \frac{1}{2.5}\right) (2.5 S_0)^2 V_2 \quad (52)$$

$$= [\eta]_{V_2} + 0.39[\eta]_{V_2}^3 \quad (53)$$

TABLE XVII

 VALUES OF CONSTANTS S_0 AND b IN EILERS' EQUATION FOR LINEAR POLYMERS (16)

Polymer	Molecular weight	Solvent and constants					
		Tetralin					
		S_0	b				
Polystyrene	600	1.4	1.15				
	2,550	2.9	1.01				
	5,200	4.3	0.92				
	23,000	15.5	0.81				
	120,000	82	0.76				
	280,000	198	0.72				
	440,000	304	0.66				
600,000	400	0.65					

Polymer	Molecular weight	Tetralin		Benzene		Methyl ethyl ketone	
		S_0	b	S_0	b	S_0	b
Polystyrene	2,400	2.6	1.01	2.75	1.09	2.4	1.35
	7,500	6.0	0.87	5.7	0.85	4.5	0.96
	28,000	19.8	0.80	20.7	0.73	10.8	1.03
	160,000	108	0.75	111	0.79
	450,000	302	0.67

Polymer	Molecular weight	Tetrachloroethane		Dioxane	
		S_0	b	S_0	b
Poly- ω -hydroxy-decanoic acid	780	4	0.78		
	1,710	6	0.78		
	2,800			4.0	0.66(?)
	5,670	15	0.78		
	6,400			8.1	0.70
	9,330	22	0.78		
	13,000			16.0	0.75
25,200	62	0.78			

Polymer	Molecular weight	<i>m</i> -Cresol	
		S_0	b
Cellulose acetate	3,150	3.7	0.825
	11,200	13.5	0.825
	23,000	31	0.825
	84,000	84	0.825
	130,000	126	0.825

which is the same as Equation 10 with $k' = 0.39$, the value found experimentally in many cases.

It is interesting to note that this behavior of the swelling factor when used in the osmotic pressure equation of Schulz gives, for $s = S/d_2$:

$$\frac{\phi}{c_0} = \frac{RT}{M} \frac{1}{1 - sc_0} = \frac{RT}{M} (1 + s_0 c_0) \quad (54)$$

The values of s_0 from the slopes of the osmotic curve are not in agreement with S_0 from viscosity except for order of magnitude. The agreement is probably as good, however, as is given by other theories.

The magnitude of the swelling factor has been the subject of several papers by Kuhn (57, 58) who, however, has calculated the distance between chain ends and attempted to determine chain extent from this and other distances. While this problem cannot be considered as completely solved, Daniels (12) has arrived at a probability function, $p(\rho)$, for the extent, ρ , or maximum distance between any portion of a randomly folded one-dimensional chain. Daniels' function for the probability has been expressed by Auluck and Kothari (3) in terms of the lengths of a link, b , and total chain length, λ , as:

$$p(\rho)d\rho = \frac{8}{(2\pi b\lambda)^{1/2}} \sum_{t=1}^{\infty} (-1)^{t-1} \exp\left(-\frac{t^2 \rho^2}{2b\lambda}\right) d\rho \quad (55)$$

This gives the most probable value of the extent, ρ_{\max} and the average value, $\bar{\rho}$, as equal to:

$$\rho_{\max} = 1.346(\lambda b)^{1/2} = 1.346 bN^{1/2} \quad (56)$$

$$\bar{\rho} = 1.596(\lambda b)^{1/2} = 1.596 bN^{1/2} \quad (57)$$

Hulburt, Harman, Tobolsky and Eyring (45) and Kauzmann and Eyring (47) have pointed out that, if this result is assumed for the three-dimensional case, Kuhn's treatment leads to:

$$\eta_{sp} = \frac{12.7}{m^{1/2}} \gamma^{1/2} M^{1/2} c_0 \quad (58)$$

where m is the average molecular weight of each carbon atom plus its side groups, M is the molecular weight of the chain and γ is the number of carbon atoms per freely orienting segment.

This, as will be seen, deviates considerably from the Staudinger law for which $(\eta_{sp}/C)_0$ is proportional to M . In fact, if $\bar{\rho}$ were taken as proportional to $N^{0.55}$ rather than $N^{0.50}$, the result would be that:

$$[\eta] = KM^{0.65}$$

which appears to be the case for many elastomers.

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THE KINETIC THEORY OF RUBBER ELASTICITY

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	PAGE
I. Introduction.....	253
Historical Excursion.....	257
II. Structure of Rubbers.....	259
1. Chemical Composition.....	259
2. Average Molecular Weight.....	261
3. Internal Flexibility of the Linear Macromolecules.....	262
III. Configurational Statistics of an Isolated Chain Molecule.....	263
IV. Model for Bulk Rubber and Its Statistical Treatment.....	267
V. Stress-Strain Relation for Unilateral Stretch.....	270
VI. General Deformations.....	272
VII. Swelling.....	273
VIII. Effect of Thermal Expansion. Thermoelastic Inversion.....	274
IX. Statistical Treatment of Highly Extended Chains.....	275
X. Molecular Significance of the Constants of the Theory.....	278
XI. Influence of Crystallization.....	279
XII. Comparison of Theory with Experiment.....	285
1. Comparison of Theory with Total Stress-Strain Curves.....	286
2. Comparison of Theory with Resolved Stress-Strain Curves..	290
3. Discussion.....	293
XIII. Brief Discussion of Other Theoretical Work on the Elastic Behavior of Bulk Rubber.....	294
Bibliography.....	297

I. Introduction

Rubbers (elastics or elastomers) are, in general, characterized by the following properties: (1) Long-range extensibility (up to 1500%), which is practically completely reversible. (2) Low initial modulus (around 10^6 dynes per sq. cm.) which first decreases and then increases up to several hundred times its initial value. (3) The elastic modulus is, over a long range of extension, a linear function of the absolute temperature.

These characteristics are so different from those encountered in other systems, such as gases, liquids and crystals, that it appears reasonable to

consider the rubbery state as a quite separate and distinct state of matter. It may also be regarded as a transition state, which has some structural details and properties in common with all three of the principal states of matter.

Rubbers resemble *solids* because there exist elastic deformations, which show that bulk rubbers possess a characteristic structure that determines their form in the absence of external forces. The elements of this structure must, however, be quite different from those in normal crystals, in which bonds of heteropolar, homopolar, metallic or van der Waals' type connect atoms or molecules into a rigid three-dimensional lattice with a definite long-range order. The high extensibility suggests that the structure of rubbers is of a much more flexible type with the long-range relationships between individual atoms or groups of atoms less rigorously defined. There must exist in rubber infrequent strong bonds which suppress permanent flow and maintain the coherence of the material. However, the small forces needed to produce considerable distortions indicate that one does not have to act against such strong bonds and that the elastic restoring forces can hardly be of any of the types listed above. That is, ordinary distortions of bulk rubber do not appreciably affect the next neighbor arrangement around individual atoms, or change the distances between atoms linked by chemical or other strong bonds. Only at very large extensions, at which some rubbers crystallize and one approaches the breaking point of the material, do these bonds come into play. For instance, ordinary chemical bonds appear to contribute to the ultimate tensile strength of rubber, which (referred to the cross section at the breaking point) is about that of copper or cellulose.

Rubbers resemble *liquids* in possessing high volume rigidity together with small rigidity of shape; their compressibility is that of ordinary liquids. In comparison with the extensibility of the material, it is quite negligible, and one may treat rubbers as incompressible for extensions up to 300 or 400%; Poisson's ratio is thus 0.5 for small deformations. Furthermore, the coefficient of thermal expansion for rubbers is of the same order of magnitude as for liquids, and their capacity to dissolve simple chemical substances such as sulfur and organic sulfur compounds is very similar to that of normal liquids, such as isoprene, benzene or carbon disulfide. These points suggest that the interactions between adjacent molecules or atom groups in bulk rubber are, for the most part, similar to those which maintain the fixed volume of ordinary liquids. They produce a certain degree of short-range (5–10 Å.) order, but no order exists over long distances (50–100 Å.). In addition to these van der Waals' forces, which do not

maintain a permanent coupling of molecule to molecule or atom to atom, there must be strong bonds which combine the atoms into large molecules and produce the elements of the structure previously mentioned. It seems that all rubbers are typical *high polymers*.

Rubbers resemble *gases* very strikingly in their thermoelastic behavior. The proportionality of stress to absolute temperature under constant strain suggests that the tension in stretched rubbers, like the pressure in gases, is associated with a change in entropy of the material when it is deformed, rather than with a change in internal energy. Quantitatively, the behavior of stretched rubbers, or of gases under pressure, is determined by their free energy, F , which in the case of simple tension may be written as:

$$F(L,T) = U(L,T) - TS(L,T) \quad (1)$$

where L represents the length of the stretched material, and the other symbols have their customary significance. The tension is:

$$Z(L,T) = (\partial F/\partial L)_T = (\partial U/\partial L)_T - T(\partial S/\partial L)_T \quad (2)$$

The same formulae hold for gases, if L is replaced by the volume, V , and Z by the negative pressure ($-\rho$). The simple and uniform thermoelastic behavior of gases, independent of their chemical composition, is due to two important characteristics: (1) the internal energy is in all cases *nearly independent* of the volume; (2) the entropy consists of two parts, one associated with the heat capacity, h , of the gas, dependent on the chemical composition, but making no contribution to $(\partial S/\partial V)_T$, and the second associated with the number of positional configurations available to the system, independent of the composition, and making a contribution to $(\partial S/\partial V)_T$, which is independent of T . The uniform and simple thermoelastic behavior of "ideal" rubberlike materials, independent of their composition, may be understood in a similar way. The internal energy of the liquidlike mass of molecules will be practically independent of its form, such strong chemical bonds as do exist being but little stretched by the relatively small forces which already produce considerable deformations of the material; $(\partial U/\partial L)_T$ will be small. As will be indicated later in more detail, the entropy again consists of two parts, one associated with the heat capacity and not contributing to $(\partial S/\partial L)_T$, the other associated with the number of configurations available to the molecules within the material. The number of these configurations will depend on the external form of the material but not on the temperature, on the general structure of the poly-

mer molecules but not on their particular chemical composition. $(\partial S/\partial L)_T$ will, accordingly, be independent of temperature, and we will have, approximately:

$$Z(L,T) = Z_0(L)T \quad (3)$$

By keeping in view all these characteristics, one arrives at a fairly good understanding of the existence of rubber elasticity, and even can proceed to the establishment of mathematical expressions which are in rather satisfactory quantitative agreement with many experimental facts.

The present development of quantum mechanics makes it possible to develop the theory of gases and solids on the application of first principles of physics only. *Practically*, however, such a method, while highly desirable, would be quite intractable mathematically. Therefore, another approach is usually adopted. One starts with a clear-cut *model* of a gas or solid. Such a model is always, admittedly, an approximation. It may, however, be an excellent approximation if it neglects only unessentials and takes care of the essential characteristics of the system under consideration. For a clear understanding of the situation, it is desirable to put all necessary approximations into the model, and then treat it rigorously as far as the quantitative mathematical-physical development is concerned.

For example, in the case of gases the simplest model is the "ideal" gas, in which one neglects the interaction between the particles. In this treatment the physical properties of the system are determined by the kinetic mobility of its molecules. *The kinetic theory of gases* was first developed for this simplified model. Later the treatment was extended, introduction of the forces between the molecules enabling one to take account of the finer details and to explain the differences in the behavior of different gases. For an understanding of the *fundamental nature* of gases, however, this extension of the theory is unnecessary; the perfect gas model exhibits all the features *essential* for the gaslike behavior of a system.

In the present state of development, the most complete theory of rubber elasticity is roughly analogous to the theory of a perfect gas. The characteristic features of rubberlike elasticity are made comprehensible, but further elaboration is required if one is to explain *quantitatively* the characteristics of individual elastomers and the differences between them.

In the case of solids, particularly crystals, the forces between the atoms determine the properties of the system, the kinetic mobility of the atoms being greatly limited. Recently it has been shown, however, that molecules or groups of molecules may have a kinetic mobility even in the solid state. For rubber like materials, particularly, kinetic mobility of the constituents

is well established. This consideration has led to a *kinetic theory of rubber elasticity*, as an analogue to the kinetic theory of gases.

Historical Excursion

Gough (12) in 1806 was the first to notice the peculiar thermoelastic properties of rubber. He observed that: (a) rubber generates heat on fast stretching, and (b) rubber extended by constant load contracts on heating. Lord Kelvin (31) pointed out in 1855 that (b) follows from (a) by thermodynamics; this indeed was one of the earliest applications of that newly developed branch of physics to an observed phenomenon. Lord Kelvin's theoretical conclusion was the starting point of fundamental work by Joule (29) in which Gough's observations were repeated and checked in a more quantitative way.

Joule's long memoir published in 1859 clearly proposes to discover by thermodynamic measurements for rubber and other similar materials whether any of the following three alternatives hold and what inferences can be drawn about the mechanism of the elastic behavior of such materials:

(1) "If the heat given out" by the compression of "elastic fluids" proved to be equivalent of the work spent, then "the natural inference" was that the elastic force and the temperature of a material "is owing to the motion of its constituent particles."

(2) "On the other hand, it was possible, secondly, to conceive of an elastic fluid which would not give out any heat by compression. This would be the case if it was made up of mutually repelling particles, the temperature of which was that of the mass. The work required to compress the fluid would be the same on either hypothesis, but in one supposition the effect would be developed in actual energy, in the other in potential form."

(3) "Thirdly, we may suppose a fluid exhibiting as heat a portion of the force employed in its compression, and retaining the rest in the potential form."

Joule's experiments have shown that at low elongations most of the work applied to stretch rubber is transformed into heat. He therefore concluded that, for rubber, the first alternative holds. The "natural inference" is then that "*the elastic force of rubber is owing to the motion of its constituent particles*" [authors' italics]. Thus, Joule and Lord Kelvin may justly be considered as the fathers of the fundamental concept of the kinetic theory of rubber elasticity.

When, in 1925, I. R. Katz discovered that rubber crystallizes at high elongations, another obvious explanation for the development of heat during stretching was available, and Joule's suggestive theory was overshadowed by an intense discussion of the two-phase structure of rubber.

Between 1927 and 1933, several authors, *e. g.*, Busse (4), Karrer (30), Mark and Valkó (36b), Meyer, Susich and Valkó (38) and Woehlich (53, 54), again expressed the idea that the elasticity of proteins and rubbers is predominantly a kinetic phenomenon, and offered qualitative support for this concept—without noticing Joule's earlier evidence. Progress was made, particularly, in recognizing the nature of the "motion of the constituent particles" in rubber, left open by Joule, because at his time but little was known about the structure of rubber. Modern investigations have shown the possibility of free rotation around the single bonds in the rubber chain (see page 262). Haller (19) seems to have been one of the first to call attention to the possibility of the coiling up of chain molecules in solution due to free rotation. Some of the aforementioned investigators (30, 38) applied Haller's suggestion to the chain molecules in solid rubber, but the manner in which the heat motion due to free rotation causes rubber elasticity was left open. In 1934, Guth and Mark (16) clarified the mechanism of rubber elasticity and worked out the first *quantitative* theory which accounted in a general way for some of the peculiar properties of rubber. In the following years the original theory of rubber elasticity was improved and developed by an attempt of Kuhn (34b) in 1936 to compute Young's modulus for bulk rubber, and, in 1937, by the calling of attention to the mutual attraction between the chains by Guth (13) and Guth and Mark (17). In all this early work, however, no clear-cut model of bulk rubber was employed.

Eyring (9) in 1932, discussed the mean square length of isolated long-chain molecules with a fixed valence angle. Guth and Mark (16) and Kuhn (34a) in 1934 developed independently the statistics of isolated long-chain molecules with free rotation. Kuhn, however, did not discuss rubber elasticity at that time, but applied this statistical treatment to rubber elasticity in an extensive article in 1936.

Recently (beginning in 1939, with the first paper appearing in 1941), James and Guth (14, 15a, 18, 22-27) developed a comprehensive theory based upon a specific model of bulk rubber. It accounts for most of the characteristic elastic and thermoelastic properties of rubber in a quantitative way and seems to be rather satisfactorily supported by all experimental facts available to date.

Still more recently, Wall (49-52), Treloar (44-47), and Flory and Rehner (10, 11) have contributed a number of interesting investigations to the problem of rubber elasticity. In 1944, at the American Chemical Society meeting in Cleveland, a general discussion of the present state of the kinetic theory of rubber elasticity brought the whole question into the focus of interest.

This review will follow principally the line of thought of James and Guth and will—in Section XIII (page 294)—attempt to give a short description of the leading ideas of the other approaches.

The kinetic theory of rubber elasticity may be developed in four stages:

(1) Treatment of isolated long-chain molecules, of given chemical characteristics, such as chain length, valence angle and internal mobility.

(2) Treatment of bulk rubber, considered as a network formed by firmly linking together such molecules, with the interaction between the molecules taken into account only in the simplest possible manner.

(3) Treatment of the process by which isolated long-chain molecules are, during cure, linked together into a coherent and (relatively) nonplastic mass.

(4) Introduction into the treatment of a more detailed account of the forces acting between molecular chains.

The first step leads to results applicable only to very dilute suspensions of isolated rubber molecules, the second leads to an approximate theory of bulk rubber the quality of which depends upon the postulated characteristics of the individual chains. The simplest assumption is that all chain segments in the network are still comparatively long (soft rubbers). It permits the detailed working out of a theory corresponding closely to that of a perfect gas. The third step is necessary if one is to give a quantitative connection between the characteristics of the isolated molecules and those of the cured material in bulk. The fourth step, finally, corresponds to the passage from the treatment of perfect gases to that of real ones.

This article, which aims at a brief survey of the present state of the theory in all four stages, will be introduced by a short discussion of the *structure* of natural rubbers and of the most important synthetic rubbers.

II. Structure of Rubbers

1. Chemical Composition

Typical rubber elasticity has been observed with substances of rather different chemical character; one essential requirement, however, is that the material must be a *high polymer* and consist of essentially linear macromolecules, in which the monomeric units are linked together by strong chemical bonds. It seems to be of secondary importance for the existence of typical rubberiness whether these bonds are identical throughout the whole chain, or whether various types of them, such as C—C, C—O, C—N, C—S, C=C, P—N, etc., alternate in a regular or irregular fashion, provided that they have dissociation energies above 50,000 cal. per mole.

TABLE I

SOME FIGURES CHARACTERIZING NATIVE AND SYNTHETIC RUBBERS

Substance	Some well-known commercial names	* Principal covalent bonds along the chains	Dissociation energy of these bonds, Eg.-cal. per mole	Principal substituents along the chains	Average molecular weight according to osmotic measurements	Density
Rubber	Rubber	C—C, C=C	70, 125	H, CH ₃	150,000–300,000	0.91
Poly-butadiene	Buna	C—C, C=C	70, 125	H	80,000–130,000	0.92
Poly-isoprene	C—C, C=C	70, 125	H, CH ₃	Around 100,000	0.92
Poly-dimethylbutadiene	Methyl rubber	C—C, C=C	70, 125	H, CH ₃	50,000–80,000	0.93
Copoly-butadiene-styrene	Buna S, GR-S	C—C, C=C	70, 125	H, C ₆ H ₅	0.95
Copoly-butadiene-acrylonitrile	Buna N, GR-N	C—C, C=C	70, 125	H, CN	0.96
Poly-isobutylene	Vistanex	C—C	70	H, CH ₃	250,000–800,000	0.91
Copoly-butadiene-isobutylene	Butyl rubber, GR-I	C—C, C=C	70, 125	H, CH ₃	0.92
Poly-chloroprene	Neoprene, GR-M	C—C, C=C	70, 125	H, Cl	1.25
Poly-cyanoprene	C—C, C=C	70, 125	H, CN
Copoly-vinyl chloride-acetate	Vynilites	C—C	70	H, Cl, COCH ₃	100,000–200,000	1.3
Poly-vinylisobutyl ether	Oppanol B	C—C	70	H, C ₆ H ₅	Around 150,000	1.0
Copoly-esters	Paracron	C—C, C—O	70, 85	H, O	1.2
Copoly-amides	Nylon	C—C, C—N	70, 90	H, O	1.2
Poly-ethylene sulfides	Thiokol	C—C, C—S	70, 60	H	1.3
Poly-ethylene poly-sulfides	Thiokol	C—C, C—S, S—S	70, 60, 50	H	To 1.6
Poly-phosphorus nitrile chloride	P—N	Cl
Proteins	C—C, C—N	70, 90	H, CH ₃ , and many others	1.3

It must be pointed out, however, that many of the more intricate mechanical and thermoelastic properties of a given rubber depend essentially on the nature and relative sequence of the linkages in the backbone structure of the material. Although, therefore, rubberiness as such does not seem to depend essentially on the specific chemical nature of the polymer under consideration, it must be emphasized that the exact numerical values of the various elastic and thermoelastic constants are significantly influenced by the detailed chemical architecture of the linear macromolecules. Table I gives a list of typical rubbers together with the character and dissociation energies of the principal bonds along the chain.

The same is true for the substituents distributed along the chains. There are typical rubbers which have only hydrogen as substituent; but there are others with CH_3 , C_2H_6 , C_4H_7 , C_6H_5 , Cl , CN and other substituents at regular or irregular intervals along the main valence chains, which constitute the irreplaceable backbone of the structure (see column 5 in Table I). It appears that the existence of rubber elasticity as such does not depend upon the presence or frequency of any specific substituent, but again it must be emphasized that the degree to which a given system exhibits required elastic, plastic and thermal properties depends to a great extent upon the nature and the mode of distribution of the various substituents. It seems, therefore, that organic chemical synthesis and the technique of polymerization will play an important role in the production of better and better rubbers, and that one main task of the theory of rubber elasticity will be to describe as quantitatively as possible the relations between the structural details and the specific mechanical and thermal performance of a rubber, thereby providing useful leads for the organosynthetic work and for the mode of polymerization and compounding.

2. Average Molecular Weight

All present knowledge indicates that the individual linear macromolecules of rubber must be *very long* to provide for the existence of typical rubber elasticity. Thus, the average molecular weight of natural rubber molecules has been found to be between 150,000 and 300,000, which corresponds to polymerization degrees between 2000 and 4000, or to lengths of the extended chains between 8000 and 16,000 Å. These molecules undergo considerable degradation during the earlier stages of processing (milling, mixing, etc.), but are by a subsequent process of polymerization (curing, vulcanization, etc.) built up into a moderately cross-linked network in which comparatively large portions of them still maintain the characteristics of the original chain molecules. Table I contains a few representative

values for the number average molecular weights of certain rubbers (compare also pages 171-178, 222-228). In view of the degrading action of the earlier stages of processing, it is difficult to predict how important a very high original degree of polymerization will be for the final properties of the cured stock; and it is equally difficult to make any definite statement about the importance of the molecular size distribution curve of the initial polymer. Again it seems that they are not essential for the existence of rubber elasticity as such but are very significant in determining the degree to which different mechanical and thermal properties can be obtained simultaneously in a given rubber.

3. *Internal Flexibility of the Linear Macromolecules*

As will be pointed out in greater detail (see pages 266 *et seq.*), a high degree of internal flexibility of the individual chain molecules is an important requirement for rubber elasticity. Cellulose, for example, or its derivatives is built up of very long main valence chains, but does not exhibit rubber elasticity to any appreciable extent. In the sense of the kinetic theory this is due to the lack of free or nearly free rotation in the individual chains and to the presence of a very strong interaction between them.

From theoretical considerations it follows that all single bonds of the type C—C, C—N, C—O, C—S, etc. can be freely rotated about their axis; but this is no longer the case if the other valences of the multivalent atoms are saturated by either H or other substituents (1, 6). The restricted rotation about the C—C bond in ethane with an energy barrier of about 3 kg.-cal. per mole (33, 55) is not the consequence of an intricate stiffness of the bond, but of an interaction between the hydrogen atoms of the two CH₃ groups. Thus, if these groups are spaced farther apart, as in CH₃—C≡C—CH₃, their mutual interaction decreases and the two CH₃ groups are practically free to rotate about the axis of the molecule. The energy barrier is then only 0.5 kg.-cal. per mole (40, 42). It seems, therefore, that the presence of a certain number of double bonds in natural rubber is of importance not only for its chemical reactivity during processing, but also for the internal free mobility of those parts of the chains which remain unaffected by the curing process. Other bonds which would have a similar beneficial influence on the free rotation of adjacent single bonds are —C≡C—, —C=N—, —C—O—C—, —C—S—C—, etc. The appropriate incorporation of such bonds in a long-chain molecule is a problem which can best be advanced by organic synthesis and polymerization technique.

Another structural detail of importance is the mutual interaction of the individual chains and the establishment of cross linkages of various types

(strength) between them. Such interactions lead to the formation of crystallized or otherwise highly organized areas in the stretched or cooled rubber and are particularly important for its behavior at low temperatures, in the later stages of extension and for the ultimate tensile strength. Permanent cross links also prevent the occurrence of irreversible displacements due to flow and hence contribute essentially to the reversible character of the deformation. These phenomena are extensively treated in the first two chapters of this volume (see pages 1 and 57) and we can, therefore, after having briefly referred to them, proceed to a more detailed theoretical treatment of long-chain molecules.

III. Configurational Statistics of an Isolated Chain Molecule

The simplest linear polymer from the chemical and geometrical point of view should be a long chain of CH_2 groups. Such a substance is known

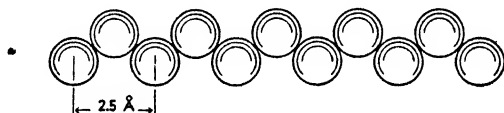


Fig. 1a.—Schematic diagram of the carbon skeleton in a chain of polyethylene in the crystallized state (3a, 3b).

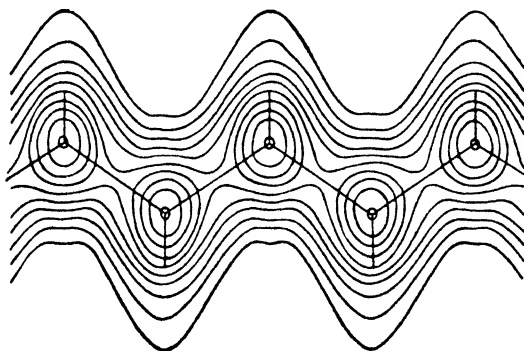


Fig. 1b.—Electronic density contour map representing five CH_2 groups of a polyethylene chain in the crystallized state (3a, 3b).

as polyethylene (polythene) and can be prepared in various ways. Representative samples have polymerization degrees of several thousands. The configuration of the extended chains was worked out by Bunn (3b) and is

shown in Figure 1 (compare also page 119). There are, however, various reasons why polyethylene does not exhibit typical rubber elasticity at room temperature.

(a) The polymerization is usually carried out under comparatively vigorous conditions (several hundred atmospheres pressure, 200° C., oxygen as catalyst) and the polymer as obtained is not soluble in any solvent. It contains a certain amount of oxygen, aliphatic double bonds and methyl groups.

(b) The straight-chain portions of the material have a high tendency for crystallization (freezing point of the crystallized phase is around 125° C.).

(c) The polymethylene chains have only a limited degree of internal free rotation (32).

It thus seems inappropriate to confine the following general treatment to simple paraffin chains, or to any specific chain. It is sufficient for the purpose of a first approximation that molecule configurations exist, differing by rotations of one part with respect to the other about any given single bond and having essentially the same potential energy. These configurations may be separated by energy barriers, provided only that they are not so high as to prevent transitions from one configuration to another in a time period which is short compared with that in which a distortion is applied to the sample. By twisting about all the freely rotating bonds, the individual molecule can take on an enormous number of configurations, all of the same energy, to the approximation just mentioned. Given the direction of one carbon-carbon bond in the chain, that of the next bond is restricted to the neighborhood of two or three definite directions. That of the second bond along the chain will be less definitely fixed, there being more different orientations of equal potential energy, while bonds only a little further down the chain will take on their positions practically independently of the prescribed orientation of the first. As long as it is not necessary to consider in detail the configurations of short segments of the molecule, one may treat it like a perfectly flexible chain which can take on any configuration without change of energy.

For the mathematical development of the theory, the flexibility of the chain has been introduced in a variety of idealized ways, as by assuming the existence of single bonds about which perfectly free rotation is possible, or of rigid links each of which can take on its orientations independently of its neighbors, etc. The general character of the results will be independent of the way in which the flexibility is introduced, but there will be differences in details, and to some degree in estimated magnitudes, from

model to model. Concerning such details, the theory will be reliable only in proportion as the model is well chosen for the particular long-chain molecules to be treated. Table II lists the most probable length of an isolated chain molecule as worked out by various authors using different ways of introducing internal flexibility.

TABLE II
STATISTICAL TREATMENT OF ISOLATED LONG-CHAIN MOLECULES HAVING DIFFERENT INTERNAL STRUCTURES

Character of chain		Maximum chain length, Å.	Most probable extension of chain, Å.	Ratio between both	
Normal paraffin	n links, length of each 1.54 Å.; angle = $108^\circ 30'$, completely free rotation about each bond				
Rubber	$n/4$ double bonds, length of each 1.34 Å.; $3n/4$ single bonds, angle between single - single bonds = $111^\circ 30'$; angle between single and double bond = $124^\circ 20'$; rotation completely free about single bond, completely hindered about double bond	<i>trans</i>	1.25 n	2.50 $n^{1/2}$	0.50 $n^{1/2}$
		<i>cis</i>	1.27 n	2.90 $n^{1/2}$	0.44 $n^{1/2}$
		Random	1.14 n	2.01 $n^{1/2}$	0.57 $n^{1/2}$
			1.21 n	2.45 $n^{1/2}$	0.49 $n^{1/2}$

We shall now treat such a linear molecule, consisting of very many units, by the methods of statistical thermodynamics (13, 14, 15a, 16, 34a, 34b, 43, 48). To a chain in thermal equilibrium with a temperature bath and subject only to the constraint that the ends have a separation, L , one may assign the entropy:

$$S = k \log C(L) + h(T) \quad (4)$$

where k is Boltzmann's constant and $C(L)$ is the partition function, namely the relative number of configurations of the chain consistent with the separation, L , of its ends. The term $h(T)$ arises from the heat capacity of the chain, and, because of its flexibility, is independent of L . For a completely flexible chain, the internal energy, u , is independent of its configuration and thus of L ; hence, we have:

$$u = u(T) \quad (5)$$

The free energy becomes:

$$F = u(T) - kT \log C(L) - Th(T) \quad (6)$$

and the tension in the chain:

$$Z(L,T) = -kT \frac{d}{dL} \log C(L) \quad (7)$$

The functions $u(T)$ and $h(T)$ drop out of the computation of Z , which becomes proportional to the absolute temperature. This will clearly be the case with any system of flexible chains which one might use as a model for bulk rubber.

We can also discuss our problem from the point of view of kinetic theory. A linear molecule immersed in a temperature bath will undergo constant changes in configuration through its thermal agitation—an internal (micro) Brownian motion. For a perfectly flexible and unconstrained molecule, each individual configuration has the same energy and, hence, the same frequency of occurrence. However, since kinked and coiled configurations are far more numerous than relatively straight and extended ones, the probability is overwhelming that at any given time the molecule will be found in a highly twisted state, with its ends separated by a distance which is small compared with the length of the extended chain. If the ends of the molecule are constrained to lie at fixed points, the thermal agitation will result in a constant jerking of the molecule against the constraints. Unless the ends of the molecule are coincident or very close together, jerks in different directions will not be equally frequent; they will result in a net force tending to bring the ends of the molecule closer together—an effective tension. At elevated temperature the thermal agitation will be more violent and the effective tension will increase. If the distance between the ends of the chain is slowly increased at constant temperature, work must be done against the forces in the jerking chain. The energy of thermal agitation will, however, remain unchanged, and the energy given to the chain appears as heat. In all these respects the isolated linear molecules would show the behavior observed with bulk rubber, and the same would be true of any system of chain molecules so connected together that the intramolecular Brownian movement is not impeded. This approach to the understanding of rubber elasticity as due to the tendency of long-chain molecules to curl up under the influence of thermal agitation is qualitatively useful. For quantitative purposes, however, statistical methods involving the enumeration of the configurations of the chain under the imposed constraints are necessary.

Methods for obtaining the equation of state of single flexible chains at *all* extensions have been developed by James and Guth (24, 25). [The somewhat different problem of the most probable statistical length of long-

chain molecules was considered also by Laskowski and Burk (35) and particularly by Treloar (45).] The difficulty of the problem and the nature of the result differ with the structure of the chain. However, all chains, regardless of their detailed structure—provided only that they are very long as compared with any chain segment which shows appreciable stiffness—have partition functions which are essentially of Gaussian form so long as the extension, L , of the chain is small as compared with its extended length. Quite generally, for long chains not too highly extended, one may write:

$$C(L) = A \exp. (-L^2/2\langle L^2 \rangle_{av}) \quad (8)$$

where $\langle L^2 \rangle_{av}$ is the mean square average of a component of the extension of the unconstrained chain under thermal agitation. In the one-dimensional problem this is the mean square extension of the chain itself, but in the three-dimensional problem it is only one-third of that quantity, to which each of the three components of the extension make equal contributions. The value of $\langle L^2 \rangle_{av}$ varies with the detailed structure of the chain. For a one-dimensional chain of N independent links of fixed length, l , one has $\langle L^2 \rangle_{av} = Nl^2$. For a three-dimensional chain, one has, instead, $\langle L^2 \rangle_{av} = \frac{1}{3} Nl^2$. For certain more realistic models of real molecular chains the root mean square extension, $(\langle L^2 \rangle_{av})^{1/2}$, is given in Table II (9, 16, 34a, 43, 45, 53).

When Equation (8) is valid, one has, by Equation (7):

$$Z = -kT \cdot d/dL \cdot \log C(L) = (kT/\langle L^2 \rangle_{av})L \quad (9)$$

For small extensions, therefore, a single flexible chain exerts an average pull directly proportional to the fixed separation of the ends. In contrast to any three-dimensional elastic body, it exerts retractive forces which vanish only as the corresponding "dimension" of the system goes to zero. At the longer extensions at which Equation (8) ceases to apply, the exact tension-extension relation shows an upward curvature, the tension ideally approaching infinity as the extension approaches the length of the completely stretched out chain.

IV. Model for Bulk Rubber and Its Statistical Treatment

While isolated, long, flexible molecules under thermal agitation behave in many ways like bulk rubbers (*e. g.*, show long-range reversible extensibility with restoring forces proportional to T), it is evident from the form of Equation (9) that such molecules do not constitute adequate models of the bulk material, of which they are known to be the essential constituents.

As the next step in the development of the theory, it is necessary to picture the structure of the bulk material as it is made up of these molecules, and to work out the elastic properties of this more complex system. This program has been carried through by James and Guth (14, 15a, 18, 22-27), whose theory will be briefly reviewed here, while a discussion of other theories will be given in Section XIII (page 294).

The picture of the structure of rubbers on which Guth and James base their computations is as follows: Masticated and uncured rubbers consist of a tangled mass of long-chain molecules, of which some may be linked together by a few chemical cross bonds, while most can move more or less freely past each other, impeded only by the tendency of the Brownian motion to keep the chains tangled. The possibility of an unlimited relative displacement of the molecules is responsible for the flow of such elastomers, whereas the tangling of the chains keeps the internal viscosity high—the higher the longer the molecular chains and the stronger their mutual overall attraction. If deformed rapidly and immediately released, they will return to their original shape almost instantaneously and with little plastic deformation because there has been time for only a little motion of the whole molecules with respect to each other.

Vulcanization or curing appears to consist in the reinforcing of cross links already present in the raw rubber *and* the introduction of new cross links. These bonds, in general, will be formed at random, sometimes connecting different parts of one and the same single molecule, but more often linking parts of two different molecules which happen to be adjacent at the time. As more and more cross links are formed, the whole mass of molecules will come to be linked together in a coherent network, very irregular in detail and quite open in structure, there being only a few bonds formed for each of the long molecules. These bonds introduce fixed relations between the molecules which will be undisturbed by latter distortions of the body, and result in the suppression of irreversible flow. On the other hand, they affect only a small portion of each molecule; the intramolecular Brownian motion is little impeded and over the greater parts of their lengths the molecules will be free to move past each other, as in a liquid or in (masticated) raw rubber. Rubbers vulcanized to this degree will show all typical elastic properties but no permanent flow. If the vulcanization is carried further, the cross links will eventually become so numerous as to suppress the intramolecular Brownian motion to a great extent and to change markedly the relationship of adjacent molecules. The extensibility and modulus of the material then approaches that of ordinary solids. Such highly cross-linked systems, and even soft rubber under high strains, in which there is known

to be induced a crystallization which radically modifies the properties of the material, will be excluded from the following considerations.

Cured soft rubber, then, consists of a coherent network of flexible molecules, linked together by bonds which give to the material a permanent structure without suppressing the internal Brownian motion of the molecular chains. A model of rubber which consists of such a network of idealized Gaussian chains would, as is evident from Equation (9), exert restoring forces proportional to the absolute temperature; alone, however, it would be quite inadequate as a model for rubber. For instance, such a model would, under the influence of the contraction of the chains, collapse into a very small volume. It is not possible to neglect completely, as is usual in the treatment of isolated flexible chains, the volume-filling property of the molecules.

The volume of a macroscopic sample will be regulated by lateral forces between the chains quite unrelated to those effective tensions along the chains which maintain the shape of the material. The chains, for the most part moving freely past each other, will jostle each other, at any boundary surface, as they would in a liquid. The bounding surfaces may be those of other solids, or free surfaces of the material at which the outward forces of the jostling molecules are balanced by the inward pull of the elastic coherent network. The effect of the sidewise thrusts and pulls will be the same as in an ordinary liquid—the production of an effective hydrostatic pressure in the material, which depends on its volume.

In the model of Guth and James, the real molecular network is replaced by a similar network of idealized flexible chains, very irregular in detail, but homogeneous and isotropic on the average and extending throughout the volume of the model. The space-filling properties of the real network are then introduced into the model by filling it with an incompressible fluid. By this means one's attention is restricted to configurations of the network which extend through the correct volume in space. (By a somewhat elaborate argument, it is possible to show that this method of representing the volume-filling properties of the molecules is adequate as long as the network is open in structure and not excessively stretched.) Further refinements may be introduced by attributing to this fluid an appropriate compressibility and thermal expansion. Under equilibrium conditions, every surface of the model must of course be in equilibrium under all the forces which act on it—the (outward) push of the hydrostatic pressure, the (inward) pull of the elastic network, and any external forces, such as stress, shear, etc.

It should be pointed out that not all individual macromolecules and not

all parts of them will be involved actively in the network. A chain chemically attached to the network at one single point will not contribute to its tendency to pull against external forces. The same may be said of closed loops or rings in chains in the network, and the molecules threaded through the network but not chemically linked to it. Such chains may be (and actually are to a certain extent) removable from the sample by solvents or, if connected into large and complicated snarls, may not be so easily separable from it. All these "inert" molecular chains will play just the role of a fluid extending through the material and thus appear adequately represented in the simplified model.

V. Stress-Strain Relation for Unilateral Stretch

Consider now a unit cube of rubber stretched by forces of magnitude Z in the z direction, being deformed into a parallelepiped of dimensions L_x, L_y, L_z with $L_x = L_y$. According to the assumption of incompressibility, we have then:

$$L_x L_y L_z = L_x^2 L_z = 1 \quad (10)$$

In the treatment of the model thus stretched the first task is to compute the pull of the irregular molecular network. This can be done for a network of arbitrary structure, provided only that every chain segment between junctions of the network is long enough for its partition function to be taken as of Gaussian form. It can be shown (24, 27) that any such network can be replaced by a simplified network which has the same number of possible configurations—*i. e.*, the same entropy—and exerts the same forces as the original network. This simplified network may consist of three sets of independent molecular chains, one set running between the x faces of the parallelepiped, another between the y faces, and the third between the z faces. Each set may be taken to consist of M chains each of N links; then, to assure the proper magnitude of the entropy changes and forces, it is necessary only to choose properly the ratio M/N . For the discussion of the problem it is by no means necessary to use this simplified model, but it does have the advantage that its behavior is easily visualized.

To determine the internal pressure, P , of the material one may consider one of the free faces of the parallelepiped, say an x face with the area $L_y L_z$. Acting on this is the outward force of the internal pressure, P , and the inward pull of M chains each with extension L_x . Equating inward and outward forces:

$$P L_y L_z = M \frac{kT}{\langle L^2 \rangle_{\text{av}}} L_x \quad (11)$$

one finds:

$$P = M \frac{kT}{\langle L^2 \rangle_{\text{av}}} L_z^{-1} \quad (12)$$

One has, in any case:

$$P = KTL_z^{-1} \quad (13)$$

where:

$$K = M \frac{k}{\langle L^2 \rangle_{\text{av}}} \quad (14)$$

is the special value of K for a particular and simple network structure; by a rather elaborate but perfectly straightforward procedure the value of K can be determined for any given network of Gaussian chains. It will be noted that the internal pressure of bulk rubber decreases when the material is subject to stretch.

To obtain the stress-strain relation for the cube, one considers similarly the equilibrium of the end faces, equating the outward push of the pressure plus the external force to the pull of the molecular chains. One finds:

$$Z = KT(L_z - 1/L_z^2) \quad (15)$$

The first term on the right is the force needed to act against the inward pull of the network, while the second term is the outward force of the internal pressure. The external force vanishes as $L_x = L_y = L_z = 1$, the hydrostatic pressure then balancing the inward pull of the network on each surface of the model. [An alternative derivation of this stress-strain equation can be carried out by consideration of the entropy and internal energy of the system, without reference to the concept of internal pressure; see James and Guth (18, 27).]

The differential Young's modulus is, of course, not a constant, since Hooke's law does not hold. Referred to the original cross section, one obtains:

$$E(L_z) = KT(1 + 2/L_z^3) \quad (16)$$

For large values of L_z this approaches one-third of its value for $L_z = 1$, a feature which conforms well with experimental stress-strain curves (see Fig. 2, page 287).

By introducing instead of L_z the extension ϵ :

$$Z = 3KT \epsilon (1 - \epsilon + \frac{4}{3} \epsilon^2 - \dots) \quad (17)$$

This form exhibits well the large deviations from Hooke's law shown by rubber at even moderate extensions.

The internal pressure in the unstressed rubber is simply related to the differential Young's modulus for zero stress:

$$P_0 = \frac{1}{3} E(1) \quad (18)$$

For the rubber sample of Figure 2, P_0 is thus about 5 kg. per sq. cm., a value which can be taken as representative for soft gum compounds. When this pressure is reduced by stretching, one might expect an increase in the volume of the material. Since the compressibility of rubber is about 10^{-4} sq. cm. per kg., the increase in volume due to complete removal of the internal pressure would be some 0.05%, an amount quite compatible with the observations of Holt and McPherson (20).

VI. General Deformations

The foregoing treatment deals with the case of unilateral stretch only. Other deformations such as shear and stretch in two perpendicular directions have been treated by James and Guth (24) by consideration of the equilibrium of forces in the model. Instead, the *elastic energy* may be derived from the theory once and for all. If the elastic energy is known, any particular deformation may be derived from it by standard procedures of the classical theory of elasticity. Obvious changes, of course, must be made to take into account the fact that the deformations are finite, rather than infinitesimal, as supposed in the classical theory.

The elastic energy becomes ($E(1) = E$):

$$W = \frac{1}{2} \cdot E/3(L_x^2 + L_y^2 + L_z^2 - 3) \quad (19)$$

with the auxiliary condition:

$$L_x L_y L_z = 1$$

As an example, the stress-strain relation for simple shear is derived from Equation (19). The shear strains, λ_x , λ_y , λ_z , are defined by the following relations:

$$\lambda_x = L_x - 1/L_x; \quad \lambda_y = L_y - 1/L_y; \quad \lambda_z = L_z - 1/L_z \quad (20)$$

The shear stress is then given by the equation:

$$\Lambda_z = dW/d\lambda_z = E/3 \cdot \lambda_z = G\lambda_z \quad (21)$$

where G is the shear modulus; Hooke's law holds for shear. The shear-stress relation (21) may also be expressed in terms of L_z as independent variable. We notice that the stress-strain relation for unilateral stretch may be written:

$$Z = dW/dL_z \quad (22)$$

Mooney (39), on the basis of the classical theory of elasticity, derived a relation for the elastic energy, from which Equation (19) follows as a special case. Mooney's treatment is phenomenological and therefore cannot lead to the dependence of the stress upon temperature nor to the absolute values of E or G .

Treloar (46) obtained Equations (19) to (22) using Wall's theory (49,50). The correctness of his results is independent of the question of the general validity of Wall's theory.

VII. Swelling

Rubbers have the remarkable property of being able to absorb large quantities of liquids without loss of shape or elastic properties. In the process of swelling, the molecules of the swelling agent do not greatly affect the structure of the material, but merely serve to increase its bulk and tend to prevent crystallization. The kinetic theory as presented here (24) makes possible a simple explanation of the elastic properties of swollen rubber.

A unit cube of rubber swells by the addition of an inert hydrocarbon until its linear dimensions are increased by the swelling factor σ . If it is then stretched or compressed until its z dimension is L_z , one obtains the following relationship:

$$L_z L_x^2 = \sigma^3 \quad (23)$$

That the stress-strain relation for the swollen cube is given by:

$$Z = KT(L_z - \sigma^3/L_x^2) \quad (24)$$

follows from a repetition of the argument of Section V. To compare this equation with the original stress-strain relation for a portion of the material which, in the unstretched state, is a unit cube, we rewrite it by reducing z by the factor $1/\sigma^2$, by which the cross section is reduced, and replacing the fractional elongation L_z/σ by L_z . Then we have:

$$Z = KT \cdot 1/\sigma(L_z - 1/L_x^2) \quad (25)$$

That is, swelling of rubber reduces its Young's modulus by a factor of $1/\sigma$, but leaves the form of the stress-strain curve unchanged.

The decrease in the rigidity of swollen rubber described by Equation (25) is well known to occur.

Relation (25) was deduced somewhat later, but independently, by Flory and Rehner (11), who consider also the swelling of unstretched rubber and compare their results with recent measurements (10).

VIII. Effect of Thermal Expansion. Thermoelastic Inversion (24)

All equations hitherto have been derived on the assumption that the elastomer does not exhibit any volume thermal expansion. If one deals with a cube of rubber having unit volume at temperature T_0 , and a coefficient of thermal expansion α , the volume becomes, at temperature T :

$$V = 1 + \alpha(T - T_0) \quad (26)$$

This leads to:

$$Z = KT \left[L_z - \frac{1 + \alpha(T - T_0)}{L_z^2} \right] \quad (27)$$

Accordingly, the stress at constant strain is not exactly proportional to T , but involves a small negative term proportional to T^2 , arising from the volume thermal expansion. The tendency of thermal expansion to decrease the stress in rubber heated under constant strain is the dominant tendency in the case of crystalline solids; for such materials, however, the decrease in stress is linear in T .

The effect of this correction term appears most clearly when one plots stress against temperature at various constant strains (see Fig. 4, page 289). Each stress-temperature curve will appear nearly straight if the range of temperature considered is not excessive; the most striking effect of the new terms in Equation (27) is the change in slope of stress-temperature curves with changing strain. If the strain is small, $(\partial Z/\partial T)_L$ has a negative value, and the behavior is that of an ordinary crystallized solid, while if the strain is large, $(\partial Z/\partial T)_L$ has the large positive value usually considered characteristic of rubber. From Equation (27) one finds, when $T = T_0$:

$$(\partial Z/\partial T)_L = KT[L_z - (1 + \alpha T_0)/L_z^2] \quad (28)$$

Thus the critical extension, L_{zc} , at which the stress-temperature curve changes its slope, the isometric thermoelastic inversion point, is given by:

$$L_{zc}^3 = 1 + \alpha T_0 \quad (29)$$

For a soft unaccelerated gum compounds with 8% sulfur content, $\alpha = 6.2 \times 10^{-4}$. For $T = 300^\circ \text{K}$. and $L_{zc} = 1.065$, the inversion should take place for a strain of about 7%.

The linear thermal expansion coefficients of stretched rubber under constant stress are (parallel to the stress):

$$\alpha_{\parallel}(L_z) = -\frac{1}{T} \frac{L_z^3 - 1}{L_z^3 + 2} + \frac{\alpha}{L_z^3 + 2} \quad (30)$$

and (perpendicular to the stress):

$$\alpha_{\perp}(L_z) = \frac{1}{2T} \frac{L_z^3 - 1}{L_z^3 + 2} + \frac{\alpha}{2} \frac{L_z^3 + 1}{L_z^3 + 2} \quad (31)$$

In the unstretched state, $L_z = 1$:

$$\alpha_{\parallel}(1) = \alpha_{\perp}(1) = \alpha/3 \quad (32)$$

as for any material.

It can be seen from Equations (30) and (31) that the changes of dimensions of the material with temperature are only slightly related to its normal volume expansion; they are principally shifts in relative dimensions needed to restore equilibrium as the effective stresses in the flexible chains vary with temperature. The coefficient of "expansion" parallel to the stress is negative, while the other is positive, a striking illustration of the thermal anisotropy of stretched rubber. These linear expansion coefficients are of the same order of magnitude, $1/T$, as the volume expansion coefficients for gases.

The change in temperature, ΔT , on adiabatic stretching can be shown to be given by:

$$\Delta T = (KT/2C_L)[L_z^2 + L_z - 2(1 + \alpha T_0)][(L_z - 1)/L_z] \quad (33)$$

where C_L designates the specific heat at constant length. ΔT has a minimum for $L_z = L_{zc} = 1 + (\alpha/3)T_0$, and becomes zero at the adiabatic thermoelastic inversion point: $L_{\text{adiabatic}} = 1 + (2\alpha/3)T_0$.

IX. Statistical Treatment of Highly Extended Chains

James and Guth (24, 25) have extended the statistical treatment of isolated linear molecules to the case of extended flexible chains approaching their maximum length.

The Gaussian distribution, Equation (8), holds only when $L \ll L_{\text{max}}$. The nature of the deviations from the Gaussian distribution may be illustrated by the example of a one-dimensional chain of N links, each of which will, in the absence of external forces, contribute to the extension of the chain an amount $+1$ or -1 , with equal probability. The number of

configurations consistent with the extension, L , of such a chain is the number of ways in which $(N + L)/2$ links can be arranged to contribute $+1$ to the extension, while $(N - L)/2$ links contribute -1 . This number is:

$$C(L, N) = \frac{N!}{\left(\frac{N + L}{2}\right)! \left(\frac{N - L}{2}\right)!} \quad (34)$$

By introducing the fractional extension of the chain:

$$t = L/N \quad (35)$$

and using Stirling's approximation for the factorials, one has, neglecting a factor very near to 1:

$$C(L, N) = \frac{2^{N+1}}{(2\pi N)^{1/2}} (1 + t)^{-(N/2)(1+t)} (1 - t)^{-(N/2)(1-t)} (1 - t^2)^{-1/2} \quad (36)$$

By neglecting the last slowly varying factor, this can be written as:

$$C(L, N) \cong \frac{2^{N+1}}{(2\pi N)^{1/2}} \exp \left\{ -\frac{N}{2} \int_0^t \log \frac{1+t}{1-t} dt \right\} \quad (37)$$

Since:

$$\log \frac{1+t}{1-t} = 2 \left(t + \frac{t^3}{3} + \frac{t^5}{5} + \dots \right) \quad (38)$$

one obtains:

$$C(L, N) \cong \frac{2^{N+1}}{(2\pi N)^{1/2}} \exp \left\{ -\frac{N}{2} t^2 - \frac{N}{12} t^4 - \dots \right\} \quad (39)$$

Deviations from the Gaussian law set in where $(n/12)t^4$ becomes appreciably different from zero—for large absolute extensions, Nt , and smaller fractional extensions, t , as N is increased. The exact fraction, $C(L, N)$, decreases more rapidly than the Gaussian fraction as t increases, and must obviously vanish as t approaches 1. The stress, being proportional to $-d/dL \cdot \log C(L, N)$, must become infinite in the same manner; the chains cannot be extended beyond their total length. The Gaussian approximation, on the other hand, leads to a stress increasing only linearly with L , which would permit one to give to the chain any extension whatever.

Instead of using the Gaussian approximation and thereby restricting the validity of the treatment to relatively small fractional extensions, more accurate relations such as Equation (36) may be used. For the particular

type of chain here considered, one obtains, with neglect of terms of the order of $1/N$:

$$Z = \frac{KT}{2} \log \frac{1+t}{1-t} \quad (40)$$

$$\text{or, with:} \quad f = Z/KT \quad (41)$$

$$\text{the inverse relation:} \quad t = \tanh f \quad (42)$$

The methods developed by James and Guth lead even more simply and directly to Equation (42). In the three-dimensional problem of a chain with independent links of fixed length l , these methods give:

$$t = \coth lf - 1/lf = L(lf) \quad (43)$$

where $L(x)$ is the Langevin function.

As a first step in developing a theory of rubber elasticity which does not depend upon the assumption of a Gaussian partition function for each chain of the network, James and Guth have considered (24) a simplified network model, such as that previously considered with Gaussian chains, but have taken Equation (43) as the stress-strain relation for the component chains. This model should represent the behavior of rubber under a wider range of strains than the Gaussian model, reproducing the effects which enter as the extensions of the component chains become comparable to their total lengths. They find as the stress-strain relation:

$$Z = (M\kappa T/l) [L^{-1}(L_z\kappa) - L_z^{-3/2}L^{-1}(L_z^{-1/2}\kappa)] \quad (44)$$

This relation involves two parameters: $K' = Mk/l$, which determines the scale of the force, just as in the Gaussian case; and κ , which is inversely proportional to the maximum stretch of the model and will depend upon the character of the sample (average degree of polymerization, etc.).

The appearance of the Langevin function in Equations (43) and (44) is most easily understood by remembering that the N links of the individual length, l , are considered to be independent of each other. In such cases it can be shown that the average contribution of each independent link to the extension of a flexible chain can be computed as if it were the only link present and the external forces were applied directly to its ends. The situation in an extended flexible chain is then completely analogous to that of a polar molecule in an electric or magnetic field. The thermal agitation of the chain tends to disorient the links, to make the average contribution to the extension vanish, while the tension of the chain, in effect, is equivalent to the uniform field of force tending to align the links. The computations

of the average contribution of a link to the extension and of the average contribution of a polar molecule to, say, the magnetic moment of a material are thus formally identical. If the link has a fixed length, and the molecule a fixed moment, the computations are identical in detail and the Langevin function appears in each result.

X. Molecular Significance of the Constants of the Theory

The theory as outlined thus far leads to a functional relationship of Z , L and T , involving parameters K (page 271), $K' (= Mk/l)$, and κ (page 277). Such relations are of immediate use in curve fitting, with the constants experimentally determined. To complete the theoretical development, however, it is necessary to relate these parameters to the molecular constants which characterize the materials. Our present discussion will be restricted to the constant, K , of the stress-strain curve (Eq. 15) for materials in which all molecular chains can be treated as Gaussian.

A general expression for K , valid for any Gaussian network, has been published recently by James and Guth (26, 27). Let N_τ be the effective number of independent links in the τ segment between junctions in the network and let λ_τ be its mean fractional extension in the unstretched state of the material. Then the simple relation holds:

$$K = \frac{1}{2} \sum_{\tau} N_{\tau} \lambda_{\tau}^2 \quad (45)$$

The sum is over all segments in the network. It is to be emphasized that this result holds for any form of network, provided only that it is isotropic on the average; the network may be completely random in character, or it may have the connectivity of a regular cubical lattice, or a tetrahedral lattice, or it may consist merely of single independent chains stretching through the material. Together with equations which permit a straightforward determination of λ (see reference 27), Equation (45) makes it possible to compute K for a network of any specified structure.

At the opposite extreme with respect to the completeness of the implied knowledge of the network structure is a relation which follows from dimensional arguments only:

$$K = \gamma k \cdot N/V = \gamma R \cdot \rho/M \quad (46)$$

Here N/V is the number of segments of the network, per unit volume, which contribute to the forces which it exerts, M is the mean molecular weight of the segments, ρ is the density of the active material, k and R are the familiar constants of the kinetic theory, and γ is a constant factor which

will depend on the mean molecular weight of the uncured material, the degree of cure, etc. Unless one possesses some knowledge concerning γ , Equation (46) hardly represents a forward step in the evaluation of K .

In practice, one never knows the detailed network structure of the material, and cannot determine K by application of Equation (45). At most, one may hope to have statistical information concerning the network structure which will permit evaluation of the summation in Equation (45) or the evaluation of the constant γ .

A theory of the process of formation of the molecular network during cure has been developed by James and Guth (27), and leads to a fairly definite value of γ . This constant, as already noted, depends on the degree of cure, and for soft gum is about 0.5.

In the liquidlike uncured material, the distribution of extensions of the molecular chains is that maintained by thermal agitation alone. If this distribution were maintained in the network built up during cure one would have $\gamma = 1$, a result derivable by use of Equation (45). Consideration of the process of network formation shows at once, however, that the cross linking of the chains into a network perturbs the thermal distribution of extensions, and in general leads to values of γ different from unity.

XI. Influence of Crystallization

Another effect which must be considered as soon as the extension exceeds certain limits is *crystallization* of the elastomer as a consequence of the stretch. It is known, however, that many rubbers particularly diene-olefin copolymers of the GR-S type, do not exhibit crystallization even at their breaking elongations; and in such cases the formulas as derived above can be applied without involving the danger of serious errors. On the other hand, *Hevea*, Butyl (GR-I), Neoprene (GR-M) and other elastomers show very definite crystallization (7, 8) at extensions above 250 or 300% and it seems appropriate, therefore, to include in this article a discussion of its effect on the stress-strain relationships.

Crystallization in rubber consists of the assembly into an ordered structure, a crystallite, of the chains within a small section of the network. The extent of these crystallites is limited, the random network structure preventing their indefinite growth. Each crystallite is thus imbedded in an amorphous matrix of uncrystallized material having the behavior already discussed. Crystallization is facilitated by the partial alignment of the chains due to stretching of the material, but is impeded by the thermal agitation of the chains. At a given temperature, crystallization increases with increasing extension of the material, and makes its first appearance

at lower extensions the lower the temperature. At sufficiently low temperatures even the unstretched material shows crystallization. Crystallites in the stretched material tend to have their long axes parallel to the direction of stretch, but crystallites produced by cooling of unstressed material show random orientation.

While crystallization is not necessary for the development of the *S* shape characteristic of the stress-strain curve of elastomers, its effect is normally to make the *S* form more pronounced. Partial crystallization changes the conditions within the material in a variety of ways. The well-known phenomenon of spontaneous elongation (11, 20) provides direct experimental evidence that oriented crystallization may tend to change the dimensions of a body. In the case of stressed rubber, in which the long crystalline fibers are generally parallel to the direction of stretch, one would expect increased crystallization, at constant stress, to cause an increase in the *extension* of the material. On the other hand, crystallization will reduce the *extensibility* of the material, by decreasing the fraction of it which shows rubberlike elasticity. Furthermore, the imbedded crystallites will have somewhat the same reinforcing action as other filler particles of corresponding dimensions, and will increase the rigidity in the same way. These factors work in contrary directions. A change in dimensions on crystallization, since it tends to increase the extension of the material, will tend to *reduce* the upturn of the stress-strain curve. Reduction of the extensibility, however, does tend to produce the *S* shape, and is normally the more important factor. In order to assess the relative importance of these effects a semiquantitative discussion of the problem is necessary and was carried out by James (28).

Several authors have experimentally determined the way in which the amount of the crystallized phase in a given elastomer increases with elongation. In the case of *Hevea* gum at room temperature, it is found that the first crystal spots appear at an elongation of 250% ($L = 3.5$) and that the intensity of these spots, which is proportional to the amount of crystallized material, increases roughly proportionally to the elongation until this is 700%. As representative of what one might find in a lightly vulcanized (below 1% sulfur) gum stock, one may take the fraction of crystallized material, q , as represented by:

$$q(L) = 0, \quad L < L_1 \quad (47)$$

$$q(L) = \frac{L - L_1}{L_2 - L_1}, \quad L_1 < L < L_2 \quad (48)$$

In order to gain a semiquantitative understanding of the variation of crystallization with temperature and extension, and some idea of the way in which it affects the stress-strain curves, a simple, essentially one-dimensional model of partially crystallized rubber will be considered here. One may represent the bulk material by a bundle of flexible chains, in which the analogue of crystallization is the consolidation into a rigid mass of adjacent sections from a number of the parallel chains, with a consequent decrease in the energy of the system. Within each crystallite the chains may be treated as essentially straight. The crystallite regions will, naturally, be assumed to be of large extent as compared to the length of the links in the chains, and relatively few in number. It can be shown that this model is only trivially different from an even simpler model, consisting of a single chain in which the analogue of crystallization is the assumption of parallelism by a large number of consecutive links, with a decrease in the energy of the system proportional to the number of links involved. We now indicate the results to be obtained by consideration of this latter model.

Let the very large total number of links in the chain be N , and the number of links involved in a relatively few crystalline regions to be N_c . We shall consider a one-dimensional model in which each link can contribute $+l$ or $-l$ to the extension of the chain. If L is the over-all extension of the chain, *i. e.*, the distance between its ends, and the length, L_c , of the crystallized sections is:

$$L_c = N_c l \quad (49)$$

we have for the total extension of the uncrystallized portions:

$$L_u = L - L_c \quad (50)$$

The number of possible configurations for the links in the uncrystallized portions is, in the Gaussian approximation:

$$C(L_u) = (N - N_c)^{1/2} 2^{N-N_c} \exp \left\{ -(L_u^2/2)(N - N_c)l^2 \right\} \quad (51)$$

The number of configurations possible for the whole system differs from this by a relatively small factor, the number of ways in which the comparatively small number of crystalline regions can be set up. One can then take as the number of configurations of the chain consistent with extension L and the crystallization of N_c links the expression of Equation (51), written as:

$$C(L, N_c) = (N - N_c)^{1/2} 2^{N-N_c} \exp \left\{ -[(L - N_c l)^2/2](N - N_c)l^2 \right\} \quad (52)$$

Let the energy of crystallization, per link, be κ . Then the energy of the system under the above conditions is κN_c , and the Boltzmann factor is $\exp \{ \kappa N_c / kT \}$.

The most probable degree of crystallization for a given extension of the chain, and one from which there will be only trivial deviations, is that which maximizes the weight function:

$$W(L, N_c) = C(L, N_c) \exp \{ \kappa N_c / kT \} \quad (53)$$

to variation of N_c . This value of N_c is fixed by:

$$-\ln 2 + \frac{\kappa}{kT} + \frac{L - N_c l}{(N - N_c)l} - \frac{1}{2} \frac{(L - N_c l)^2}{[(N - N_c)l]^2} = 0 \quad (54)$$

Hence:

$$\frac{L - N_c l}{(N - N_c)l} = 1 - \left[1 - 2 \ln 2 + 2 \frac{\kappa}{kT} \right]^{1/2} = \rho(T) \quad (55)$$

Solving for the length of the crystallized section of the chain, we obtain:

$$N_c l = [L - \rho(T)Nl] / [1 - \rho(T)] \quad (56)$$

a linear function of L , corresponding to the observations already noted. $N_c l$ is, of course, a non-negative quantity. Crystallization will appear only when:

$$L > L_1 = \rho(T)Nl \quad (57)$$

The higher the temperature the larger will be $\rho(T)$, and the greater the extension at which crystallization begins, again in agreement with observation.

The stress-strain relation for this linear model is easily worked out in terms of the internal energy and entropy functions of L . Instead, we shall turn to the consideration of the three-dimensional material, taking Equations (47) and (48) as basic, and carrying out the discussion in terms of forces rather than of entropy and internal energy.

We shall consider the extension of the material, L , as the sum of a part L_c contributed by the crystallized portion of the material and a part L_u contributed by the uncrystallized portion:

$$L = L_u + L_c \quad (58)$$

The contribution of the essentially inextensible crystallized portion will be directly proportional to its amount. We write:

$$L_c = \lambda q \quad (59)$$

The contribution of the uncrystallized portion must then be:

$$L_u = L - \lambda q \quad (60)$$

In the unstretched state of the material this portion contributes to the unit initial length an amount $1 - q$. In the stretched material its relative length will then be:

$$L_r = (L - \lambda q)/(1 - q) \quad (61)$$

In discussing the forces exerted by the material one might, as a first approximation, neglect the inhomogeneities in the stress distribution within it. In doing so one will neglect the filler action of the crystallites, but will retain in the theory the effects of increased extension and decreased extensibility of the crystallized portion of the material. To this approximation and neglecting changes in density of the material on crystallization, the stress per unit original cross section is the same for the crystallized and uncrystallized parts. Let the stress-strain relation for the uncrystallized material be written as:

$$Z_v = Z_v(L_r) \quad (62)$$

to distinguish it from the relation:

$$Z = Z(L) \quad (63)$$

describing the behavior of the material as a whole. [It is with relations such as Equation (63) that we have heretofore been concerned.] Using the approximation of stress homogeneity:

$$Z = Z_v \quad (64)$$

and introducing Equation (61), one has:

$$Z = Z_v[(L - \lambda q)/(1 - q)] \quad (65)$$

Given the dependence of q upon L , this relation expresses the stress-strain curve for the entire body in terms of that for the uncrystallized portions. By introducing Equations (47) and (48), it becomes:

$$Z(L) = Z_v(L), \quad L < L_1 \quad (66)$$

and

$$Z(L) = Z_v(L_r) = Z_v \left(\frac{\lambda L_1 + [L_2 - L_1 - \lambda]L}{L_2 - L} \right), \quad L > L_1$$

According to Equation (59), as q approaches 1, L_c approaches λ , while under the same conditions, by Equation (48), L approaches L_2 . If one

assumes that both relations hold up to the point of complete crystallization, at which $1 - q$ and L_u vanish, one must write:

$$\lambda = L_2 \quad (67)$$

whence:

$$L_r \equiv L_1 \quad (68)$$

According to this result, crystallization will progress at such a rate, with increasing strain, that the fractional extension of the uncrystallized material remains constant after the onset of crystallization. On the assumption of homogeneous stresses, the total stress also will remain constant—a result strikingly different from the observed rapid upturn in the stress-strain curves. This behavior is, of course, that found with the single chain model, in which the constancy of average stress in crystallized and uncrystallized regions is inherent. In these models, crystallization appears as a sharp phase change, completely analogous to the condensation of a vapor, in which, while the two phases coexist, the volume may be varied enormously while the pressure remains constant. As with the vapor-liquid systems, these models lead to sharp phase changes with changing temperature, at constant stress. That this does not occur in real rubbers is due to the irregularity in structure of the molecular network, and the associated variability in local conditions, which has no analogue in our model or in the vapor-liquid system.

It is possible to avoid this result by assuming that λ is less than L_2 . If the maximum relative length possible for the *uncrystallized* material is L_m :

$$L_r \dot{<} L_m \quad (69)$$

one finds for the limiting extension of the body:

$$L_{\max} = \frac{L_m L_2 - \lambda L_1}{L_m + L_2 - L_1 - \lambda} \quad (70)$$

under which conditions the fractional crystallization is:

$$q_{\max} = \frac{L_m - L_1}{(L_m - L_1) + (L_2 - \lambda)} \quad (71)$$

(Crystallization will, of course, play a role only if $L_m > L_1$.)

However, even on this basis one must go to unreasonable lengths to account for an increase in stresses due to crystallization. Stresses will be increased above those in the absence of crystallization, at the same strain, only when $L_r > L$. Now one has, from Equations (48) and (61):

$$L - L_r = (L - L_1) \left(\frac{\lambda - L}{L_2 - L} \right) \quad (72)$$

Hence L_r will exceed L only when the second factor on the right is negative, or L exceeds λ . This, in turn, will be possible only if L_{\max} exceeds λ , or, as follows from an investigation of Equation (70), if L_m exceeds λ . In other words, in order to account for an increase in stresses due to crystallization, on the assumption of homogeneous stresses, it is necessary to assume that the uncrystallized chains have an average extension in the direction of stretch which is greater than that possible for crystallized chains.

In the case of natural rubber, in which the crystal fibers are constructed from essentially unbranched chains, the increased stresses due to crystallization appear for average extensions of the chains which are markedly smaller than those of the chains involved in the crystals. It is consequently not possible to account for the increased stresses on the assumption of a homogeneous stress distribution. It appears, then, that in rubber the initial increase in rigidity with increased crystallization is due to the filler action (15b) of the increasingly numerous crystallites. This will cease to be true only when crystallization is so far advanced that it is no longer possible to apply to the remaining uncrystallized material the same statistical and mechanical theories which would be valid in the absence of the crystals.

XII. Comparison of Theory with Experiment

In explanation of the method to be used in comparing this theory with experiment, we may survey briefly the approximations which have been made. A rather elaborate attempt has been made to treat the changes in entropy of a random molecular network when the bulk material is deformed, as this accounts for much the greater part of the elasticity of the material. It has been necessary to neglect steric hindrances between chains (an approximation which can be shown to be significant only for compact networks such as highly vulcanized materials or extreme deformations) and, in the non-Gaussian model, to carry out the reduction from an irregular network to a regular one in an approximate way which will be increasingly in error as the deformation is increased. By including thermal expansion in the model phenomenologically, there have been introduced terms in the entropy which occur also in ordinary liquids, and also some terms in the internal energy. On the whole, however, the effects of changes in the internal energy have been ignored. There have been neglected van der

Waals' forces between the atoms in a single molecule, which may affect the behavior of the material for small extensions by changing both the internal energy and entropy, and also van der Waals' forces between essentially independent chains of atoms. At the smaller extensions one may expect these latter forces to be largely taken into account by inclusion of the thermal expansion, but at large extensions they give rise to crystallization, a large effect which is entirely outside of the domain of the present theory (see, however, Section XI). On the whole, it is apparent that the theory is essentially one of entropy effects, valid at most for extensions which do not induce crystallization. It will be reasonable and desirable to resolve both theoretical and experimental results so as to separate forces due to entropy changes from those due to changes in internal energy, and to deal with these separately, anticipating the better agreement for the entropy effects.

The division of the total force in unilaterally stretched materials into parts associated with the entropy and internal energy is expressed in Equation (2). Since:

$$Z_U = (\partial U / \partial L)_T = Z - T(\partial Z / \partial T)_L = Z - Z_S \quad (73)$$

the two terms in Z can be determined separately as soon as $Z(L, T)$ is given, whether experimentally or theoretically. Proceeding from Equations (13) and (44), respectively, for the cases of Gaussian and independent link chains, respectively, one finds for the entropy forces:

$$Z_S = KT\{L_z - [1 + \alpha(2T - T_0)]L_z^{-2}\} \quad (74)$$

$$Z_S = K'T\{L^{-1}(L_z\kappa) - 3\kappa[1 + \alpha(2T - T_0)]L_z^{-2}\} \quad (75)$$

respectively. The forces associated with the internal energy are:

$$Z_U = K\alpha T^2 L_z^{-2} \quad (76)$$

$$Z_U = 3K'\kappa\alpha T^2 L_z^{-2} \quad (77)$$

in the two approximations. In both cases the isothermal and the adiabatic inversion points are given, respectively, by:

$$L_{sc}^3 = 1 + \alpha(2T - T_0) \quad (78)$$

and

$$L_{ad}^3 = 1 + 2\alpha(2T - T_0) \quad (79)$$

1. Comparison of Theory with Total Stress-Strain Curves

Experimental stress-strain curves obtained under conditions carefully enough controlled to permit satisfactory comparison with the theoretical

results are not abundant in the literature. Most older experimental results are incomplete, and, in particular, do not permit a resolution of the observed stresses into parts Z_S and Z_U . To make possible a more satisfactory comparison of the theory with experiment some careful and complete observations were made recently at the University of Notre Dame (2, 5, 7, 8, 41).

To illustrate the general agreement between theory and experiment, we shall compare Equations (15) and (44) with total stress-strain curves.

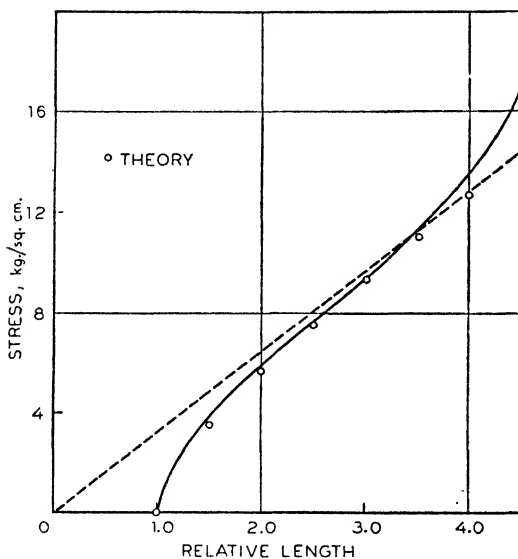


Fig. 2.—Comparison between theoretical and experimental stress-strain curves of soft rubber (24). The solid line represents an experimental curve; the circles are theoretical values, computed according to Equation (15). The dotted line is the asymptote approached by the theoretical values at large extensions.

Figure 2 shows the degree of agreement of Equation (15) with experimental data obtained by S. L. Dart at the Notre Dame Polymer Physics Research Laboratory. The knee in the experimental curve is well represented by the theory out to the point at which upward curvature begins in the former. In fitting the theory to experiment, the one adjustable parameter here is the vertical scale of forces. One striking feature of the theoretical curve, for which one may look in such experimental curves, is that the differential Young's modulus, the slope of the stress-strain curve, given by Equation (16), falls by a factor of 3 as one goes from $L = 1$ to the

linear portion of the curve at larger strains. Another is that linear extrapolation backward of this part of the curve brings one to zero stress for zero relative length.

It seems clear, then, that the downward curvature of the stress-strain curve at low extensions is associated with changing internal pressure in the material. This effect cannot be understood by consideration of single flexible molecules. The later upward curvature, bringing about the characteristic S shape of rubber stress-strain curves is shown by Figure 3 for

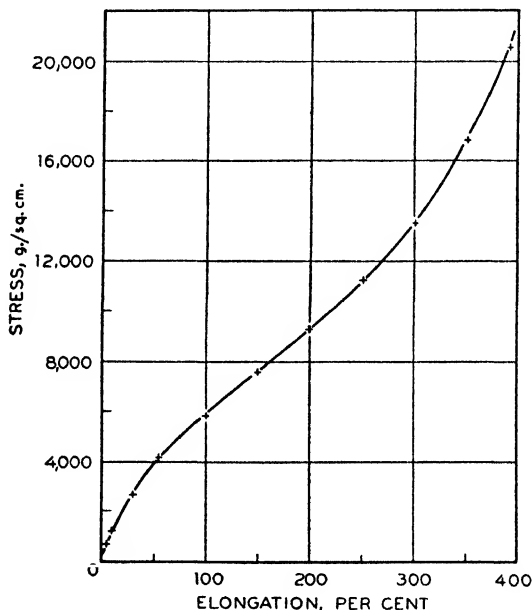


Fig. 3.—Typical experimental stress-strain curve of soft rubber (24).

the first experimental stress-strain curve obtained by Villari. Again the theoretical Equation (44) represents the upward curvature well.

The same behavior is shown by compounds which are known not to crystallize up to 400% extension. Thus, it is clear that the upward curvature is due to the behavior of the chains of the network as they approach maximum extension. This effect can be understood by consideration of single flexible molecules; it corresponds to the upward curvature in the stress-strain curves for highly extended molecules. Figure 4 shows iso-

metrics, *i. e.*, stress-temperature curves at constant length. Note that while Z_S should be proportional to T , this does not hold for the total stress $Z = Z_U + Z_S$. The observed linear dependence of Z upon T shows, however, that Z_U is sensibly independent of T .

Quite recently, Treloar (47) studied extensively stress-strain relations at constant temperature for two types of gum stocks under various deformations. He studied: (1) a two-dimensional extension of a sheet, as in a

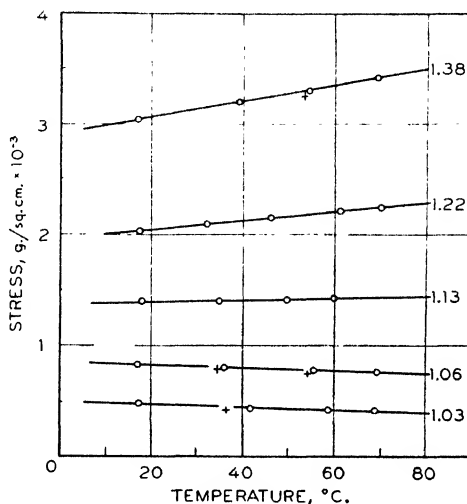


Fig. 4.—Stress-temperature relationships (isometrics) at various constant relative lengths, according to Anthony, Caston, and Guth (2).

balloon; (2) simple elongation; (3) pure shear; and (4) elongation combined with shear in a plane at right angles to the elongation. The same 8% sulfur-rubber compound was used as in the earlier work of Meyer and Ferri (37) and of Anthony, Caston and Guth (2). For this compound, agreement between experiment and theory was obtained in general. By using the value of K obtained from two-dimensional extension, where theory and experiment check up to almost 200% extension, agreement with experiment was obtained for the other deformations up to 50%. Treloar mentions that closer fit to the shear and elongation data would be possible by adjusting the value of K in the theoretical formulae in each case separately.

2. Comparison of Theory with Resolved Stress-Strain Curves

A. UNACCELERATED HEVEA GUM (2)

This material was an unaccelerated Hevea gum stock (2), containing 8 parts sulfur and 100 parts pale crêpe rubber, cured for three hours at 147° C. It shows little permanent set and no crystallization for extensions up to 350%, at room temperature. At higher temperatures greater extensions are possible without crystallization. For this compound, $a = 6.2 \times 10^{-4}$.

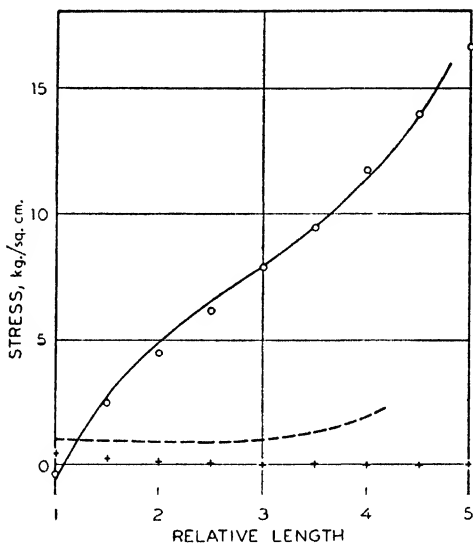


Fig. 5.—Comparison between experimental and theoretical stress-strain curve for a Hevea gum sample cured without accelerator (24): —, entropy contribution, experimental; O—O, theoretical; ---, internal contribution, experimental; +—+, theoretical.

The experimental value of L_{zc} is approximately 1.10 as compared with 1.065 as given by Equation (78). Z_S was found to be proportional to T , to within the experimental error. Figure 5 shows the experimental values for both Z_S and Z_U in comparison with the values predicted by Equations (75) and (77) for a model with chains of independent links, with $K' = 24$, $\kappa = 0.12$.

B. ACCELERATED HEVEA GUM (5)

This stock (5) was an accelerated pure gum compound containing 5 parts sulfur, 3 parts diphenylguanidine, 1 part zinc oxide, and 100 parts pale

crêpe. It was cured for thirty minutes at 147° C. This compound showed little permanent set. Crystallization began at 250% extension at room temperature, and at somewhat higher extensions when the temperature was raised. For this compound, $\alpha = 7 \times 10^{-4}$. This leads to a calculated value of $L_{zc} = 1.07$, against 1.14, the value given by Guth and James (18). More recent work at Notre Dame, still unpublished, gives an improved experimental value of $L_{zc} = 1.09$, in better agreement with the theory. Z_S was found to be proportional to T , to within the experimental error.

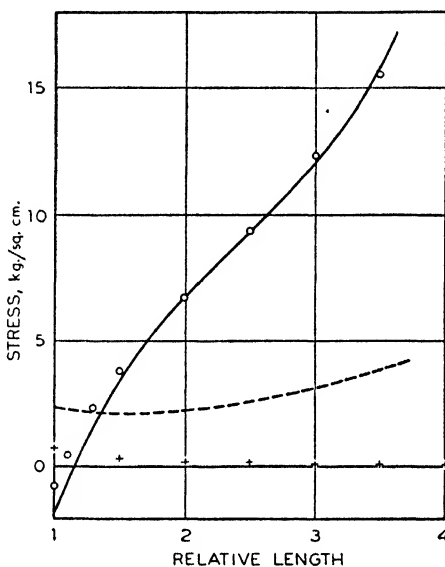


Fig. 6.—Comparison between experimental and theoretical stress-strain curve for a *Hevea* gum sample cured with accelerator (24): —, entropy contribution, experimental; O—O, theoretical; ---, internal contribution, experimental; +---+, theoretical.

Figure 6 shows experimental values for both Z_S and Z_U as functions of L , measured at 20° C. The indicated theoretical values were computed by Equation (25), with $K' = 30$, $\kappa = 0.143$. In this case, the fit was made in the middle of the range of L , since the discrepancy between the observed and computed thermoelastic inversion points indicated the presence of additional entropy terms in the forces measured at low extensions.

Figure 7 compares experimental (unpublished experiments of Dart) and theoretical values for the temperature rise in this material on stretching. These experiments give the isometric inversion point (ΔT at a minimum)

at $L = 1.07$ and the adiabatic inversion point ($\Delta T = 0$) at $L = 1.15$, in excellent agreement with the theoretical values of 1.065 and 1.13, respectively. Theoretical and experimental values of ΔT agree well over the

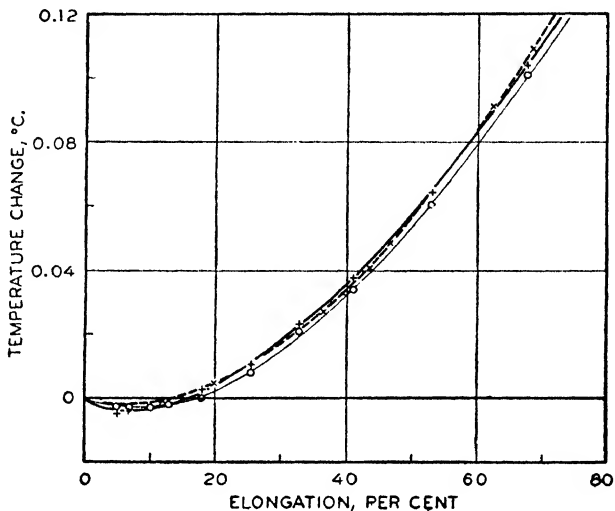


Fig. 7.—Change of temperature on stretching of a *Hevea* gum sample (same as in Figure 6) (24): +—+, values measured after extension; O—O, values measured after retraction; X—X, theoretical values.

whole range considered. Figure 7 gives the data of Joule (29) for another vulcanizate. It is of interest that the same trend is shown as in the modern data.

C. ACCELERATED HYCAR GUM (41)

The composition of this stock was as follows: 1 part sulfur, 1 part crude lauric acid, 5 parts zinc oxide, and 100 parts Hycar OR. This compound, like most synthetics, exhibits considerable permanent set if stretched to higher extensions. Curing is not enough to restrict plasticity; it is necessary, in addition, to use reinforcing agents such as carbon black. We have wished to avoid consideration of compounds in which the reinforcing material adds a new element to the behavior of the material, and have accordingly been forced here to deal with extensions not exceeding 130%. Within this range the Gaussian approximation equations, (74) and (76), are valid. No crystallization whatever was observed on stretching this

material. α was not observed with this compound. Assuming $\alpha = 1.1 \times 10^{-4}$, one computes $L_{zc} = 1.065$, as compared with the observed $L_{zc} = 1.10$. Z_S was found to be proportional to T , to within the experimental error.

Figure 8 compares experimental and theoretical results for this material. Again the fit was made with reference to moderate rather than very small extensions of the material. No estimate of κ is possible.

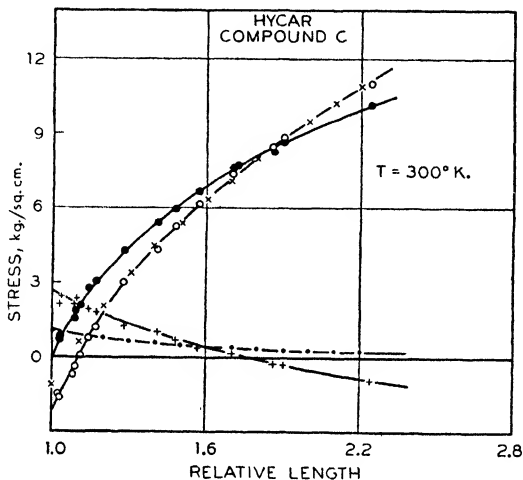


Fig. 8.—Comparison of theoretical and experimental stress-strain curves for an accelerated pure Hycar OR gum stock (24): 1, F , ●—●, total force; 2, $B(L)T$, ○—○ (exptl.). ×—× (theor.); 3, $A(L)$ +—+ (exptl.). ●—● (theor.).

3. Discussion

The proportionality of Z , to T at constant L , shown by all these samples, is in complete accord with the theory. The terms in T^2 appearing in Equation (76) are too small to produce an appreciable disturbance of this proportionality over the temperature range investigated.

The observed entropy stress-strain curves are in satisfactory agreement with the theory in all cases, over the whole range of extensions here considered. At the very highest extensions of compounds A and B (page 290), the observed stress begins to increase more rapidly than the theoretical. This may be considered as an effect of incipient crystallization, or it may be due to the approximate replacement in the theory of an irregular network by bundles of chains all with the same fractional extension in the unstretched state of the material. A more satisfactory approximation would certainly require the use of chains with a variety of initial fractional ex-

tensions. This would lead to just the behavior here observed—a more rapid increase in stress at large extensions than one would expect from the behavior at moderate extensions, due to the increasing relative importance of the shortest chains.

Compound B shows in addition an appreciable discrepancy in Z_s for L near 1, associated with a nearly equal and opposite discrepancy in Z_v . Compound C shows a similar discrepancy which vanishes for $L = 1.2$, that is—more rapidly than in the case of compound B. The variability of this discrepancy and its rapid decrease with decreasing internal pressure in the material suggests that it is due to van der Waals' forces neglected in the theory. The close agreement of the theoretical and experimental thermoelastic inversion points indicates that the actual discrepancy is even smaller than it appears to be in Figures 5, 6 and 8.

Aside from the small effect just mentioned, synthetic rubber C gives fair agreement with the theory. It is thus proved that synthetics behave quantitatively in the same way as natural rubber. In general, results obtained with synthetic rubbers agree less well with theory than the results obtained with *Hevea*. It is to be emphasized that rubberlike elasticity requires the presence of a coherent network of flexible molecular chains, but does not depend on the special nature of the chains. The form of the stress-strain curves for small extensions (at least in the absence of excessive van der Waals' forces) is then universal; variability in the behavior enters when plasticity is not completely suppressed, or the network approaches its maximum extension.

Experimentally, the entropy effects account for 80% or more of the total stress. As was to be expected, this theory gives a less satisfactory account of the smaller internal energy force. For very small extensions the predicted force is about half that observed. Whereas the theory predicts that this force will continually decrease as L increases, actually in the natural rubber compounds it passes through a minimum and then increases. In the case of the Hycar compound C, this rise does not appear. The effect appears to be due to the increasing importance, as the chains are straightened and aligned, of those van der Waals' forces which eventually lead to crystallization of the natural compounds.

XIII. Brief Discussion of Other Theoretical Work on the Elastic Behavior of Bulk Rubber

We now turn to a brief discussion of other theories, which intend to derive quantitative expressions for the elastic behavior of rubberlike materials. For a more extensive discussion, see James and Guth (25, 27).

The first attempt to derive, on a statistical basis, the fundamental elastic properties of rubber as a three-dimensional structure is that of Kuhn (34b). He considers a liquidlike mass of independent long-chain molecules as convertible into a solid piece of rubber by a fictional process of sudden "freezing" in which each individual chain molecule is immobilized in the position and configuration it happens to occupy at the instant of freezing. The distribution of chain configurations in this liquidlike mass is assumed to be the same which Kuhn, in an earlier article (34a), derived for the form of threadlike molecules in solution. "Liquid" and "solid" rubber differ in this picture in that in the liquid state each individual molecule is free to change its configuration, whereas in the solid state this configuration is fixed. Kuhn postulates further that, when the solid material as a whole is stretched, each molecule takes on a *new* fixed configuration each of its dimensions being changed in the same proportion as the corresponding dimensions of the bulk material.

More specifically, James and Guth (27) make the following comments to Kuhn's theory: "The references sometimes made to it as a 'network theory' of rubber are certainly not justified. Kuhn nowhere introduces or makes use of this idea, and the constraints on molecular configurations implied by a network structure are quite different from the total constraint which he pictures as existing. Actually, Kuhn's physical picture of the structure of rubber cannot be correct, and it does not even correspond to the mathematical formalism which he develops.

"According to this picture there is, for each shape of the material, just one configuration possible for the constituent molecules. There would then be in the entropy no shape dependent term such as that appearing in Equation (2.4), and correspondingly no retractive forces associated with the entropy, in complete contradiction to observation. It is because of a fundamental inconsistency in his statistical theory that Kuhn avoids arriving at such an obviously false conclusion."

James and Guth were able, however, to give a consistent, if somewhat artificial, interpretation of Kuhn's formalism. Unfortunately, the model arrived at this way does not correspond to physical reality. Nevertheless, their consideration permits a thorough understanding of the similarity of Equation (82) to the stress-strain Equation (15) (Eq. 2.4 of James and Guth) derived by a consistent application of statistical mechanics to the most general network model.

On the basis of a simplified model for the structure of bulk rubber, Kuhn computes its modulus of elasticity to be:

$$E = \frac{1}{3} G_0 kT \quad (80)$$

where G_0 is the number of independent chain molecules per unit volume. Equation (80) certainly represented at that time (1936) a very interesting step in the right direction. On the other hand, Kuhn's work also calls attention to the need for a more precise formulation of the structural model

for rubberlike materials, and for an extension into the range of larger strains. Specifically, it seems that the "freezing" of the individual chain molecules at certain prespecified points—namely, first at the ends, then in the middle and finally in the quarter-points—is necessitated by the lack of a definite network model. The factor $^{7}/_3$ depends on this specification and is therefore subject to corresponding uncertainty. Kuhn uses Equation (80) to compute from the experimentally known value of E at a given temperature T the number, G_0 , of molecules per unit volume, and from G_0 calculates the molecular weight of the rubber under consideration. It turns out to be of the same order of magnitude as the osmotic molecular weight of rubber in dilute solution. Considering the uncertainty of factor $^{7}/_3$ and the fact that the "freezing operation" eliminates the individual molecule as a well-defined entity, it seems that one *should not expect* any close agreement between the computed sizes of the long-chain molecule which travels independently in solution and those parts of it which move freely between points of constraint in the bulk material.

Treloar (44) has recently pointed out that an extension of Kuhn's computation without approximations leads to the stress-strain relation:

$$Z = ^{7}/_3 G_0 k T (L - 1/L^2) \quad (81)$$

If only the end points of each individual molecule are frozen into fixed positions, one arrives at:

$$Z = G_0 k T (L - 1/L^2) \quad (82)$$

This equation corresponds to relation (15) (page 271), according to which G_0 may be, on the basis of the network model, interpreted as the number of independently moving chain segments.

Wall (49-52) has presented a theory of quite different character. He renounces the calculation of individual molecular entropies and consider, the macroscopic system in its entirety. He does not specify his model and postulates rather than derives his distribution function, both for the unstretched and the stretched state. He then proceeds to compute the probability of the stretched and unstretched state and hence the change in entropy. Wall's final result agrees with Equation (82).

James and Guth (27) have pointed out that nowhere does Wall make use of the properties of a network, and show that his mathematical postulates are inconsistent with any such interpretation. In the one-dimensional case, Wall's formalism leads to a result different from that given by the network theory; in the three-dimensional case, apparently by chance, it leads to the same form of stress-strain curve. Wall's formalism implies the presence in the material of components other than

flexible molecular chains. Unfortunately, no physical significance can be attributed to such a model, or to Wall's formalism, unless this be modified in some essential respect.

Another theory, recently advanced, is that of Flory and Rehner (11) who make use of a simplified and special network of tetrahedral structures. They arrive at a stress-strain relation equivalent to Equation (82) and, in particular, include the treatment of swelling.

Their development of a theory of a molecular network is in some respects incomplete, reliance being placed on certain obviously reasonable postulates. It can be shown by the method of James and Guth (25, 27) that these postulates can be derived mathematically or, at most, deviate from such derivable results only in unimportant ways. It is therefore understandable that the stress-strain relation of Flory and Rehner agrees with Equation (15).

Flory (10) recently has also taken into account the effect of the initial molecular weight of the rubbery material before the process of cross linking (curing or vulcanization) on the elastic properties of the cured material.

Objections have been raised by James and Guth to Flory's treatment. They also point out the inadequacy of Flory's consideration of theories other than his own.

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VULCANIZATION

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	PAGE
I. Introduction.....	299
II. Structural Transformations in Rubber.....	301
1. Structural Pattern.....	301
2. Thermal Decomposition and Cyclization.....	302
3. <i>Cis-trans</i> Isomerization.....	305
4. Polymerization.....	307
III. Reactivity in Relation to Constitution.....	308
1. Additive and Substitutive Tendencies.....	308
2. Vulcanizing Tendencies of Hydrorubber and Butyl Rubber..	313
IV. Cross-Linking Processes.....	315
1. Action of Dibenzoyl Peroxides and Azo Compounds.....	315
2. Action of Nitro Compounds.....	317
3. Action of Light.....	319
4. Hydrogen Bonding.....	323
5. Insolubilization.....	323
V. Specific Reactivity of Vulcanizing Agents.....	324
1. Sulfur.....	324
2. Sulfur Monochloride.....	335
3. Grignard Reagents.....	336
VI. Constitution of Sulfur Vulcanizates.....	337
1. Proportion of Sulfur.....	337
2. Decrease in Unsaturation during Vulcanization.....	338
3. Dispersability and Molecular Integrity.....	340
4. Overcuring and Reversion.....	344
5. Accelerator Action.....	346
6. Effect of Zinc Oxide.....	355
VII. Conclusions.....	357
Bibliography.....	359

I. Introduction

After more than a century of technological experience of vulcanization, opinion is still divided over the true nature of the phenomenon. In what measure does the vulcanized state result from the chemical modification (in

detailed structure or in the formation of intermolecular links) of the original rubber molecules, and to what extent does it spring from colloidal changes involving physical rearrangement of the form and manner of association of long-chain molecules? Since Carothers and his colleagues suggested that the change of the α -polymer of chloroprene into the μ -polymer is due to cross linking in a three-dimensional structure, the interpretation has been widely accepted as generally applicable to vulcanization processes, although no direct proof of its correctness has been forthcoming. Increasing knowledge, however, of vulcanization phenomena, and especially of acceleration, reversion and softening processes, all of which seem to have but slight connection with the formation or destruction of cross links, has caused doubts to arise in many minds. Some chemists, indeed, view the interpretation with wholehearted suspicion, and are inclined to believe that primary valence forces may not really be concerned in vulcanization. Yet the physical properties of vulcanizates cannot rationally be considered apart from the molecular entities which compose them, and in consequence little real progress has been made toward the establishment of a case for regarding vulcanization as a mere manifestation of colloidal behavior.

There can be no doubt that the molecular entities brought together in a typical vulcanization change quite considerably in one way or another as the result of the chemical or thermochemical treatment received. This being so, it would seem that the most urgent necessity from all points of view is the determination of the chemical character of the transformed molecules. It is true that the elaborateness of the structural detail in the original rubber molecules renders the chemical task far from easy, but fortunately much can be learned about the main lines of reaction between rubber and vulcanizing agents by submission of low-molecular polyisoprenes and simple olefins to vulcanization treatment. The most uncertain factor in the chemical behavior of long-chain polyolefins is the incidence of intramolecular and intermolecular reaction, and on this matter—one on which information is badly needed—there is but little guidance to be found in the chemical literature.

The conversion of materials into the vulcanized state clearly does not involve a uniform operation. The rubber before vulcanization has low tensile strength, limited elasticity (characterized by low recovery, high retentivity, high flow and a narrow temperature range), a certain degree of thermoplasticity, a good degree of solubility and marked tackiness; after vulcanization it has high tensile strength, extensive elasticity (characterized by high recovery, low retentivity, low flow and a wide temperature range)

and has lost its thermoplasticity, solubility and tackiness. But these separate physical characteristics of vulcanizates vary so considerably from one product to another, none remaining constant, that the quality of a vulcanizate can only be judged on a group of properties, being superior with respect to some and more or less satisfactory with respect to others. This physical variability must be presumed (at any rate at the outset) to correspond to an underlying variability in chemical structure, but the chemical factors concerned in vulcanization may none the less be uniform as regards some prime cause, *e. g.*, the establishment of cross links, although it is nonuniform as regards others, *e. g.*, the chemical character of the cross links, or the incorporation of sulfur atoms which are not concerned in cross linking. The definite recognition of a prime chemical cause, if such exists, is of high importance in connection with the industrial development of all elastomers, natural and synthetic, but since no general agreement has been reached by chemists no coherent theoretical treatment of vulcanization is yet possible. In these circumstances it has seemed best to view progress in the knowledge of vulcanization almost entirely from the chemical structural standpoint, since in the nature of things specialized colloidal concepts can be relied on to assume their rightful importance as the facts concerning the chemical constitution of vulcanizates both became adequately known, and in due course show their capacity or lack of capacity to furnish the basis for a coherent interpretation of the varied phenomena observed.

In the following review it has been found convenient to consider certain basic structural transformations of rubber and its analogues, which are constantly referred to in the literature as essential or auxiliary participators in vulcanization, in a preliminary section, the relevance of which, it is hoped, will be apparent later.

II. Structural Transformations in Rubber

1. Structural Pattern

Although the molecular chains of rubber are composed of innumerable mono-olefinic units arranged end to end, it is preferable, owing to the fact that the olefinic double bond ordinarily extends its activating influence to adjoining groups, to consider the basic units to be the dimethyloctadiene system, $\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}\cdot\text{CH}_2$. This unit of pattern is, comparable with the unconjugated unit, $\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot$, of the vegetable and fish oil acids, and the conjugated unit, $\cdot\text{CH}:\text{CMe}\cdot\text{CH}:\text{CH}\cdot$, of the carotene pigments. The fact that two methylene groups

separate each pair of double bonds in the rubber system, whereas one or none separates each pair in the other systems, must be recognized as a source of important differences in the detailed reactivity and molecular transformability of the various materials. Analogies drawn, therefore, between the chemical behavior of rubber and that of these polyolefinic materials of quite different structural pattern are likely to be very misleading. The classical chemistry of aliphatic olefins is mainly concerned with additive reactions occurring at the double bonds: but in the methylene-interrupted unsaturation of the drying oils each of the isolated methylene groups shows, comparably with that in the system $\text{.CO.CH}_2\text{.CO.}$, a considerable chemical reactivity; and, if one of the methylenic hydrogen atoms becomes detached, the double bonds on either side show (probably owing to resonance in the system .CH:CH.CH:CH:CH.) a strong tendency to become conjugated by the migration of one of them. This tendency toward the assumption of a conjugated form affects very greatly the polymerizability of the drying oil acids; furthermore, the enhanced reactivity of the single methylene groups expresses itself in a marked capacity for substitution reactions to take the place of additive reactions where the experimental conditions are favorable. In the case of rubber the individual methylene groups are flanked on only one side by double bonds, so that their reactivity, although greater than that of methylene groups in saturated chains, is less impressive than that of the single methylene groups of the drying oils; moreover, because of this lesser reactivity, and because two double bond shifts would be necessary to convert the rubber system into an isomeric conjugated system, the tendency toward conjugation is practically nonexistent (20, 22). This lack of capacity for conjugative isomerization on the part of rubber has been demonstrated to hold at high temperatures (up to the cracking point), under oxidation by molecular oxygen, and under the action of alkalis and of many other chemical reagents: hence it can be assumed to hold under all ordinary conditions of reaction, including those of vulcanization.

2. *Thermal Decomposition and Cyclization*

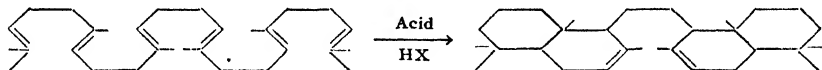
In Staudinger's well-known researches on the hydrogenation of natural rubber it was shown that complete hydrogenation ensued when the dissolved hydrocarbon was heated at 100 atm. pressure in the presence of extremely large proportions of nickel catalyst. The various hydrogenation products obtained, as judged by their viscosity molecular weights, were all considerably degraded, except that of Staudinger and Leupold (80),

which retained practically unchanged the molecular weight of the original rubber. Under the conditions of hydrogenation employed the rubber was liable to undergo two important side reactions, thermal decomposition and cyclization, the occurrence of the latter being deduced from the low hydrogen content of the rubber at the stage of complete saturation. A re-examination of the hydrogenation of rubber (19) has shown that, if the temperature of reaction is maintained at a point sufficiently high to insure rapid union of the gaseous reagent, but below that at which thermal decomposition (cracking) and cyclization of the rubber becomes serious ($230^{\circ}\text{C}.$), hydrogenation can then be carried out in the presence of moderate amounts of nickel catalyst to any desired stage of hydrogenation without trouble arising from the subsidiary reactions. If, however, the temperature is allowed to rise above the optimum range, hydrogenation becomes accelerated but there is then a measure of cracking; the extent of cracking can be fairly well controlled by adjusting the temperature. The regularity with which, given satisfactory temperature control and complete exclusion of oxygen, complete hydrogenation of the rubber can be effected without any reduction of its viscosity molecular weight forms one of the most cogent reasons for accepting the macromolecular hypothesis of rubber constitution: the individual chains retain their integrity, but the product, as Staudinger reported, is a good deal more plastic at room temperature than is the original rubber.

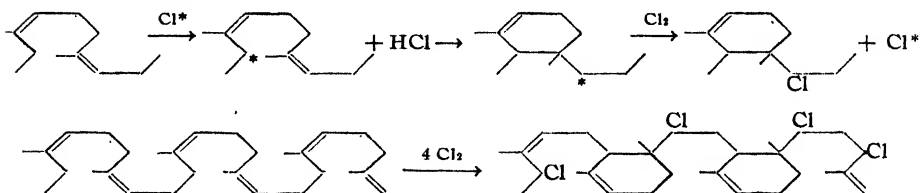
It has often been suggested that degradation of the rubber chains occurs during prolonged vulcanization at temperatures around $140^{\circ}\text{C}.$ Detailed studies, however, of the effect of thermal treatment of rubber in complete absence of oxygen leaves no doubt that degradation is inappreciable below $230^{\circ}\text{C}.$, but that above this temperature the progressive splitting-off of isoprene and dipentene occurs (9). The rubber molecules break in the first place, in accordance with Schmidt's rule, between a pair of adjoining methylene groups, so giving large fragments with active (radical) ends; thereafter, resonance in the new end groups facilitates and permits the detachment of single isoprene units or cyclized double isoprene units (but not of larger fragments) in methodical fashion. Such high-temperature thermal degradation of rubber hydrocarbon can hardly have a place in ordinary processes of vulcanization, and if any serious thermal degradation of the rubber substance actually occurs during curing it must be due to the degradation of chemically modified rubber chains—presumably those of rubber-sulfur systems. Of course the access of oxygen at vulcanization temperatures is likely to cause a minor degree of oxidative scission of rubber molecules; but, since *milled* rubbers are usually employed

for curing in any case, this degradation has no important influence (at any rate so far as molecular magnitude is concerned) on the success of vulcanization. Another common suggestion is that cyclization of the rubber chains occurs to greater or smaller extent during vulcanization, and this possibility deserves some consideration.

The low-molecular polyisoprenes, dihydromyrcene ($C_{10}H_{18}$) and squalene ($C_{30}H_{50}$), show a strong tendency to become cyclized when they are heated at *ca.* 100° in the presence of acids—even of organic acids; furthermore, a process commonly called cyclization occurs generally among low- and high-molecular polyisoprenes when they are treated with one or other of a variety of acidic chemical reagents. Squalene gives a *tetracyclo-derivative* when it is refluxed with formic acid (34), the reaction doubtless proceeding by the Whitmore ionic mechanism, and only failing to bring about complete cyclization of the hydrocarbon (*i. e.*, to give a *pentacyclosqualene*) by reason of the interruption occurring in the polarity sequence of the double bonds caused by the symmetry of the molecule about the middle C—C

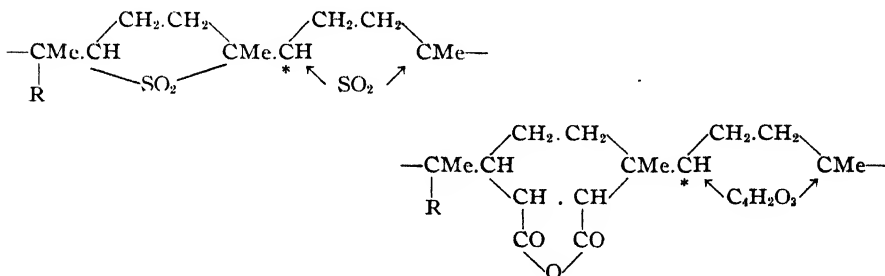


bond. As seen above, the thermal cyclization of rubber, which with little doubt is a radical reaction, begins at temperatures around 200° and is not likely to occur appreciably during vulcanization reactions. A somewhat similar cyclization, however, probably also dependent on radical initiation, accompanies all substitutive halogen processes, and may possibly have a counterpart among vulcanization reactions. Nevertheless, there



are two things to be said about the possible occurrence of cyclization during vulcanization: first, that although cyclization by radical action is feasible, that by acid catalysis (Whitmore mechanism) is not likely to be at all important because of the unsuitable reaction conditions; and, secondly, that even if extensive intramolecular cyclization were to occur, that in itself would not confer, so far as present knowledge of cyclized rubbers indicates, the characteristic properties of good vulcanizates. An uncertainty, however, arises with regard to the second point, because cyclization depends

on the reaction of one olefinic unit with a neighboring one in the same molecule, and is to be distinguished from true olefinic polymerization [$nA \rightarrow (A)_n$] only by its purely intramolecular character. If this type of reaction becomes intermolecular it at once involves molecule linking, and on general considerations it seems not unlikely that cyclizing processes are ordinarily accompanied by the formation of occasional intermolecular links, or in very favorable circumstances (*e. g.*, high concentration of the hydrocarbon and raised temperature) by fairly frequent cross links. Many of the known so-called cyclized and chemically isomerized rubbers seem likely from their insolubility to be partly polymerized. The cyclized rubber obtained by thermal treatment under hydrogenation conditions, however, remains soluble. Cyclizing reaction is probably especially characteristic of addition processes in which the reagent is bifunctional, and may well apply to sulfur dioxide and maleic anhydride additions promoted by peroxide catalysts (R), but not to maleic anhydride addition effected at



temperatures above 200° , in which case reaction appears generally to be substitutive at α -methylene carbon atoms.

3. *Cis-trans* Isomerization

Many olefinic substances which are capable of existing in *cis* and *trans* forms show a ready capacity for isomerization. Often the change from *cis* to *trans* can easily be brought about by the action of light, or by the action of specific chemical reagents with or without light, but the reverse isomerization is usually more difficult to accomplish. In the case of many conjugated polyolefinic materials the *cis* to *trans* change can occur progressively in one double bond after another, but the corresponding change in unconjugated polyolefinic materials is practically unknown—doubtless solely because of the noncrystalline nature of the substances and the consequent difficulty of recognizing the change when it occurs. Current opinion is in favor of the conclusion, based on x-ray evidence (48, 49, 52), that the

hydrocarbons composing natural rubber and gutta-percha differ from one another only in chain length and in the *cis* and *trans* configuration, respectively, of their double bonds, but up to the present no clear evidence of interconvertibility of the substances has been obtained. Ultraviolet light may well cause a progressive change-over of the *cis* bonds of rubber but this, if it actually occurs, is effectively masked by a species of vulcanization which rapidly sets in. Ferri (23) has concluded from x-ray data that the materials which are derived from rubber and gutta-percha, respectively, by treatment with chemicals such as zinc chloride, toluene-sulfonyl chloride and titanium chloride contain both *cis* and *trans* bonds, and are in fact configurationally intermediate between the original substances. It seems likely, however, that any *cis-trans* changes produced by this treatment would be accompanied by other structural changes, and especially by cyclization. A similar production of *cis-trans* changes has been considered by Garvey (27) to be the essential feature in vulcanization. Thus the conversion of a proportion of the *cis* links of rubber into *trans* links is held to result in the production of corresponding kinks in the otherwise straight rubber chains, thereby assisting in the interlocking of molecules by mechanical entanglement, and in fact serving to produce a sort of "molecular felting" which is identified with the vulcanized state. It is pointed out that the kinked molecules would be likely to become comparatively straight again by free rotation about single bonds under the influence of thermal agitation, and such straightening of chains with the consequent loss of felting power is advanced as the cause of the well-known phenomenon of reversion in vulcanizates. The suggestion is based on observation of the viscosity changes and gelling which occurred in solutions of rubber when the latter were treated with sulfur monochloride and finally evaporated. The increases in viscosity which ensued on the addition of the sulfur chloride are difficult to correlate simply with the concentration of the reactants, but oxidation clearly entered markedly into the reaction under the conditions employed, and caused very serious reversion of gels and inhibition of gel formation. The occurrence of such oxidation affords a much more satisfactory explanation of the reversion effects observed than the *cis-trans* changes advocated. Moreover, there is good reason to reject the idea that rubber chains are straight, since this would mean abandoning the fundamental concept of organic chemistry concerning freedom of rotation about single C—C bonds and the tendency toward assumption of random positions in space (in relation to the axis of rotation) by the groups attached to the rotating carbon atoms—a concept which has proved so valuable in recent years in the interpretation of the physical be-

havior of elastomers. In addition to these considerations the occurrence of *cis-trans* change during vulcanization is reported to be inconsistent with x-ray diffraction results (30).

4. Polymerization

The term "polymerization" has been used of recent years to specify molecule linking, whether or not the reacting molecules are exactly alike or simpler substances are eliminated in the process. Likewise the term "depolymerization" is frequently used in connection with rubber to describe not only reactions of thermal decomposition—the nearest practicable approach to transforming the polymeride into its original diene units—but also, and indeed most often, those of oxidative degradation in which the chains become shortened by severance at points which do not coincide with the boundaries of the original diene units. Naturally, with molecules so large and potentially multifunctional as are those of rubber it is in practice no easy matter to say by what precise mechanism molecule linking occurs. It is useful, however, to draw a distinction between *true* polymerization, signifying the union of molecules which are structurally of the same kind (although not necessarily of exactly the same chain length) by ordinary polymeric mechanisms, and cross linking, signifying the union of the molecules by heterogeneous mechanisms—oxidative, reductive and the like. Activation by free radicals may enter into either of these processes, but is here considered principally in connection with the latter.

Since natural rubber resists thermal alteration until it approaches its cracking point, and even then does not assume vulcanized properties, thermal polymerization can be dismissed from consideration as a factor in ordinary vulcanization. Any change, therefore, of a *true* polymeric type which occurs under conditions of curing and contributes in some degree toward producing the ordinary vulcanized effect must be initiated by double bond activation, since the molecules of natural rubber contain no unstabilized or unusually reactive end groups. For the purpose of polymerization the hydrocarbon can be considered as composed of reactively independent trialkylethylene molecules which are partly immobilized, but not seriously reduced in activity, by being linked together in long chains. These units are likely to be susceptible to the same activating influences that cause polymerization in monomeric trialkylethylenes, but may not be able to use fully such opportunities of activation as are available owing to reduced mobility. The restriction in free movement, indeed, seems particularly likely to insure that no chain reaction of many steps can occur to cause reaction to run on from molecule to molecule by the

interaction of some one unit in one molecule with some unit in a second, and this last unit with some unit in a third molecule, and so forth: the successful process would be likely in fact to result largely in two-molecule linkings corresponding to the dimerization of a simple olefin, but here complicated by the fact that several different olefinic units in one rubber chain might react in succession with units in quite different polyolefinic molecules. The means of activation which are usually successful with olefins are light of short wave length, radicals or paramagnetic molecules, chemical activators of the boron trifluoride type, and the hydrogen ion. Since sulfur and the usual active accelerators of vulcanization appear to be uniformly without activating effect when applied under favorable conditions to polymerizable olefins, and since light and powerful chemical activators are normally absent during vulcanization, the only feasible activators are hydrogen ions, traces of oxygen, and neutral radicals. The hydrogen ion is unlikely to be present in very effective concentration, the only acidic bodies normally appearing in the vulcanizing mixture being hydrogen sulfide in small amount, and such quantities of fatty acids as have escaped neutralization by zinc oxide. Radicals remain as possible promoters of polymerization, and there is some probability that a number of the well-known accelerators can yield such radicals by thermal decomposition. But many of the common basic accelerators do not appear themselves to break down into radicals, hence it seems very unlikely indeed that true polymerization is a necessary contributor to the vulcanization mechanism. Current ideas as to the likelihood of polymerization contributing largely to vulcanization are founded principally on the fact that the α -polymer of chloroprene passes spontaneously on keeping into the μ -polymer which resembles in its general character vulcanized rubber. The exact nature of this process, which is remarkable in being accelerated by primary aromatic amines, has not been determined.

III. Reactivity in Relation to Constitution

1. *Additive and Substitutive Tendencies*

One of the notable properties of olefinic substances is their capacity to undergo reaction at the carbon atoms immediately adjoining the double bonds. This capacity is comparable with the reactivity characterizing the α -carbon atoms of carbonyl compounds, but is usually weaker than the latter and apparently much less likely to be of ionic nature. The ease of displacement of hydrogen atoms from α -methylene groups decreases in passing along the series, $\text{.CO.CH}_2\text{.CO.}$, $\text{.CO.CH}_2\text{.CH:CH.}$, $\text{.CO.CH}_2\text{.}$,

.CH:CH.CH₂.CH:CH., and .CH:CH.CH₂., but the tendency is sufficiently developed in even the last of these to make a considerable difference to its chemical reactivity. The unsaturated system occurring in rubber, *viz.*, .CMe:CH.CH₂.CH₂.CMe:CH., falls between the two last members of the series, since each of its methylene groups is not only adjacent to a double bond, but is separated from a second double bond by only one carbon atom. The second double bond has of course less effect on the methylene group than the first, but its influence is still substantial. It may be said that the ease of displacement, or detachment, of a hydrogen atom from the methylene groups in the above series decreases from the first member to the last, but whereas such displacement tends to be unavoidably of ionic character in the carbonyl compounds, there is an apparently* strong tendency for it to be of neutral (*i. e.*, radical) character in the olefins, *unless* the reagents used are highly polar materials such as caustic alkalis or mineral acids and the reaction media liquids of strongly dissociating type. The reactions of rubber are generally conducted in nonpolar media, *e. g.*, in solvents of low dielectric constant, or without any solvent, and the nonpolar media appear greatly to assist the radical type of reaction in which the electron pair forming the >C—H link is symmetrically severed to give the neutral atoms >C· and H· instead of the charged atoms >C: and H as in polar reaction. Curiously enough, the methyl groups attached to the ethylenic carbon atoms of rubber not only promote and direct in the normal way all *polar* reactions immediately affecting the double bonds, but seem by their presence to assist in quite an important degree the *radical* type of reaction. This is particularly to be seen in the greater tendency to autoxidation in air shown by natural rubber in comparison with synthetic polybutadiene rubbers, but it is shown in other reactions also. Hydrogen displacement and the process of addition at double bonds are both to be regarded as constituting different potential reactivities of the three-carbon system, .CH₂.CH:CH. or .CH₂.CMe:CH., and the degree to which each is exercised depends on the experimental conditions. The first is the cause of numerous substitutive reactions to which rubber is prone. It is of interest that one of the α -methylene hydrogen atoms in the hydrocarbon system .CH:CH.CH₂.CH:CH. is sufficiently labile to be detached as an ion by caustic alkalis at high temperatures in strongly polar solvents, but this lability is not sufficiently developed in the rubber system for the hydrogen atom to become detachable under the same con-

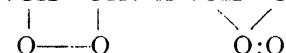
* There is much that is obscure in the reactions of olefins under nonpolar conditions and the steps in the processes are difficult to establish kinetically.

ditions; nevertheless the hydrogen atoms of both systems are reactive in nonpolar conditions.

It is also to be noted that additive reactions occurring at the double bonds of rubber and of similar olefins in nonpolar media appear to be usually of nonionic type, taking place by multistage chain mechanisms. It is a remarkable fact that, until recently, the additive dichloride of rubber has remained unknown; and this is because under usual reaction conditions the first molecular proportion of chlorine applied to the rubber attacks the latter wholly substitutively ($.CH_2.CMe:CH.CH_2 + Cl_2 \rightarrow .CHCl.CMe:-CH.CH_2 + HCl$), but the additive chloride can easily be obtained if chlorination is carried out with such thermally unstable chloro compounds as phenyliododichloride, $PhICl_2$, or sulfonyl chloride, SO_2Cl_2 (5). The latter reagent must be used in conjunction with a little peroxide as catalyst, and the reaction takes another course if antioxidants (even those indigenous to natural rubber) are present. Bromine, unlike chlorine, reacts at once with rubber at 0° in the presence of a trace of alcohol to give the additive dibromide. The additively formed chloride and bromide are both very stable compounds, whereas the substitutively formed chloride is very unstable, decomposing in air and almost quantitatively undergoing double decomposition with inorganic salts such as silver nitrate at 80° . The ease of the latter reaction indicates the existence of a strongly polarized link between carbon and chlorine which can undergo ionic dissociation under favorable conditions. These and other similar halogenation reactions almost certainly involve complex mechanisms. In the case of molecular chlorine and bromine the halogen may possibly add at the double bond in the first place to give, as suggested by Stewart (81), activated dihalides of high energy content, the fate of which on deactivation—to yield normal dihalide, halogen-substituted olefin, cyclized monohalide or (by reaction with a further molecule of halogen) a halogen-substituted dihalide, $.CHX.-CHX.CHX.$ —varies according to the experimental conditions, the character of the olefin and the energy associated with the dihalide. Other halogenating agents yield by thermal decomposition, or peroxide catalysis, either atomic halogen atoms to attack the double bonds, or organic radicals to detach hydrogen atoms from the α -methylene groups of rubber, so enabling halogen to enter or cyclization of the rubber to take place.

The interrelationship of α -methylene and double-bond reactivity is well illustrated in autoxidation processes. The first products of autoxidation are normally peroxides; and these being unstable decompose more or less rapidly according to the olefinic constitution. Conjugated cyclic dienes such as cyclohexadiene undoubtedly add oxygen at the terminals of the

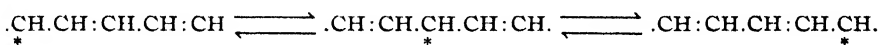
diene system as in (I) (p.3 12), but open-chain conjugated dienes just as certainly undergo oxidative reaction at individual double bonds to quite a considerable extent, as is shown by the reaction products obtained (*e. g.*, as in II), although reaction still occurs largely by addition of oxygen (often polymolecularly) at the terminals of the diene system, comparably with (I). It may be that oxidative scissions of the type shown in (II) are mere secondary reactions made possible by decomposition of some of the 1,4-peroxide molecules. Certainly, never yet has a 1,2-peroxide, *e. g.*,



ground for suspecting that it never does appear as a tolerably stable molecule. It is conceivable, however, that the oxygen absorbed by some olefin molecules first adds to one ethylenic carbon atom of a double bond as in (III*b*), and momentarily couples with the second ethylenic carbon atom to form a very unstable 1,2-peroxide; but then owing to the instability of the structure the O.O link becomes ruptured to form the biradical (III*c*), which automatically breaks down by severance of the —C—C— bond. On passing to unconjugated systems which contain α -methylene groups the peroxides actually formed are found to be hydroperoxides having .OOH groups situated on the α -methylene carbon atoms as in (IV*b*): and this seems to apply whether the reaction is promoted photochemically or thermally. The stages by which these .OOH groups are formed require much laborious effort to establish kinetically, but one important point at least has become clear. Small amounts of hydrogen have been found among the volatile autoxidation products formed in diffused daylight or ultraviolet light from a number of olefins, and it seemed reasonable at first sight to conclude that the first stage of reaction in the thermal or photochemical process (or in both) consists in the scission of the C—H bond. The energy, however, which must be supplied from some source to bring about this scission is very considerable, and experiment (2) has shown that the scission resulting from *photochemical* activation at least is far too slow to account for the rates of oxygen absorption observed, so that it must be concluded that molecular oxygen assists in the removal of α -methylene hydrogen in spite of observations to the effect that the rate of oxidation is independent of the oxygen concentration. Conceivably the hydrogen is removed as *OOH, and the reaction proceeds as in (IV). Alternatively, reactions may be initiated by addition of oxygen at one of the ethylenic carbon atoms forming the double bond, and thereafter proceed by detachment of an α -methylene hydrogen atom—probably not intra-

molecularly as in (Va), since the reaction satisfies the criteria for a chain reaction, but rather intermolecularly as in (Vb). The two-stage intramolecular process would necessarily involve change in the position of the double bond, whereas the intermolecular process would start reaction chains (and but few additions of oxygen molecules to double bonds would be necessary to initiate effective reaction) by promoting the continual removal of hydrogen atoms from molecules of olefin, followed by successive interaction of the derived organic radicals with oxygen and olefin as in the last two stages of reaction (IV).

The latter might involve some degree of double-bond shift, since change in the position of the double bond is known to occur with the utmost facility in the photooxidation of the highly autoxidizable substances containing the system $\cdot\text{CH}:\text{CH}.\text{CH}_2.\text{CH}:\text{CH}\cdot$, in which loss of hydrogen from the methylene group according to scheme (IVa) would leave a resonating system:

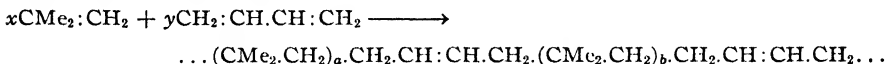


Whether any double-bond shift occurs during the oxidation of monoolefins or of polyolefins having the unsaturation pattern of rubber is not yet known with certainty, but it is quite definitely known that double-bond shifts during oxidation do not occur sufficiently frequently during the oxidation of rubber to produce any significant degree of conjugation. It must be recognized, however, that rubber represents a difficult case for the production of conjugation because two double-bond shifts per diene unit are necessary to this end. Autoxidations of rubber and of other olefinic substances are known to be autocatalytic, and the scheme finally arrived at must provide for both photochemical and thermal methods of activation.

2. *Vulcanizing Tendencies of Hydrorubber and Butyl Rubber*

The presence of some form of aliphatic unsaturation is normally a necessary condition of effective vulcanization by sulfur. Usually the unsaturation takes the form of olefinic double bonds, although the unsaturation of carbonyl groups and of the sulfur groupings of Thiokol may perhaps be included in the same category. Staudinger and Fritschi (79) made an attempt to vulcanize fully saturated, but somewhat degraded, hydrorubber with sulfur monochloride and failed, although natural rubber vulcanized easily under the same conditions. More recent attempts to vulcanize undegraded (as well as somewhat degraded), fully saturated

hydrorubber with sulfur according to the usual techniques have also failed (66), and the same applies to fully saturated synthetic polymers such as the polyisobutenes. The industrial difficulty presented by this lack of vulcanizing capacity on the part of saturated compounds has been overcome in the example of polyisobutene in a very reasonable way by mixing with the molecules of the ethylenic monomer (which alone would yield a fully saturated product on polymerization) a proportion of conjugated diene molecules sufficient to provide occasional double bonds in the polymeric chains (74), thus:



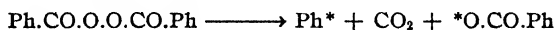
What constitutes a sufficient degree of unsaturation in the polymer molecules has been fixed by experiment at between 1 and 2% of that present in natural rubber, as determined by the iodine value. With this degree of unsaturation the polymer becomes satisfactorily vulcanizable and can then be classed as a true rubberlike elastomer. Presumably the unsaturated units are distributed fairly evenly along the lengths of the rubber chains, since perfect mixing of the hydrocarbon ingredients can be assured before polymerization is begun, although monomers do not always combine exactly in the proportions taken, and may vary in their degree of participation from one reaction yield to another. A corresponding provision of residual unsaturation can be fairly easily made in the case of hydrorubber, by refraining from carrying the hydrogenation quite to completion. In practice, however, the somewhat unsaturated products, although they are capable of combining with sulfur, have failed on test to respond satisfactorily to the most usual conditions of sulfur vulcanization. The reason for, or the inevitability of, this result has not yet, however, been established. It is unlikely that difficulty would arise from faulty distribution of the surviving unsaturation along the rubber chains, such as would amount in the extreme to the admixture of much fully saturated hydrorubber with a little unchanged rubber. Maldistribution of this kind is quite unlikely on grounds of probability, and could not arise unless a rubber molecule when once adsorbed on the catalyst did not become desorbed until long sequences or even the whole of the olefinic centers had been saturated—a contingency which is not realized in polyolefins even when the double bonds are as close together as they are in conjugated compounds. There would be no abnormality if some or many of the surviving double bonds changed position in contact with the catalyst (67), but this would hardly be expected to destroy the possibility of satisfac-

tory vulcanization. The relative difficulty of cross linking where the double bonds are thoroughly isolated appears to be illustrated by the need which has been found (47) in connection with the vulcanization of Butyl rubber to avoid compounding the polymer with olefinic materials such as natural rubber, terpenes and unsaturated fatty acids. These ingredients doubtless undergo ready reaction under vulcanization conditions, often in preference to the less reactive, widely spaced olefinic units of the elastomer.

IV. Cross-Linking Processes

1. Action of Dibenzoyl Peroxides and Azo Compounds

The idea that neutral organic radicals can be produced at moderate temperatures with sufficient frequency to initiate and effectively propagate reactions between neighboring molecules is nowhere more attractive than in the field of cross-linking processes. One likely source of such radicals which has attracted attention of recent years is the group of peroxides, and most convenient among these is dibenzoyl peroxide. The hypothesis of radical activation as applied to common organic reactions is not yet soundly established although the peroxides themselves have long been used to catalyze additive and polymeric processes. Dibenzoyl peroxide breaks down fairly rapidly at temperatures above 100° into fragments which show an unexpectedly strong capacity to combine with themselves or with other molecules in their vicinity (35). The active fragments are phenyl and benzoyloxy groups:



and it appears legitimate to deduce from the studies of Gelissen and Hermans (29) and others that these can ordinarily combine with colliding olefin molecules by one of three processes (21):

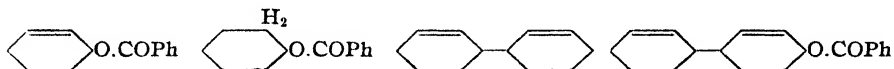
(1) Extraction of a hydrogen atom from a reactive methylene group leaving an active olefin radical ($\text{.CH:CH.CH}_2 + \text{R}^* \rightarrow \text{.CH:CH.CH}^* + \text{RH}$).

(2) Union with an olefin system at the expense of expelling an active hydrogen atom therefrom ($\text{.CH:CH.CH}_2 + \text{R}^* \rightarrow \text{.CH:CH.CHR} + \text{H}^*$).

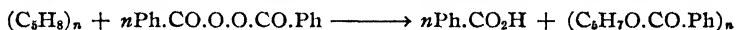
(3) Addition at one end of a double bond, leaving an active radical at the other ($\text{.CH:CH.CH}_2 + \text{R}^* \rightarrow \text{.CHR.CH.CH}_2$).

The more complex active radicals so formed can in turn interact with one another, or with other olefin molecules to give a variety of products including principally benzoyloxyolefin, diolefin and benzoyloxydiolefin. Whether the fragments derived from dibenzoyl peroxide are truly free

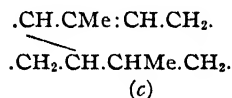
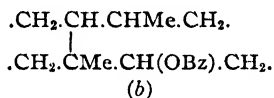
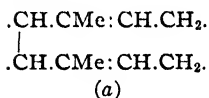
radicals or not, there is no doubt that their union with olefins and polyolefins occurs with singular facility at vulcanization temperatures to give products according to the above theoretical scheme. The most significant item of their varied reactivity is the power to cross link olefinic and aromatic molecules, with or without the attachment of phenyl or benzyloxy groups to the cross-linked products. This is illustrated in the case of cyclohexene by the appearance *inter alia* of the four products in considerable yield:



Since dibenzoyl peroxide reacts very easily with rubber at 140°, the reaction following a course already known to approximate the scheme (59):



there is every reason to regard the vulcanization as proceeding by cross linking with some attachment of benzyloxy or phenyl groups (in addition to benzyloxylation, etc. without cross linking), in one of three ways:



Since both the coupling and the substituting reactions in the interaction of dibenzoyl peroxide with cyclohexene occur principally at the α -methylene positions, it is not unreasonable to expect a similar substitutive coupling to be attainable at the alpha positions of ketones, acids, nitriles, etc. Methyl ethyl ketone does in fact undergo cross linking to quite a considerable extent when heated with dibenzoyl peroxide, yielding thereby a cyclized derivative of the diketone, $Me.CO.CHMe.CHMe.COMe$; and even crotonic ester gives a few units per cent of the cross-linked derivative, $EtO_2C.CH:CH.CH_2.CH_2.CH:CH.CO_2Et$ (7). Acetic acid similarly gives the corresponding cross-linked derivatives, succinic acid (42). It is not surprising therefore, that the cross linking of even saturated synthetic polyesters has recently been achieved by vulcanization with dibenzoyl peroxide, although it is stated that partly unsaturated polyesters (formed by using a proportion of maleic acid in place of saturated dibasic acid) require much less peroxide to reach a satisfactory state of cure than do the fully saturated compounds (26).

The vulcanizing action of diazo compounds doubtless resembles in mechanism that of dibenzoyl peroxide, since many of these nitrogenous

substances break down when heated to give free radicals and gaseous nitrogen (35) ($R.N:N.X \rightarrow R^* + N_2 + X^*$). Buizov (13) first drew attention to the activity of diazoaminobenzene in vulcanizing rubber, but Levi (45) found that all diazoamino compounds of the type $R.N:N.NXR'$ (where R is an aryl, R' is an aryl, aralkyl or arylamino group, and X is hydrogen, a metal, or an alkyl, acyl or aralkyl group) are vulcanizing agents—many of them energetic ones. Phenyldiazoaminobenzene, when heated alone, evolves a molecule of nitrogen, with formation of *o*- and *p*-aminobiphenyl ($Ph.N_2.NHPh \rightarrow Ph.C_6H_4.NH_2 + N_2$), and only those diazoamino compounds which decompose with evolution of nitrogen are successful as vulcanizing agents. Azo and azoamino compounds of the types $R.N:NR$ and $R.N:N.C_6H_4.NH_2$ are ineffective. Levi reports that diazoamino compounds, like dibenzoyl peroxide, are energetic polymerizing agents of diolefins; and it seems probable that, for rubber, a cross-linking reaction similar to that formulated above is the essential result. Certain other thermally decomposable azo compounds, such as N,N' -dichloroazodicarbonamide (24), probably belong to this group of vulcanizing agents. The vulcanizates obtained from natural rubber by use of diazoamino compounds are reported to show good resistance to solvents, but to be porous and of rather poor aging quality; those from synthetic rubber, on the contrary, are stated to be nonporous and to age normally.

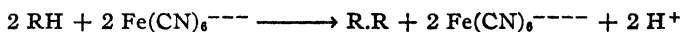
2. Action of Nitro Compounds

The vulcanizing action of nitro compounds such as *m*-dinitrobenzene and *sym*-trinitrobenzene has excited a good deal of interest; and it has sometimes been suspected that these substances add chemically to the rubber. Although both soft and hard vulcanizates can be obtained, there is no published evidence of the formation of definite adducts; and indeed any possibility that these reagents add to the double bonds of the rubber, as has been suggested, is remote in view of the fact that the additive capacity of these compounds has been pretty thoroughly explored, and is confined to the formation of molecular compounds, mostly with polynuclear aromatic compounds. Inorganic oxides are recommended as auxiliary reagents for obtaining best results; and Ostromislensky, who first brought nitro compounds into use, regarded them as oxidizing agents which became destroyed during reaction. Blake and Bruce (3) have shown that the unsaturation of rubber decreases progressively and markedly during vulcanization with *m*-dinitrobenzene or *sym*-trinitrobenzene, and at the same time the nitrogen content steadily rises. Wright and Davies have reported

the production of ammonia, volatile amines and probably azo- and azoxybenzene as by-products (92). Aromatic nitro compounds have of course long been used, together with alkalis, as oxidizing agents for certain classes of organic compounds, including those containing alkyl groups attached to carbonyl or benzenoid systems. These alkyl groups are oxidized, the nitro groups being simultaneously reduced to azo, azoxy and simpler compounds. There can be no doubt that the nitro compounds act oxidatively during their vulcanization of rubber and possibly they serve in part to link together α -methylene groups and in part to saturate double bonds by subsidiary reactions. At present, however, oxidative molecule-linking action of this sort has not been demonstrated with simple olefins and polyisoprenes. It is of some interest, however, that nitro compounds have been reported to vulcanize satisfactorily the Buna type of synthetic rubber (84).

An indication of the complicated subsidiary reactions likely to occur with this type of reagent is probably to be found in the behavior of nitric oxide and nitrosyl chloride with rubber and allied olefins. In the case of nitric oxide at least one-quarter of the combined nitrogen is invariably liberated as free nitrogen, and the remainder together with its combined oxygen forms reaction products identical with or analogous to those to be expected from higher oxides of nitrogen. Simple olefins yield substitutive and additive products consisting partly of monomeric nitro-olefins, and partly of dimeric nitrosites, but very largely of complex nitroxylated bodies of small unsaturation and considerable molecular weight. With rubber, however, the introduction of nitro groups is accompanied by oxidative chain scission, but ultimately insoluble materials are formed having an empirical composition between $C_{10}H_{15}NO_2$ and $C_{10}H_{15}NO_3$. Thus chain shortening, chain linking and modification of chain structure seem to occur side by side or consecutively, giving complex, nonuniform products (6). When nitrosyl chloride is used as reagent somewhat analogous complex changes occur, the derivatives becoming insoluble (22).

Vulcanization of the rubber of specially prepared latex has been reported to occur in the absence of air when the latex is heated with potassium ferricyanide at 100° . Since alkaline ferricyanide is well known as an oxidizing agent of dehydrogenating habit, the possibility exists of an oxidative cross-linking reaction of the type:



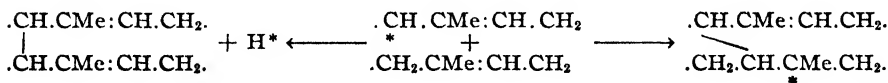
as suggested by Spence and Ferry (75). No such cross-linking reaction has, however, yet been observed with simple olefinic compounds.

3. Action of Light

Although the photochemical detachment of hydrogen atoms from rubber molecules cannot be regarded as constituting the usual primary stage in the autoxidation of rubber, it appears to be the fundamental cause of the gelling of solutions of rubber (18, 21) when the latter are exposed to sunlight or ultraviolet light. It is suggested that the hydrogen atoms are detached in sufficient numbers to cause a mild degree of cross linking of the rubber molecules through the combination of the stripped molecules with adjacent molecules. The reactions must be of chain-reaction type, in which rubber molecules RH. combine to give linked molecules R.R (or R.RH), R.RH.R (or R.RH.RH), etc.

- (1) $\text{RH} \rightarrow \text{R}^* + \text{H}^*$
- (2) $\text{R}^* + \text{RH} \rightarrow \text{R.R} + \text{H}^*$ or R.RH^*
- (3) $\text{R.RH}^* + \text{RH} \rightarrow \text{R.RH.R} + \text{H}^*$ or R.RH.RH^* , etc.
- (4) $\text{RH} + \text{H}^* \rightarrow \text{R}^* + \text{H}_2$
- (5) $\text{R}^* + \text{H}^* \rightarrow \text{RH}$
- (6) $\text{R.RH}^* + \text{H}^* \rightarrow \text{R.RH}_2$, etc.

The distinction between the alternative products shown for the linking reactions (2) and (3) is that the first product in each case is deemed to arise by displacement of hydrogen from a rubber molecule by a hydrocarbon radical (simple or otherwise), and the second by the addition of a similar hydrocarbon radical to the double bond of a rubber molecule, for example:



It is not, of course, necessary to assume that the hydrogen atoms removed are invariably those attached to those α -methylene carbon atoms nearest the methyl groups, although these seem likely to be removed with the expenditure of a smaller amount of energy than those attached to the other α -methylene groups or to the doubly bound carbon atoms. Also, since there are very numerous olefinic units in each rubber chain, any molecule is theoretically able to form one, several or many cross links with its neighbors, the precise number and position of the linkages produced depending on the activation efficiency (quality of irradiation), the effective proximity of neighboring units, and the absence of hindering agents such as oxygen which, by combining with the chain-starting radicals, would prevent the propagation of reaction chains.

Porritt first observed that rubber solutions gel when they are subjected to the action of ultraviolet light in the absence of oxygen (63), and thereby brought to notice a phenomenon which, because of its apparently close relation to vulcanization, has aroused interest out of all proportion to its practical importance. Pummerer and Kehlen (65) realized its outward similarity to vulcanization, but suspected polymerization to be the cause, while Meyer and Ferri (50), by showing that it could be brought about in complete absence of oxygen, at once removed the possibility that it could result from the formation of oxygen links between the rubber chains, and themselves attributed the gelling to the grouping of the rubber molecules "in a tridimensional network through the formation of transverse chemical linkages between the chains." The phenomenon has since been briefly examined by Spence and Ferry (76), comprehensively by Stevens (82) and most recently by Naunton (57). The essential facts are admirably set out by Naunton.

Gels, termed photogels, can be produced by the action of diffused light or (more rapidly) of ultraviolet light on rubber solutions. With certain solvents such as carbon tetrachloride gel formation is accompanied by some degree of combination of the solvent with the rubber, whereas with others it is not. The speed of gelling is increased if small proportions of well-known photosensitizers such as aldehydes and ketones are included. For every set of experimental conditions there is a limiting degree of gelation beyond which it is impossible to proceed whatever the length of irradiation. Under the best experimental conditions discovered (covering choice of solvent, activator, source of light, etc.) it has proved impossible to obtain a final (dry) product which, rated by the standards of sulfur vulcanization, is more than lightly vulcanized. If photogelling is attempted in the presence of oxygen or air, the oxygen becomes slowly absorbed and the viscosity of the rubber solution decreases through oxidative degradation to a limiting value: if, however, insufficient oxygen is present, the viscosity falls until all the oxygen has been absorbed, whereupon gelation begins, provided the degree of degradation has not been too great for the particular gelling conditions (*i. e.*, nature of solvent, concentration of activator, etc.) Gelling, unlike the initial degradation with its steady decrease in viscosity, is not attended by a uniform increase in viscosity. The effect of the oxygen absorption is to delay gelling, and the larger the amount of oxygen the greater the delaying action, and the weaker the resulting gel. Benzene solutions are much more sensitive to the initial amount of oxygen than carbon tetrachloride solutions, given equality of treatment with respect to the concentration of any activator employed. Generally speaking, in-

crease in the proportion of the activator (up to an ascertainable point) accelerates gelation in either solvent; if, however, oxygen is present at the outset, the gelling of rubber-benzene solutions is much more delayed than that of rubber-carbon tetrachloride solutions. Very rigorous removal of oxygen from rubber and solvent aids gelling.

Photogels revert to solutions when exposed to further irradiation in the presence of oxygen, and although gel formation with certain exceptions (*e. g.*, Neoprene gels) takes place throughout the whole volume of irradiated solution, reversion takes place progressively from the surface in contact with the oxygen or air. Photogels in carbon tetrachloride are much more stable than those in benzene and take longer to revert. In this behavior photogels resemble gels obtained by the treatment of rubber solutions with sulfur chloride; and both of these gels after complete reversion give solutions of the same viscosity whether made from lightly or heavily milled rubber. Provided the degradation has not gone too far, it is possible to regel the reverted solution by further irradiation in the absence of oxygen; but reverted weaker gels obtained from highly masticated rubber, or those produced in the presence of a larger amount of initial oxygen, or stronger gels which have been reverted by too long irradiation in the presence of too much oxygen, cannot be regelled without the addition of further amounts of activator. In general, the smaller the rubber molecules in a given solution the slower will be the gelling and the weaker the final gel.

The solvents which combine with the rubber promote gel formation more readily than those which do not. Gelling in such solvents is less easily influenced by activators or retarders; and the gels thus formed are firmer and more stable to reversion. Moreover, the more degraded rubbers which refuse to gel in inactive solvents will gel in active solvents. Certain antioxidants, *e. g.*, phenyl- β -naphthylamine, have been reported to accelerate the *photochemical* oxidation of rubber solutions (4): these same compounds delay gelling, and the ultimate gels are weaker than those obtained in the absence of the antioxidant.

In the presence of larger amounts of activator the effects of such antioxidants are smaller. The presence of an antioxidant appears to have no delaying effect upon reversion, and may even slightly accelerate it; but gels which have undergone reversion in the presence of an antioxidant are found to regel under conditions which will not cause the regelling of a reverted product which has been formed in the absence of such antioxidant. Pro-oxidants delay or inhibit gelation, and "peptizing" agents such as thionaphthols entirely prevent gelling, in both the presence and the rigidly enforced absence of oxygen.

Most of the synthetic rubbers form photogels, the simple butadiene polymers (*e. g.*, Buna 85) more readily, the butadiene interpolymers much less readily, and the chloroprene polymers (*e. g.*, Neoprene M) less readily than natural rubber. In the case of the butadiene rubbers the speed of gelation and the firmness of the gel are less influenced by the presence of oxygen. The gels do not revert when irradiated in contact with oxygen and will often undergo syneresis with separation of much firmer gels, which can be dried and which will give higher tensile strengths than the corresponding gels from natural rubber. Antioxidants delay gel formation, and here again the delay is not greatly affected by varying amounts of oxygen. Gel formation with the Neoprenes invariably takes place inward from the wall exposed to the light, whereas with natural rubber and the straight butadienes gel formation takes place through the mass simultaneously.

Oxygen thus appears to hinder photogelling, not so much by combining with, and so rendering innocuous, the radical centers as they are formed, as by effecting oxidative degradation of the rubber chains in the normal manner. This is understandable in view of the independence of the autoxidation process of any hydrogen-removal procedure prior to the actual attack by the oxygen molecules; and it accounts for the smaller sensitivity to oxygen of butadiene rubbers during photogelation than of natural rubber, since the latter is intrinsically the more readily oxidizable. Antioxidants have a direct effect on gelling by destroying the radical centers of the rubber chains, but may have a secondary effect insofar as they can become mildly pro-oxidant under strong illumination. Activators presumably become effective by themselves dissociating to produce active radicals, either directly under the influence of light or indirectly through interaction with rubber radicals (so leading to longer chains or more extensive reaction), and the different specific capacities of solvents to assist the process doubtless spring from the same cause.

The foregoing evidence appears to be qualitatively quite consistent with the simple hypothesis of photogelling outlined at the beginning of the section; and very direct evidence of the essential correctness of the hypothesis has now been contributed by Bateman (2) as the result of a close study of the secondary results attending the irradiation of rubber. He finds that irradiation with ultraviolet light of highly purified and meticulously out-gassed rubber hydrocarbon *in vacuo* ($p < 10^{-6}$ mm. Hg) immediately effects slight but significant decomposition. This can be followed by accurate measurement with a McLeod gage of the amount of the gaseous mixture which results. Such measurements at various wave bands show that

the short ultraviolet region is the more effective; but, although there is a marked reduction at *ca.* 270–280 $m\mu$, activity is retained as far as 370 $m\mu$. The over-all efficiency in the range 220–370 $m\mu$ is represented by a quantum yield of the order of 10^{-4} . Since comparative experiments reveal that photooxidation has very different characteristics, the mechanism of oxidation must, in general, be other than one in which oxygen participates subsequent to dissociation of the hydrocarbon. Although the composition of the gaseous product varies to some extent with wave length, microcombustion analysis indicates that hydrogen is the main constituent. This correlates with the efficiency drop at 270–280 $m\mu$, as the energy of quanta at longer wave lengths is less than the dissociation energy of normal C—H bonds. Retention of activity as far as 370 $m\mu$, however, suggests that weaker C—H linkages are also present. Examination of the rubber thus altered by light is severely restricted by the rapidity with which it becomes insoluble. It develops swelling behavior in benzene akin to vulcanized rubber; and the decrease in plasticity which it shows also points to the occurrence of considerable cross linking.

4. Hydrogen Bonding

Amide groups are known to interact with one another extensively, probably owing to the formation of hydrogen bonds. Similar bonding might be expected to produce insolubility in polyhydroxy derivatives of natural rubber, or perhaps to enter to some extent into vulcanization changes. All oxidative treatments of rubber, however, which give high percentages of hydroxyl groups result in such gross degradation that any associative effect due to hydrogen bonding which there may be does not become apparent. In respect to vulcanization, the low concentration of hydroxyl groups present initially, even in well-milled rubber, is not increased by the curing process, and thiol groups which may be produced in the process show no tendency (73) to participate in hydrogen bonding.

5. Insolubilization

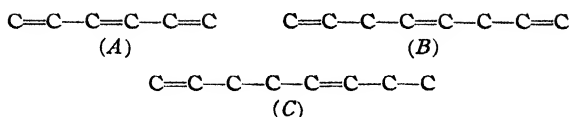
One of the most embarrassing phenomena encountered in connection with the chemical modification of rubber is the unexpected development of insolubility. Often it arises more or less rapidly after a derivative of rubber has been removed from solution and thoroughly freed from traces of solvent *in vacuo*. The most plausible cause of this change is the appearance of a certain degree of cross linking—presumably rendered easy by the close

proximity of the individual molecules in the solid condition. Highly oxidized rubber becomes more viscous on thorough drying, the change being accompanied by loss of water, presumably largely intermolecularly. The maleic anhydride adduct of rubber shows marked insolubilization on being recovered from its solution, possibly owing to the cross-linking action of residual traces of the peroxide used in preparing the adduct; and various other modified rubbers—including the thiocyanogen, hydrogen sulfide and nitrosyl chloride derivatives—show comparable changes which cannot be regarded as the normal results of the proportions of polar groups introduced. The insolubility of gel rubber itself is believed to be due to occasional cross links between the rubber chains, although, since the protein impurity of natural rubber is concentrated in this fraction, the links may possibly be largely between hydrocarbon and protein. The change is in the opposite direction from that brought about in rubber and its derivatives by oxidation, and, just as minute percentage proportions of oxygen are effective in reducing the molecular weight of rubber, the occurrence of a very minor degree of cross linking may be very effective in producing insolubilization. No other explanation of this change has so far been forthcoming.

V. Specific Reactivity of Vulcanizing Agents

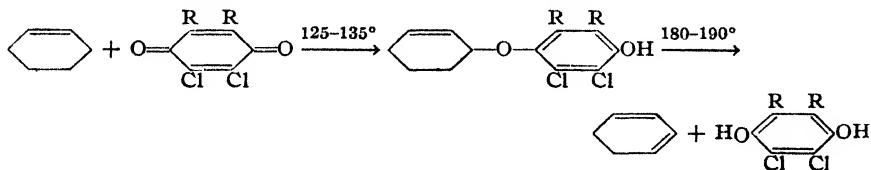
1. Sulfur

It is an astonishing fact that no comprehensive formal investigation of the action of sulfur on polyolefinic substances has been carried out, in spite of the great interest this subject possesses in connection with vulcanization. Many workers interested in vulcanization theory have speculated on the course of reaction, but their speculations have for the most part rung changes on the conceivable ways in which sulfur could add to the olefinic double bonds, with and without causing molecule linking. All of these suggestions, from the early ones of Prins (64) onward, lack experimental foundation and deserve slight consideration as serious contributions to vulcanization theory. Sulfur, indeed, has never been recognized by organic chemists as belonging to the group of additive reagents for olefins, and the meager information available about its reactivity toward polyenes has indicated that its behavior is neither simple nor homogeneous. There is no doubt that sulfur reacts fairly freely with olefins at temperatures above 100°; this applies particularly to olefins which contain α -methylene groups. It is necessary, however, to distinguish carefully between the reactivities of the different allied polyolefinic systems:



since neglect of differentiation has in the past been responsible for much confusion in the discussion of reaction mechanisms. Over the field of polymerization phenomena it is very noticeable that sulfur is not employed as a polymerizing agent for polyolefins, and among allied compounds has sometimes been reported to be a definite inhibitor: nevertheless it is not unlikely that substances containing the very sensitive methylene-interrupted system (B) may behave with sulfur as they do with oxygen, so becoming conjugated and thereafter being liable to undergo polymerization. An observation of Whitby, in fact, suggests very strongly that a substance of this type (linseed oil) is affected in just this way (87). The constitution of system (B), however, is sufficiently different from that of the rubber system (C) to cause a marked difference in behavior toward both oxygen and sulfur: indeed there is no sound experimental ground at all for believing that sulfur serves as an effective polymerizing agent for rubber.

Sulfur has been used for many years as a dehydrogenating agent for hydroaromatic compounds (to convert them into the corresponding aromatic compounds) but latterly selenium, platinum, palladium, and sometimes substituted quinones, have been found to act with greater efficiency. Platinum and palladium remove the hydrogen *catalytically* at temperatures between 170° and 300°, and are able to attack even saturated hydroaromatic compounds: sulfur and selenium, on the other hand, although they function over much the same temperature range, are capable of dehydrogenating only unsaturated hydroaromatic systems and are themselves converted into their hydrides in the process. Now since ethylene and other olefins which contain no α -methylene groups show great stability toward sulfur, it seems fairly certain that the attack on these latter reagents begins at the labile hydrogen atoms of the α -methylene groups, and an apparent pointer to the mode of reaction is afforded by the observed dehydrogenating action of various quinones. Thus the complex quinone, dichloroquinizarin quinone, when heated with cyclohexene at temperatures a little below the

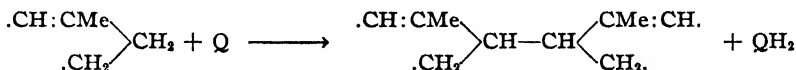


usual vulcanization range combines to form a hydroquinone-substituted olefin, and this when heated at a higher temperature undergoes an elimination reaction, to yield a cyclic diene and the hydroquinone (16).

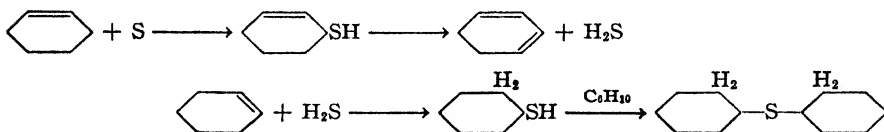
Chloranil is able to effect both stages of the dehydrogenation at 140° in the case of representative hydroaromatic substances (1). Possibly the vulcanization of rubber by certain active quinones (Q), including chloranil, begins in just this way, the conjugated units so formed combining with the ethylene units in other rubber molecules in Diels-Alder fashion:



On the other hand, some more direct mechanism ending as follows may really be responsible:



However this may be, it would seem at first sight that Meyer and Hohenemser in demonstrating that sulfur and cyclohexene combine when heated together in a closed vessel at 140–150° to give cyclohexyl mercaptan and dicyclohexyl sulfide (51) went far toward establishing that the quinone-dehydrogenation mechanism holds good for the action of sulfur on olefins also.



This conclusion would mean, if it were applied to rubber, that any cross linking which occurs during vulcanization is achieved only by the formation of sulfide bridges, and at the expense of saturating two double bonds per cross link formed. The probable incorrectness of this conclusion is indicated by much of the chemical evidence connected with vulcanization, but its essential falsity appears at once if the evidence of Meyer and Hohenemser is somewhat amplified. As far as can be gathered from the published record of these authors, the saturated mercaptan and sulfide each account for about 20% of the cyclohexene consumed, the remainder of the reaction product apparently consisting of high-boiling oils. Jones and Reid (38) repeated the experiment using ethyl tetrasulfide as the source of sulfur, and obtained the same two identified products in yields amounting to about 13% and 20%, respectively, of the cyclohexene consumed.

Recent repetitions (7) have shown that, over a wide range of sulfur concentration (from 2 to 30% by weight of the cyclohexene taken), only very small amounts of hydrogen sulfide and mercaptan are ever formed at 140–150°; instead, the product consists of a mixture of mono-, di-, tri-, and tetrasulfides of the general formula $R.S_x.R'$ ($x = 1$ to 4) in which the amount of monosulfide is very small.* The constitution of the polysulfide groups, whether of the disulfide type with coordinated sulfur ($.S.S.$ or $.S.S.$), or



most usually of the chain type ($.S.S.S.S.$), is unknown. Desulfuration of these sulfides with Raney nickel containing adsorbed hydrogen gives monomeric hydrocarbons still showing some unsaturation, although some part of any original unsaturation which groups R and R' may have possessed is likely to have been destroyed by hydrogenation. These results, as far as they go, give no indication at all of any significant degree of carbon-to-carbon cross linking having occurred, or, to put it in another way, all cross linking effected in the vulcanization reaction is of the nature of sulfur bridging. Only when these *primary* products of the action of sulfur are heated to *ca.* 160° or above, or alternatively when the original reactants are heated to the higher temperature, is any considerable amount of hydrogen sulfide, monosulfide or mercaptan formed. If the distillative separation of the sulfurated products is attempted in anything but an efficient molecular still operating below the vulcanization temperature, then extensive degradation of the sulfides, with formation of large amounts of hydrogen sulfide, monosulfide and mercaptan, is inevitable; and in this event the products ultimately isolated are of course not the original ones formed. 1-Methylcyclohexene gives exactly comparable results when it is heated with sulfur at 140–150°; and in the case of both cyclic olefins the radicals R, R' contained in the sulfides appear to retain a considerable degree of the original olefinic unsaturation (7). Much difficulty attends the exact determination of the degree of this residual unsaturation in cyclohexenic derivatives because of the inherent tendency of the latter to undergo a measure of substitution in the presence of the halogen reagents which are usually employed in the determination of unsaturation; but carefully conducted elementary analysis gives hydrogen values which lie about half-way between those required for sulfides displaying the original mono-olefinic condition of both the groups (R and R') and those required for sulfides containing saturated groups R and R'. There is thus a strong sug-

* The monosulfide may be a decomposition product. The simplest sulfide from isobutylene appears to be the disulfide $R.S.S.R.$

gestion that the vulcanizates $R.S_x.R'$ contain one saturated and one unsaturated hydrocarbon radical, so that the products from cyclohexene would tend to be cyclohexyl-cyclohexenyl sulfides.

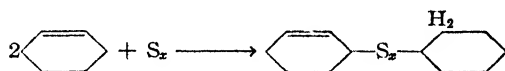
Two other features of the cyclohexene reactions are of interest, *viz.*, the hydrogen/carbon ratios of the sulfides formed, and the extent to which simple dehydrogenation of the cyclohexene ring occurs. In all experiments the hydrogen/carbon ratio of the mixed sulfides differed insignificantly, or not at all, from that of the parent hydrocarbon, and in no example investigated did the cyclohexadiene or benzene derived by dehydrogenation of cyclohexene (determined spectrographically as benzene) amount to more than 2% of the cyclohexene consumed in sulfide formation. Thus the reaction cannot be regarded as proceeding according to the simple two-stage reaction scheme involving dehydrogenation and hydrogen sulfide addition formulated above; and hence some less simple reaction scheme probably involving active radicals and a chain mechanism must be involved.

With open-chain polyisoprenic hydrocarbons, a somewhat different result is to be observed. No dimers or trimers of the hydrocarbon such as would be formed by direct carbon-to-carbon cross linking of the monomer molecules have been found. Instead, those molecules that react at all (which, during several hours' heating at 140–150°, is by far the minor proportion*) give largely monosulfide derivatives of two types (7). It is to be expected from what has been said above that chemical reaction which brings about molecule linking in a mono-olefin may, in a polyolefin, occur intramolecularly as well as intermolecularly. It is no surprise, therefore, to find that much (usually the major part) of the sulfurated product is a monomeric cyclic monosulfide and the remainder mainly a dimeric sulfide, $R.S.R'$, with some proportion of polysulfide apparently of the type $R.S_x.R'$. This applies whether the hydrocarbon is dihydromyrcene, $H[.CH_2.CMe:-CH.CH_2.]_2H$, geraniolene, $CH_3.CMe:CH.CH_2.CH_2.CMe:CH_2$, or squalene, $H[.CH_2.CMe:CH.CH_2.]_3[.CH_2.CH:CMe.CH_2.]_3H$; and the remarks made above still hold concerning: (a) the retention unchanged of the original hydrogen/carbon ratio in the sulfurated products, and (b) the production of a (roughly) half-way degree of saturation in those of the olefinic units

* For example, dihydromyrcene undergoes about 14% conversion into sulfurated products when heated for five hours at 140° with a half-atomic proportion of sulfur, so giving products containing up to 42% of sulfur (*i. e.*, > three atoms per $C_{10}H_{18}$). The same hydrocarbon undergoes 14% conversion when heated for three hours at 180° with a quarter-atomic proportion of sulfur, giving, then, products containing up to 24% of sulfur (*i. e.*, > 1.5 atoms per $C_{10}H_{18}$).

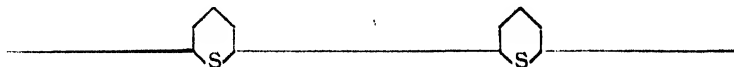
that react (*i. e.*, halfway between the original degree of hydrocarbon unsaturation and that which would be attained if all the *reacting* olefinic units became saturated). The accuracy of the unsaturation values determined directly for these simpler olefins is a little uncertain for reasons mentioned later.

The net result, therefore, of the action of sulfur on simple mono-olefins at *ca.* 140° appears to be that pairs of molecules become cross linked by the sulfur, and that approximately one double bond is lost between each two interacting molecules. If this conclusion is correct, it means, apparently, that where vulcanizing reaction results in the formation of a sulfide, R.S.R', the radicals R and R' are on the average, respectively, unsaturated and saturated:

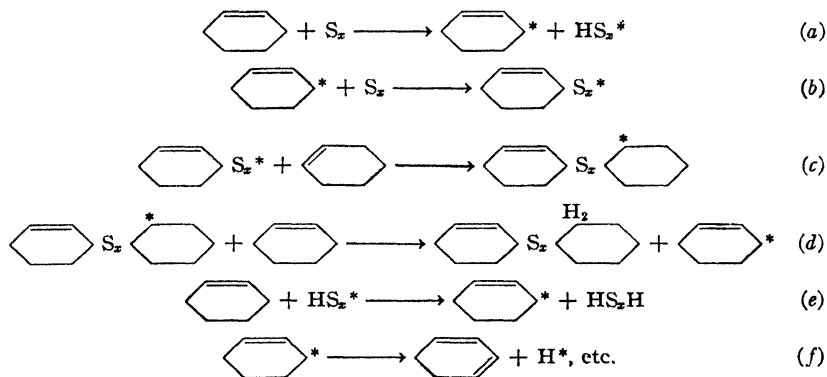


In other words, *one double bond is lost by the hydrocarbon system for each sulfur atom that becomes chemically incorporated.* It will readily be seen that, if the hydrocarbon system here concerned were an immensely complicated one such as the rubber system, and the reaction products were accordingly inseparable by existing techniques, the deduction might erroneously, but with apparent justification, be drawn from the over-all analytical determinations available that each sulfur atom entering reaction is expended in attacking one double bond in some particular molecule, thereby saturating it. It must necessarily follow, of course, that where the product is a di-, tri- or tetrasulfide, R.S_x.R', a good deal less than one double bond is lost per atom of sulfur incorporated, so that the net average loss of unsaturation per atom of sulfur incorporated is likely to fluctuate as the assemblage of sulfides formed in particular operations changes. Only where the proportion of mono- to polysulfide is high (which present indications suggest is most likely to happen where the over-all uptake of sulfur is quite low) could the result "one double bond lost per atom of sulfur incorporated" be realized.

In the case of polyolefins such as the polyisoprenes, the olefinic units which become directly linked by sulfur may be taken largely from the same molecule; and to the extent that this happens intramolecular cyclizing action occurs. The introduction of one or more cyclic sulfide units into a long rubber chain:

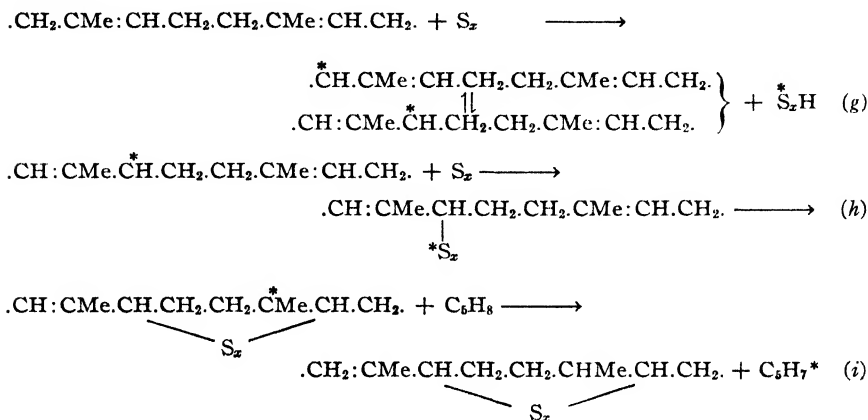


is clearly ineffective for vulcanization purposes if cross linking is the required condition, but if the establishment of secondary valence links between the combined sulfur atoms of different molecules (or between sulfur and carbon, or sulfur and hydrogen) enters at all into the vulcanization scheme as a necessary or desirable subsidiary to primary linking or bridging, then sulfur expended in cyclizing action (and there is apparently no other way of expending it except to form sulfur bridges) may well be of real importance. Unfortunately, insoluble high-molecular polyolefinic materials do not lend themselves to the very certain determination of the relative numbers of sulfide rings and bridges formed during vulcanization treatment, but the analogy afforded by the behavior of the low-molecular polyisoprenes—dihydromyrcene, geraniolene and squalene—suggests it may be high. The existence and effectiveness (or otherwise) of secondary valency links in vulcanizates may safely be left to future physicochemical demonstration when the lines of organic reaction are laid bare, but it is of present interest to consider the mechanism whereby both intramolecular (cyclic) and open-chain (cross-linked) sulfides could be formed. If the reaction between elementary sulfur and the olefins may be considered to have a chain mechanism, as seems very likely, stages (a) to (f) below could be reasonably postulated in the case of cyclohexene to fulfill the saturation requirements outlined above:



Corresponding to this series there would be for the intramolecular type of reaction a similar series which may be expressed for the polyisoprenic group by stages (g) to (i), in which S_x is normally S. Here the point of attack by sulfur at one or other of the resonating systems ($\cdot\text{CH}\cdots\text{CMe}\cdots\text{CH}\cdot$ and $\text{CMe}\cdots\text{CH}\cdots\text{CH}\cdot$) which would be formed by the detachment of a hydrogen atom from the olefinic unit $\cdot\text{CH}_2\text{CMe}:\text{CH}\cdot\text{CH}_2$ has been so

selected as to give a six-membered ring (one of two isomers possible), although alternative five- or even seven-membered rings may conceivably be formed:



There are experimental reasons for believing that *epi*-sulfides containing the grouping $\cdot\overset{\text{C}}{\diagdown}\text{C}\text{---}\overset{\text{C}}{\diagup}$ do not occur at all among these intramolecularly

formed sulfides, but the possibility of their appearance in some degree has not been finally excluded (7). It should also be mentioned that, although the dehydrogenation-hydrogen sulfide addition mechanism appears to be excluded by the paucity of conjugated hydrocarbon found at the end of operations and by the formation of polysulfides, there is nevertheless a possibility that this simple mechanism plays some part, since any conjugated material formed would probably be consumed preferentially in the hydrogen sulfide addition reaction, giving unsaturated mercaptans which might then add to cyclohexene to form semiunsaturated sulfides. This consideration raises the question of the effectiveness of hydrogen sulfide in producing molecule linking, which is of particular interest in relation to the part (if any) played by the hydrogen sulfide formed by the action of sulfur on rubber during vulcanization operations. It might be supposed that this reagent adds readily to olefins: on the contrary, reaction is rather difficult to induce unless the reactants are irradiated, or less effectively, brought into contact with an active iron sulfide or iron oxide catalyst. Liquid hydrogen sulfide has been found to add easily and fairly completely in the "abnormal" direction (*i. e.*, in the direction opposed to the Markownikoff rule) to the double bond of propene or of 1-butene in ultraviolet light, giving thereby mixtures of mercaptans and alkyl sulfides (86).

Likewise, addition of the gaseous or liquid reagent in the "normal" direction has been achieved in the case of isoprene and of propene up to a 25% yield (8). The most painstaking efforts, however, to bring about smooth and continuous addition of liquid or gaseous hydrogen sulfide to solid or dissolved natural rubber have failed (7). Under photochemical activation the liquid reagent, used with solutions of rubber, gives (very slowly) ungelled products containing up to 2% of sulfur, provided a reaction sensitizer such as acetone is present. Under the influence of active iron catalysts, and using an excess of the liquid, ungelled products containing about 1% of sulfur (doubtless products of "normal" addition) have been obtained. With either procedure, small amounts of gelled products containing a considerably higher proportion of sulfur than that usually obtained (maximum, 10%) are prone to appear. Where solid rubber has been heated with an excess of liquid hydrogen sulfide at 150° for 14 hours, products containing up to *ca.* 4% of sulfur have been obtained. These show very definitely, on superficial examination, true physical characteristics of vulcanization; but direct comparisons of their tensile properties, etc., with those of comparable sulfur-vulcanized samples are not available (7).

It is noteworthy that Jones and Reid have reported (38) that sulfur is an effective catalyst for the addition of hydrogen sulfide to simple olefins, although it may be remarked that these authors obtained rather poor yields of the mercaptan and the sulfide addition product, and they used amounts of the "catalyst" so large that it might well have figured as the reagent. Where sulfur was officially the reagent, their results compare favorably indeed with those in which abundant hydrogen sulfide was also supplied, so that suspicion arises as to the true origin of the products. Yet their conclusion—that not only hydrogen sulfide but (at a faster rate) also alkyl mercaptans add to olefins in the presence of sulfur to give products of "normal" addition—has been found by the most careful re-examination* (7) to be amply justified. Apparently the (slow) ionic addition of hydrogen sulfide is catalyzed by sulfur or metal sulfide, the catalyst polarizing the double bond by co-ordination, so giving a "normal" reaction; and this can occur alongside the (rapidly propagated) radical olefin-sulfur reaction which yields mercaptan and sulfide as secondary products above 160°. A little disulfide, R.S.S.R', is formed side by side with monosulfide in the addition of hydrogen sulfide to the simpler olefins, thus suggesting that active radicals R.S* play a considerable part in bridge formation, and

* A stainless-steel autoclave was employed which doubtless could be relied on to give traces of iron sulfide with sulfur. Whether elementary sulfur alone is effective is uncertain.

carbons, of consecutive substitution and additive reactions for each sulfur atom entering combination. The loss of one double bond for each sulfur atom incorporated, which has so often been claimed—on the basis of rather unsatisfactory technique of unsaturation determination—to hold over a very wide range of rubber-sulfur combination, is difficult at present to account for unless cyclic or bridged *monosulfide* derivatives are formed to the exclusion of polysulfides $R.S_x.R'$. The formation of hydrogen sulfide in small amount during rubber vulcanization appears to be quite unavoidable, but in the case of impure rubber hydrocarbon may arise in part or largely (at least in the early stages of sulfur intake) from the nonrubber impurity. The influence of this gas on the progress of rubber-sulfur vulcanization is possibly of some importance, since the complete removal of the gas from the scene of reaction by continuous high-vacuum pumping causes the rate of rubber-sulfur combination to be depressed (7). Conversely, an artificial increase in the concentration of the gas causes, as previously noted by Buizov and Popova, the rate of combination to increase. Since the rate of hydrogen sulfide addition to rubber, even at high concentrations of the reagent, is ordinarily very slow, the increase in the rate of vulcanization seems unlikely to be due to the addition of the hydrogen sulfide to the double bonds of the rubber to form cross links; hence it may be necessary to envisage the existence of a catalytic influence of hydrogen sulfide on the rate of rubber-sulfur combination. It is somewhat curious that this is so, for the catalytic effect of sulfur on the addition of hydrogen sulfide to the simpler olefins seems unchallengeable.

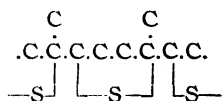
The adverse influence of atmospheric oxygen on the rate of rubber-sulfur combination is probably indicative of a chain reaction mechanism. If all traces of oxygen are removed from the reactants by adequate evacuation before reaction is begun in sealed vessels, the rate of sulfur combination is markedly increased (7).

One of the most important pieces of evidence concerning the cross linking of rubber by sulfur is that afforded by the action of methyl iodide on vulcanizates at 24°. Selker and Kemp (72) have recently reported that part of the combined sulfur is removed as trimethylsulfonium iodide, and that the sulfur so removed is linked to the α -methylene carbon atoms of the rubber chain. Moreover, the sulfur linkages in a GR-S stock apparently do not differ chemically from those present in a rubber vulcanizate.

The direct carbon-to-carbon linking of olefins which is promoted so effectively by dibenzoyl peroxide might be expected to have a counterpart in the reaction between sulfur and olefins. This expectation is abundantly realized where aromatic olefins containing active α -methylene groups are

concerned (although the temperature of reaction required is usually somewhat above normal vulcanization temperature). Among aliphatic olefins, however, no such cross linking has yet been reported; and, indeed, many special experiments to produce this effect in some degree with sulfur have consistently failed. It is to be remembered that carbon-to-carbon cross linking could quite well occur intramolecularly as well as intermolecularly in the case of rubber chains. Among carbonyl compounds the occurrence of carbon-to-carbon cross linking by the action of sulfur is exemplified by acetophenone ($2 \text{ Ph.CO.CH}_3 + \text{S} \rightarrow \text{Ph.CO.CH}_2.\text{CH}_2.\text{CH}_2.\text{CO.Ph} + \text{H}_2\text{S}$) (37).

Midgley (54) has submitted ebonite containing approximately one atom of sulfur per C_6H_8 unit to pyrolysis at high temperatures, and obtained thereby a mixture of four dimethyl- and methylethyl-thiophenes, from which evidence he concludes that ebonite probably has the skeleton:

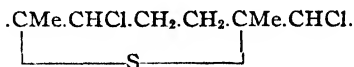


This deduction, if it were sound, would suggest two possible modes of reaction by sulfur, one similar to the cyclizing addition of maleic anhydride referred to earlier, and the other involving α -methylene attack by the sulfur to form .SH groups, followed by addition of the latter at near-by double bonds, so giving carbon-sulfur rings. There is very good reason, however, for doubting the diagnostic value of evidence such as this obtained by pyrolysis at very high temperatures (up to 700°).

2. Sulfur Monochloride

The formation of satisfactory vulcanizates from natural rubber by the action of sulfur monochloride in the cold is strong evidence in favor of the cross-linking hypothesis of vulcanization. The halide behaves as a true bifunctional additive reagent toward ethylene at room temperature, so serving to link pairs of hydrocarbon molecules together and liberating at the same time crystalline sulfur ($2 \text{ CH}_2:\text{CH}_2 + \text{S}_2\text{Cl}_2 \rightarrow \text{CH}_2\text{Cl.CH}_2.\text{S}.\text{CH}_2.\text{CH}_2\text{Cl} + \text{S}$) (31). The empirical composition of rubber vulcanizates formed by use of sulfur chloride afford some evidence that the reaction with rubber proceeds comparably with that observed with ethylene (53); and it appears that the linking of molecules in each case is entirely or largely independent of the sulfur liberated, since part of this at least can be re-

covered even with rubber. Under vulcanization conditions the interaction of halide and rubber is doubtless almost entirely of intermolecular type, but when the reaction is conducted in solution an intramolecular reaction may well occur which gives sulfide rings:



3. Grignard Reagents

Lightly oxidized rubbers which contain free hydroxy, epoxy, and other oxygen groups capable of reactivity with Grignard reagents have been found to undergo a species of vulcanization when placed in solid condition in contact with ether solutions of magnesium alkyl halides or zinc alkyls; if they are first dissolved in benzene, they give gels (55). The solid vulcanizates show marked improvement in tensile strength over the original rubber, and revert to the original unvulcanized condition when treated with water or acetic acid. The gels can also be caused to revert to the original sol condition by addition of water or excess of acid; they can be "peptized" by addition of excess of Grignard reagent, zinc alkyl, anhydrous aluminum chloride, magnesium bromide, etc., and "depeptized" to give the gel again by cautious addition of a restricted amount of acetic acid. The cycle of gelling, "peptizing," "depeptizing" and reverting can be repeated (55). This production of vulcanization appears to be due to genuine cross linking, the links being formed by interaction of >C—O—MgX or >C—O—ZnX with one another in virtue of the strong tendency of oxygen under Grignard conditions to form oxonium salts—probably of the type $\text{>C—O—Mg—O(MgX)X—C<}$. Such complexes would naturally be sensitive to excess of Grignard reagent or other metallic halide which could compete in oxonium salt formation with the limited amount of Grignard reagent already combined. In the "peptized" state each oxygen atom may well have entered the oxonium condition—possibly to give complexes of the type >C—O(MgX)(X)(MgR) .

This phenomenon is of the greatest interest in two respects: first, in that it shows how serviceable quite feeble cross links—easily produced, easily disrupted—can be in forming sufficiently effective constraints between the rubber chains to give a true vulcanized condition; and, secondly, in that it permits a very rough upper limit to be assigned to the number of cross links per molecule required to be formed (say ten for moderately degraded rubber) in order to give a real degree of vulcanization.

VI. Constitution of Sulfur Vulcanizates

1. Proportion of Sulfur

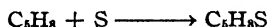
Various workers have established that soft rubber vulcanizates formed from the ordinary mixtures of compounding ingredients by heating them at constant temperature for different periods of time contain, up to a point at which the free sulfur approaches exhaustion, percentages of combined sulfur which are proportional to the time of heating. With the advent of organic accelerators it soon became clear that the proportions of 3–5% of combined sulfur, which were formerly thought to be necessary for the production of good vulcanizates, were no longer required, since much smaller proportions served to produce the desired physical properties. Moreover, different accelerators, even when used in proportions that would give equivalent physical properties under the same conditions of vulcanization, did not bring about the combination of the same proportion of sulfur—and in fact the variations were so wide that the proportion of combined sulfur in vulcanizates lost all general significance (32).^{*} If, then, the essential part of vulcanization is considered to be either the addition of sulfur to the double bonds of the rubber, or the production of sulfur bridges between the rubber chains—or, indeed, as has been most often supposed, both function together in a combined additive cross-linking reaction—the almost complete lack of relationship between the proportion of combined sulfur and the resulting physical properties becomes very disturbing. Yet, quite definitely, the reaction of sulfur with the rubber is a necessary feature of sulfur vulcanization, so that apparently either the production of good physical properties is independent of cross linking altogether, or cross linking is not purely a matter of sulfide bridges. The latter alternative would include three important possibilities: (a) that production of good physical properties depends in some degree on the establishment of direct carbon-to-carbon cross links or of heteroatom (*e. g.*, oxygen or accelerator fragment) bridging; (b) that the chemically incorporated sulfur is distributed very variably between intermolecular sulfide bridges and intramolecular dispositions; and (c) that secondary valence links, probably easily ruptured and redistributed, between the sulfur atoms (or sulfur and carbon atoms) of different chains, constitute an important and indispensable auxiliary to a foundation of not very numerous primary valence cross links. The two alternatives are fundamental issues in the consideration of the constitution of vulcanizates; and it is necessary to try to determine in what degree their

^{*} The anomalies are due in part to the specific action of zinc oxide.

respective claims to acceptance are supported or opposed by the complex phenomena connected with organic accelerator action.

2. *Decrease in Unsaturation during Vulcanization*

Spence and Scott concluded from their early work on the unsaturation of sulfur vulcanizates that the proportion of combined sulfur corresponds exactly to the decrease in unsaturation, and consequently that the sulfur adds entirely to the double bonds. The reaction was thought to be representable by the simple equation (77, 78):



but it is now known that the maximum amount of sulfur with which rubber can be induced to combine considerably exceeds one atom per C_5H_8 of the rubber (83). The idea that sulfur reacts by adding to the double bonds of rubber has remained as a background to thought on vulcanization questions, although the later workers have had suspicions as to its correctness; but the acquisition of accurate knowledge concerning the relation between the combination of sulfur and the concomitant loss of unsaturation by the rubber has been severely hindered by the high insolubility of all vulcanizates. If the insolubility of the vulcanizates arises from the fact that the original rubber chains have been joined together by cross links—perhaps to form a single large molecule—then it seems reasonable to suppose that dissolution of the vulcanizates will not be possible until some of the links (original or new) holding the structure together have been broken, and this presumably can only occur by oxidative or thermal degradation, or by the action of specific chemical reagents. It has proved possible in practice to bring most vulcanizates into solution by heating them for a period with a suitable high-boiling solvent. Blake and Bruce (3) have used *p*-dichlorobenzene as the high-boiling solvent in preference to the not completely stable tetrachloroethane which had previously been employed for the purpose by Kemp (40, 41). In this medium (b.p., 172°) complete dispersion of samples occurs in a few hours, thereby giving solutions which can, after dilution, be used directly for the determination of unsaturation. Whether the dispersion effected is due to thermal degradation or to oxidation is not immediately obvious. Any serious thermal effect among C—C bonds at *ca.* 172° is very unlikely. On the other hand, recent observations indicate that oxidation very definitely assists in, but is not essential for, dispersion, since samples heated with boiling *p*-dichlorobenzene in an atmosphere of not specially purified nitrogen take 2.5 to 3.5 times as long to disperse as they do in air (33), and samples sealed in most meticulously evacuated

tubes (high vacuum) take from 3 to 6 times as long to disperse as similar samples treated in contact with air, but still do disperse (7). In view of the effectiveness of quite small proportions of oxygen in drastically reducing, even at room temperatures, the average molecular weight of rubber by chain scission, it is not unlikely that sufficient links become oxidatively severed, when oxygen is available, to aid materially in complete dispersion—and this could quite well happen without the unsaturation of the vulcanizates being much affected. Whether the small changes of unsaturation which would be caused by this oxidation are too small to be distinguished from the experimental error must depend on the accuracy of the method of determination employed, but the best technique at present available has revealed (7, 33) no difference between the unsaturation of samples dispersed in air and in nitrogen, respectively. The Blake and Bruce method of effecting dissolution, used in conjunction with Kemp's iodine value procedure, affords the best means yet disclosed for determining the unsaturation of vulcanizates. There is, however, a potential source of serious error in the method, and this concerns the extent to which the halogen reagent employed in the iodine value determination enters into more or less firm combination with the bound sulfur atoms of the vulcanizate, so giving the appearance of having been absorbed by olefin bonds. Halogens, like alkyl halides, tend to become strongly coordinated on the sulfur of sulfide groupings .C.S.C.; and this coordinated halogen may later be more or less completely liberated as hydrogen halide (and so become capable of estimation) as the result of the hydrolytic action of water. The error arising from this source may well be significant, and indeed very serious where the proportion of combined sulfur in a vulcanizate is high: its probable existence must be borne in mind in connection with the results which follow.

In the low-sulfur vulcanization of natural rubber effected by the aid of organic accelerators, neither the proportion of combined sulfur nor the percentage reduction in unsaturation bears any direct relation to the physical properties of the vulcanizate (12, 33). It has been reported, however, that the proportion of sulfur which combines for each double bond that is lost often (but not always) considerably exceeds one atom. The curve expressing the combined sulfur-unsaturation relationship remains practically linear during the combination of most of the sulfur, but after the optimum cure has been reached, and nearly all the sulfur has entered combination, the unsaturation values decrease gradually, but in some instances quite considerably, as the heating is continued. Of course any oxidation of the rubber which occurs during vulcanization, and there is no reason to suspect that this is at all important, will cause an independent reduction of un-

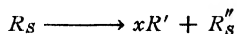
saturation indistinguishable from that due to vulcanization. Insofar as the optimum physical properties of vulcanizates can be judged by the tensile strength alone, the reduction in unsaturation accompanying the production of the optimum cure is remarkably small, usually amounting to between 1 and 4% of the total unsaturation. Moreover, observation of the change of tensile strength with decrease in unsaturation shows that, for stocks vulcanized with both sulfur and accelerators, those displaying the least decrease in unsaturation have the highest tensile strength; also, for both accelerated and unaccelerated stocks, the highest tensile strengths are displayed when the loss of double bonds per atom of combined sulfur (ranging from 0.4 to 1.7 double bonds per atom) is smallest (12, 33). Of course these relationships do not allow for sulfur which reacts with rubber and is then lost as hydrogen sulfide; also, insofar as the reaction mechanism involves free radicals capable of attacking either α -methylene groups or double bonds (see page 310) there can be no close correlation between the number of double bonds lost and the sulfur consumed.

3. *Dispersibility and Molecular Integrity*

The role of chemical cross links in the formation of highly insoluble colloids is a matter of hypothesis, the hypothesis resting on experimental observations connected with the building up of these complex materials and their behavior toward solvent media. There is no direct way of verifying that the cross links actually function in the manner supposed, even where the exact nature of the presumptive cross linking material is known, as in the case of divinylbenzene introduced into polymerizing styrene: consequently, in those colloid examples in which the existence of cross links is not only a matter of hypothesis, but their nature a matter for speculation, there is good reason for paying special attention to any signs of lack of structural coherency which appear when the colloid is brought into intimate contact with liquids or solids of apparently innocuous chemical character.

If the cross-linking hypothesis is assumed to be valid for rubber-sulfur vulcanizates, then the extreme smallness of the amount of sulfur which would theoretically be required to link together all the molecules of rubber by the minimum number of sulfur bridges can give the impression, which may well be false, that the whole of the molecules of rubber in the vulcanizates (even in low-sulfur vulcanizates) have become joined to form one large molecule, or at worst to form a few such molecules. The same impression is conveyed if the sulfur consumed in vulcanization is assumed to be primarily used in forming intermolecular C—C bonds by dehydrogenation ($\text{>CH}_2 + \text{S} + \text{>CH}_2 \rightarrow \text{>CH.CH<} + \text{H}_2\text{S}$) instead of sulfur bridges

Yet Williams has reported that various relatively simple substances, mostly organic bases or their derivatives, can be used in toluene solution to disperse both unaccelerated and accelerated rubber-sulfur vulcanizates, and from the resulting mobile solutions the vulcanizates can be precipitated fractionally, or as a whole, by the addition of alcohol (90). The process of dispersion according to Williams' observations does not *appear* to need oxygen, and since it can be effected at temperatures below 100° it hardly seems likely to involve the thermal rupture of C—C or C—S bonds. Moreover, in the same way that ordinarily there is no direct relationship between the physical properties of the vulcanizates and the amount of combined sulfur, so there is none between the same properties and the ease of dispersion. The fractions obtained from any vulcanizate by progressive precipitation show quite appreciable differences in sulfur and nitrogen contents and in physical appearance. Also, excellent vulcanization is seen to be compatible with a considerable degree of heterogeneity in the distribution of sulfur over the vulcanizate. As the total vulcanizates, but not all of the fractions, leave insoluble vulcanized films on evaporation of their solutions, there is apparently ground for the revolutionary belief that linkage by C—S—C bonds or C—C bonds is unnecessary for producing the vulcanized condition. Somewhat similar results had previously been obtained by Williams (90) in the case of rubber which had been lightly vulcanized by sulfur in solution at room temperature with the aid of an accelerator. Such sulfur vulcanizates can subsequently be dispersed in a few hours as the result of adding small amounts of the same or a different accelerator, and in some cases regelled on being kept, and again dispersed by addition of more accelerator. Prolonged standing during gelling or frequent regelling tends to give nondispersable gels. Williams suggested that the vulcanizate R_S formed by the chemical combination of rubber "units" R with sulfur S breaks up in presence of the accelerator or dispersing agent into x smaller "units" R' , which are more active chemically and colloiddally than R , together with a smaller chemical unit R''_S :



Thus Williams considers the vulcanization to consist of an initial chemical reaction followed by colloidal changes. A comparable phenomenon to dispersion is presented by the softening of rubber through milling into it substituted hydrazines, their organic or inorganic salts, or (less efficaciously) certain of their addition and condensation products (91); also by incorporating in latex or rubber substances such as naphthyl or xylyl mercaptan or mercaptobenzothiazoles. The softening effect is intensified if the tem-

perature is raised or the amount of softening agent increased, but the character of the change—whether purely physical, arising from decrease in or redistribution of the forces between the rubber molecules, or due to chemical action—is left in doubt. Sol rubber undergoes rapid dispersion in the presence of phenylhydrazine, but gel rubber, which in the absence of air resists dispersion by the base, is reported to succumb rapidly if air is admitted (91). This behavior is curious in view of the strong antioxidant properties of organic bases.

The facts connected with the dispersion of vulcanizates and the softening of rubber by nitrogenous materials need careful scrutiny, and especially the contribution (if any) of oxidation to the process, since oxygen is particularly liable to attack insidiously. Recent observation has shown that considerable amounts of piperidine, so far from assisting the oxidation of acetone-extracted crêpe rubber in benzene solution, effectively inhibit reaction for long periods (7) and no different result has ever been reported. Nevertheless, undiluted piperidine brings crêpe rubber (M , 353,000; N , 0.33%) into solution in a few hours at room temperature. The rubber recovered from solution by precipitation contains only the original proportion of nitrogen, but shows consistently nearly 20% diminution in molecular weight (M , 285,000). In contrast to this, precipitation of the rubber by a less polar solvent (ethyl acetate), or evaporation of the piperidine in high vacuum, increases the nitrogen content to 0.7 and 1.75%, respectively. Milled crêpe rubber behaves similarly, but is dispersed more slowly—possibly because of the superior physical compactness of the specimens. Turning to simple unaccelerated rubber-sulfur vulcanizates (no zinc oxide), dispersion is effected at room temperature by undiluted piperidine more rapidly than with the original crêpe rubber, and dissolution in a 10% solution of piperidine in benzene occurs easily, whereas attempted dispersion in a 10% solution of tertiary butyl alcohol in benzene leads only to swelling. Careful tests show, however, that if the sulfur vulcanizate is *prepared* under high-vacuum conditions instead of in the presence of air it will disperse with very much greater difficulty in piperidine-toluene than do equivalent specimens formed in contact with air. Solutions of rubber-sulfur vulcanizates in piperidine-toluene can be diluted indefinitely by benzene, or the piperidine removed by extraction with aqueous acid, without precipitation occurring. Moreover, the vulcanizates recovered by precipitation with alcohol have exactly the original nitrogen and sulfur contents, but will not now dissolve in benzene. The weaker bases, pyridine and phenylhydrazine, reduce the viscosity of rubber solutions considerably, but have a less intense dispersing action on unaccelerated rubber-sulfur vulcanizates

than has piperidine. Nevertheless, when phenylhydrazine hydrochloride, mercaptobenzothiazole and thio- β -naphthol are introduced into different portions of rubber (1 part per 200 parts of rubber) and the mixtures milled, the molecular weight of the rubber falls progressively in each case, and in 20 minutes is reduced by 57–61%, whereas the control specimen is only reduced by 45%. The rubber recovered from the milled phenylhydrazine hydrochloride mixture by dissolution of the latter in benzene and precipitation of the hydrocarbon with alcohol shows no significant change in nitrogen content and has almost exactly the same molecular weight as the mixture (7).

The utilization of zinc oxide in the formation of rubber-sulfur vulcanizates is found by Brown and Hauser (12) to slow down considerably the decrease in unsaturation of the rubber as vulcanization proceeds while simultaneously reducing the rate of sulfur combination. At the same time the tensile strength improves considerably as compared with a simple rubber-sulfur mixture. The zinc oxide proves to have a very pronounced effect in hindering dispersion by piperidine (7): the vulcanizates swell but do not dissolve. This effect increases beyond the stage of optimum cure: indeed, the overcured stiffened specimens not only do not dissolve, but show reduced swelling. The most remarkable effect, however, is obtained when rubber is vulcanized with tetramethylthiuram only (7, 90). The vulcanizates then do not disperse in piperidine at all. The result, therefore, of using tetramethylthiuram disulfide as a vulcanizing agent or zinc oxide as a vulcanization accessory is to give thoroughly coherent products.

What happens then in the softening and dispersion processes? No chemical action is reasonably to be expected between an organic base (or its salt) and a hydrocarbon, and indeed dihydromyrcene can be heated at 140–160° with an equimolecular quantity of phenylhydrazine in pure nitrogen for 24 hours without any attack on the hydrocarbon occurring; also, rubber is recovered after dispersion unchanged in nitrogen content. Similarly, dispersion of unaccelerated rubber-sulfur vulcanizates by bases takes place easily, and without (so far as has been found at present) any change occurring in nitrogen or sulfur content sufficient to be recognizable by elementary analysis. There can be no doubt at all that oxygen is thoroughly effective in aiding the dispersion of vulcanizates or of gel rubber where it is available in sufficient quantity, and it is not inhibited by powerful antioxidants.* The promotion of oxidation is probably the main effect pro-

* There is no question here of diffused daylight reversing the usual antioxidant effect of piperidine, as strong illumination is reported to do with phenyl- β -naphthylamine.

duced by the milling of most chemical softeners into rubber; but many careful observations would have to be ignored entirely if oxidation were to be held mainly responsible for the dispersion of vulcanizates by high-boiling solvents where pains are taken to exclude oxygen. Some other degradative mechanism must assist. In the case of dispersion of vulcanizates by organic bases of strong antioxidant tendency, oxygen cannot be responsible, and indeed the most rigid exclusion of air does not prevent dispersion. With regard to Williams' conclusion, based on dispersion experiments, that it is unnecessary to assume the presence of bridges in vulcanized rubber in order to account for the characteristic properties of the vulcanized state, it may be noted that all grades of dispersability of vulcanizates (by bases) from the complete undispersability of thiuram-accelerated rubber to the easy dispersability of rubber-sulfur are to be found. Also, in the examples of rubber vulcanized by sulfur monochloride or by light, where the existence of cross linking can hardly be doubted, the vulcanizates are still very easily dispersed in solvents if they are subjected to very mild autoxidation, although the ease of dispersion of the sulfur chloride product decreases as the number of cross links mounts. Rather, it seems that the true deduction to be drawn from dispersion experiments is that all vulcanizates are cross linked, but that the chemical nature as well as the number of the cross links differs from product to product as the essential details of curing change. Certain of the cross links are clearly resistant to the action of bases, but others, no less real, and no less essential to the production of good physical properties, easily succumb.

4. *Overcuring and Reversion*

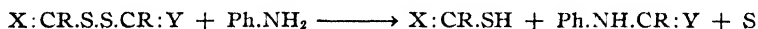
The resistance to dispersion by piperidine of rubber-sulfur-zinc oxide stocks increases with duration of heating during curing, and continues after the physical properties of the vulcanizate begin to deteriorate. Also, in low-sulfur stocks deterioration of physical properties amounting to softening (*i. e.*, reversion) of the vulcanizate occurs on unduly prolonged curing; and here again the onset of the deterioration does not coincide with increased ease of dispersion by piperidine, but instead the reverse holds (7). If, therefore, the development of good vulcanized properties is dependent on the increasing formation of cross links, the appearance of overcuring or reversion must mark a change in the chemical nature of the cross links rather than their destruction. This being so, it appears that the more ephemeral types of cross links give the better physical properties in the vulcanizate. In conformity with this conclusion are the previously mentioned results of Selker and Kemp to the effect that the combined sul-

fur removable from vulcanizates by methyl iodide at 24° is sulfide sulfur, linked to the α -methylene carbon atoms of the chains. It is found that in well-cured rubber stocks the less the quantity of sulfur present which is removable by methyl iodide, the higher is the tensile strength; also, when overcure sets in conversion of nonremovable to removable sulfur occurs; in addition to this, the sulfur which combines on overcure is completely removable (72). Complete devulcanization is stated to be achieved with methyl iodide at 100°. It is of interest that the sulfur linkages in GR-S rubber stocks do not appear to differ chemically from those present in pale crêpe rubber stocks.

There arises from the foregoing considerations with respect to the dispersion, overcuring and reversion of vulcanizates the question: what kind of cross links could be ruptured by organic bases, or by prolonged heating at vulcanization temperatures? No certain answer is available at present, but there are indications as to where the solution may lie. These turn around the intrinsic properties of the disulfide grouping and the constitution of rubber hydrocarbon. The disulfides, as might be expected from the position of sulfur in the periodic scheme, bear some resemblance to peroxides, and show a readiness to undergo scission between the sulfur atoms. They are thus readily hydrogenated to give mercaptans, and hydrolyzed by aqueous alkalis to give mercaptans and unstable, actively oxidizing substances apparently of thioperoxide type:



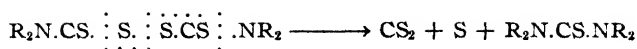
This scission takes place with such readiness if the disulfide group is flanked by double bonds that cold dilute alkalis or organic bases are able to effect it (25). With the latter, however, the reagent may be incorporated and sulfur lost:



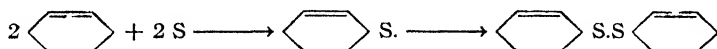
Saturated disulfides are a good deal more resistant to hydrolytic and ammoniolytic fission than are those with double bonds immediately adjoining the disulfide group, but in between these two types come disulfide structures which are likely to figure importantly in rubber vulcanizates. These latter are likely to have their S.S groups attached to α -methylene groups of the rubber, as in (a), and therefore to be flanked by allylic systems in which the potential electronic shifts would foster the peroxide type of scission as they do in the simpler system (b). The potency of such shifts in the allylic system is demonstrated by the ease with which the chlorine atoms of ordinary (substituted) chlororubber (c) separate as chloride ions in the

of vulcanization," but not all accelerators are necessarily peptizing agents since "certain accelerators appear to act as peptizing agents only at high temperatures, and other materials which act as accelerators of vulcanization appear to have little action as peptizing agents." There are thus exceptions to the rule that organic accelerators as a class possess peptizing qualities as an intrinsic property. The basis of the accelerating action of the exceptions can most conveniently be considered later, since Williams doubtless had in mind substances of the thiuram group which combine accelerator action with the function of providing some sulfur for the vulcanization; but with regard to those accelerators which *are* effective peptizers it must be borne in mind that their action is relatively slight on rubber itself compared with that which they can exercise on rubber which has already combined with some sulfur. If one takes into consideration that basic substances of all kinds, inorganic and organic, have a positive and usually strong accelerating influence on vulcanization, whereas acidic substances tend to retard it in a degree proportional to their acidity, there is justification for asking whether the substances of basic type do not produce a definite structural effect on the rubber hydrocarbon which is normally the prelude to the action of sulfur. Although no general effect of this nature has been recognized it is profitable to inquire whether the best known and most effective accelerators are able to exercise any incipient or well-marked vulcanizing effect in the absence of sulfur. For the purpose of this inquiry it is necessary to exclude accelerators of the thiuram group which liberate free sulfur under vulcanization conditions. Garvey (28) has examined by plasticity tests the effect on rubber (in the presence of zinc oxide) of a number of popular accelerators. With the exception of the thiuram group, he found only mercaptobenzothiazole, dibenzothiazyl disulfide, and an ester of dimethyldithiocarbamic acid to show any signs of vulcanizing activity, and even with these satisfactory curing did not take place. Apart from Garvey's observation, there is but little indication in the literature to suggest that accelerators, alone or in the presence of zinc oxide, have any specific action. The source of the incipient vulcanizing action of the three compounds is not immediately obvious, but it is interesting in this connection to compare the direct vulcanizing action of thiuram compounds with that of mercaptobenzothiazole compounds.

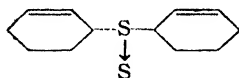
The thiuram disulfides, $R_2N.CS.S.S.CS.NR_2$ [$R = Me, Et, .(CH_2)_5.$], are exemplified by the tetramethyl compound ($R = Me$). This substance undergoes ready and unavoidable thermal decomposition at 140° , yielding tetramethylthiourea, sulfur and carbon disulfide (7, 11), and the reaction occurs even at 100° in the presence of rubber:



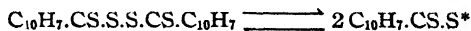
The sulfur is largely or wholly used up in promoting vulcanization and the carbon disulfide rejected. When cyclohexene and the thiuram disulfide are heated at 140°, thiourea and carbon disulfide are again formed, together with a very small amount of cyclohexadiene and a moderate yield of a distillable yellow liquid, C₁₂H₁₈S₂, which appears to be a disulfide formed according to the scheme:



although the possibility of a co-ordinated sulfur derivative of the monosulfide:



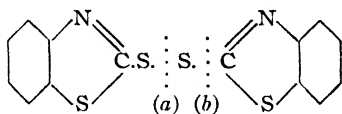
has not yet been experimentally excluded. 1-Methylcyclohexene behaves exactly in the same way, the molecule-linked derivative being then C₁₄H₂₂S₂. In both cases appreciable amounts of hydrogen sulfide are formed, but in neither case does the inclusion of zinc oxide make any very obvious difference in the nature of the organic reaction products. When the accelerator is heated with rubber at 140°, tetramethylthiourea and carbon disulfide again become recognizable as by-products, and again hydrogen sulfide is formed in a proportion which seems to be fairly representative of low-sulfur vulcanizations. Farmer and Michael suggested that tetramethylthiuram disulfide, like dibenzoyl peroxide, decomposes under the action of heat, probably to give radical fragments (21), the latter helping, as they do in the case of dibenzoyl peroxide, to bring about direct carbon-to-carbon linking. Some evidence of the likelihood of such decomposition among aromatic disulfides had earlier been published by Schönberg (69). Thus thionaphthoyl disulfides decompose thermally into radicals:



and in Schönberg's view the same tendency probably applies to thiuram disulfides, although here the position of equilibrium is likely to favor the left-hand side (70). It is not easy to demonstrate experimentally that the fragments, as formed, are radicals and not ions, but the fact that the relatively small over-all proportion of sulfur ordinarily liberated by decomposition of the disulfide during the vulcanization of rubber can be used with such great effectiveness in cross linking itself indicates that the sulfur frag-

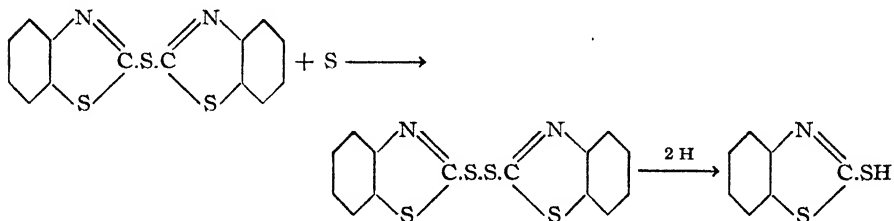
ment at least is generated in very active, and indeed truly atomic, condition (probably as \ddot{S}). In this condition it could presumably attack the double bonds directly; alternatively, of course, it could attack the α -methylene groups. It is interesting that the decomposition of the thiuram disulfides differs from that of dibenzoyl peroxide, Ph.CO.O.O.CO.Ph, in producing three potentially active fragments instead of two; and although the two nitrogenous fragments unite to some extent and so prove, to be unprofitable in starting reactions, the extent of this union appears to be smaller with rubber than with simple olefins.

Radical action may possibly be important also with accelerators of the mercaptobenzothiazole group, but the matter needs careful experimental examination. Dibenzothiazyl disulfide passes largely into mercaptobenzothiazole when heated at 140° in a closed vessel with 1-methylcyclohexene, but there is formed also in very small yield a high-boiling sulfo derivative of the hydrocarbon. In contrast to this, the same disulfide remains practically unchanged (especially when no air is present) if benzene or cyclohexane is substituted for the olefin. It appears, therefore, that the disulfide reacts to some small extent with the olefin, but the bulk of it gets reduced to mercaptobenzothiazole—possibly by the hydrocarbon itself, but possibly by hydrogen sulfide formed in the production of the sulfur derivative, or by dissolved oxygen. The deduction which may be drawn is that, although the scission at (a) occurs readily enough, that at (b) is only slightly favored:



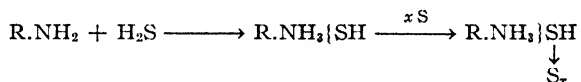
so that little sulfur is available for vulcanization. The mercaptobenzothiazole, on the other hand, is stable and does not react appreciably with the olefin. This means that one of the most popular of all accelerators does not react directly with, or undergo decomposition in the presence of, a simple olefin at ordinary vulcanization temperatures. Nevertheless, the mercapto compound is well known to be so much more rapid in its accelerating action (in the presence of sulfur) than the disulfide that the latter may be conveniently used as a safe antiscorch derivative of the former. It seems strongly unlikely, then, that the accelerating activity of free mercaptobenzothiazole can ever result from its own thermal decomposition, or from its own direct attack on rubber: as against this, mercaptobenzothiazole is invariably (and necessarily) used in technological practice in

conjunction with zinc oxide; but the possibility that the zinc salt of the mercaptan is more likely to attack the rubber than is the mercaptan itself, or, alternatively, is likely to decompose extensively at vulcanization temperatures to yield free radicals, requires examination. If some degree of decomposition of the zinc salt does in fact occur at vulcanization temperatures, a similar decomposition would be likely to apply to numerous derivatives of mercaptobenzothiazole, $C_6H_4:(NCS).SR$ (in which the character of R varies very considerably), and doubtless also to comparable derivatives of dithiocarbamic acids, $NR_2.CS.SR'$. Thus there may well be a satisfactory explanation of the incipient vulcanizing activity observed by Garvey, but it is unknown how far the latter would be due to: (1) the action of radical fragments from the accelerator in producing a few C—C links between the rubber chains; (2) the liberation of very small amounts of atomic sulfur; or (3) the detachment of α -methylene hydrogen atoms from a few rubber units followed by disproportionation, and union of the resulting conjugated units with ethylenic units in other molecules. It is of interest in connection with this subject that the source of the activity of dibenzothiazyl monosulfide as an accelerator has been reported to be its capacity to yield mercaptobenzothiazole at vulcanization temperatures (93), the cause of its slowness of action being the necessity for it to form intermediately the disulfide by combination with sulfur, and thereafter for the latter to undergo reduction by the hydrocarbon or maybe by hydrogen sulfide.



Thermal stability of the zinc salts and other derivatives of mercaptobenzothiazole and the dithiocarbamic acids is a matter which appears possibly to lie at the root of the ultra-accelerator action. Before pursuing it further some thought may be given to the cause of the effectiveness in acceleration of the large group of basic amino compounds which in the main cannot form zinc salts and do not contain sulfur. It must be admitted that no very satisfying explanation of their activity has as yet been advanced. Taking the most direct view, we might suppose that the characteristic feature of these compounds, *i. e.*, their basicity, or in other words the coordinating

power of their basic nitrogen atoms, must provide the real foundation of their accelerating activity, especially as acidic materials are known to hinder vulcanization. Presumably the coordinating capacity is directed toward one or other of the reactants—either tending to detach hydrogen atoms from the α -methylene groups of the rubber, or enhancing the reactivity of elementary sulfur. If the former were the true basis of their influence, the detachment of the hydrogen atoms as ions rather than as neutral atoms would presumably be most assisted, and the way would be open to some sort of ionic vulcanization reaction. But if this were the main factor in acceleration—applying to the whole range of nitrogenous basic accelerators—there would then be great difficulty in explaining why technologists are able to obtain widely varied effects in vulcanization by selecting accelerators, or mixtures of accelerators, from a list so long that (as a recent writer says) no one has the least idea when or why to use most of them: indeed, success in vulcanization might be expected to run parallel to the strength of the organic bases. If, on the other hand, the accelerator is assumed to function as a sulfur carrier, first coordinating with elementary sulfur and later discharging this in active (presumably atomic) form at the seat of potential reaction, there is then the necessity to suppose that those nitrogenous accelerators which contain no sulfur atoms capable of serving as coordination centers use hydrogen sulfide formed in the rubber-sulfur reaction as an auxiliary reagent (71):



This view conflicts seriously with experimental observations to the effect that, if hydrogen sulfide is supplied artificially to enable the accelerator to combine with sulfur, this does not promote accelerator action but hinders it, and the adverse action is not overcome by the use of extra zinc oxide (10). Nevertheless, there is no doubt that sulfur-containing accelerators at least show signs of forming coordination compounds with elementary sulfur (S_8) (43, 56): it would be surprising, in view of the intense coordinating powers of sulfur, if they did not. As regards the significance of such coordination, Lewis, Squires and Nutting (46) point out that the peculiar shape of the curves representing combined sulfur-time of cure may be easily explained if it is assumed that the accelerator and sulfur react to form a sulfur complex which, in turn, reacts with the double bonds of rubber, and so regenerates the accelerator. But there is nothing in the literature of a truly positive or compelling nature to support the notion

that sulfur coordination is the all-important factor in acceleration, or to explain the wide variability in effect which is obtained by using different accelerators.

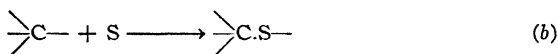
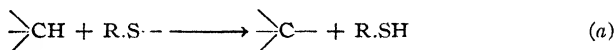
Clearly some more helpful hypothesis is needed, and such a hypothesis must necessarily be based on some attribute which the miscellaneous array of accelerators possess in common, but display in almost infinite variety as determined: (a) by accelerator structure, and (b) by reaction conditions. In this connection, the thermal instability of accelerators, already briefly referred to above, deserves further consideration.

Little is known in detail about the fate of accelerators used in vulcanization, but evidence is not lacking that many of them suffer decomposition in the process. The question therefore arises: is decomposition a necessary condition of their efficacy? Hardman and White (32) noted that lead and zinc dithiofuroate and zinc ethylxanthate have highly transient accelerating activity if the latter is judged by the course pursued in both sulfur combination and the building up of good tensile strength: the activity while it lasts is effective, but it is short-lived (15 to 30 minutes). At the opposite extreme from this is the behavior of accelerators such as hexamethylenetetramine and triphenylguanidine, both of which promote steady increase in the tensile strength and the incorporation of sulfur over a long period. Most accelerators, whether or not they are structurally capable of forming zinc salts, are stated to fall between these extremes. Qualitative tests show that many of the most active accelerators undergo some low or high degree of decomposition when they are heated at ordinary vulcanization temperatures, even at atmospheric pressure. But many accelerators, or accelerator mixtures, are so rapid in action that they bring about rapid vulcanization at temperatures well below 140° C.—sometimes even at room temperature—and precautions have to be taken against premature vulcanization (scorching). Compounds of the dithiocarbamate group, $RR'N.CS.SM$ (RR' = alkyl groups or pentamethylene and M = metals or organic radicals), are typical examples of this class. A quite important degree of variation of the accelerating capacity can be achieved by changing the groups RR' , but the most interesting variations from the present point of view are those which are obtained by changing the character of M , on which depend the solubility or insolubility of the accelerator and the time and temperature of onset of vulcanization. Philpott (62) has pointed out that the extreme low-temperature effectiveness exhibited when M is piperidyl decreases considerably (although excellent activity at higher temperatures still remains) as M becomes in turn zinc and lead. Moreover, a characteristic activity somewhat different from

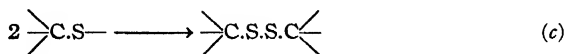
that due to zinc or lead appears when M is cadmium. Also, an activity inferior at low temperatures and about equal at moderate temperatures (115–140°) to that of the piperidyl salt appears when M is sodium. Added to this are all the gradations of activity accruing when M varies over the wide range of possible organic radicals. Many organic radicals, like the heavy metals, delay vulcanization; but it is necessary to distinguish between *true delay action*, *i. e.*, action showing a delay in time between the first-raising of the temperature of the rubber mix and the effective onset of vulcanization (whether the temperature of vulcanization being employed is high or low), and *temperature-delayed action*, *i. e.*, action which needs a relatively high temperature before it sets in effectively, and so is delayed until the required temperature has been attained by the mix. From what has been said earlier about the structural changes which must occur before the thiuram monosulfides become capable of functioning as accelerators, it is plain that these "proaccelerators" are likely to show a time lag, that is, they belong to the class of time-delayed accelerators; but when vulcanization once sets in it is rapidly completed. Accelerators, on the other hand, like the lead or cadmium salts of the dithiocarbamic acids mentioned above, or of benzothiazyl disulfide, owe their freedom from scorching to the comparatively high temperature at which really effective vulcanizing action first begins, so that they exhibit a temperature lag in coming into action. The range of possible variation in temperature lag among the more popular accelerators is considerable, and that in time lag very useful. Akin to the delayed action shown by many accelerators, but quite distinct from it, is "multiple accelerator action," by which is meant the enhanced or modified accelerating action obtained by mixing with the accelerator to be employed a small proportion of a second accelerator, termed the secondary accelerator or activator. The results obtained in this way are surprising (88) and exceedingly useful.

It has been recognized for many years that most delayed-action accelerators are chemical derivatives of known powerful accelerators, $R.SH$, in which the place of the active (mercaptan) hydrogen atom is taken by a more or less easily displaceable organic group, M (58, 85). Thus the success of these compounds in achieving the desired end depends on the fact and ease of scission of the $.S-M$ bond; and it has been thought that when this scission has occurred (by "hydrolysis") the real accelerator is then present and is ready to effect vulcanization. Implicit in this view of delayed action is the notion that the degree of delay provided is closely dependent on the strength of the $.S-M$ bond. But the particular atom of M which is linked directly to sulfur may be S, N, Se or C, so that only in a very formal sense

can M be regarded as a group esterifying the mercaptan $R.SH$ and this is especially the case where the atom linked to S is S , so giving the rather peroxide-like disulfide group; furthermore, hydrolytic conditions of reaction do not prevail during vulcanization. The cause of scission must usually be thermal decomposition, even where the link $.S-M$ is such that hydrolysis could be accomplished under suitable conditions; and, in order that the supposed true accelerator may be generated, hydrogen atoms must be gained ($R.S-M \xrightarrow{2H} RSH + MH$). But in the numerous accelerators belonging to the mercaptobenzothiazole group, the free mercaptan is known to be unable to function as an accelerator, so that the important grouping—*i. e.*, the *true* accelerator—is not $R.SH$ or $R.S-M$, but $R.S-$. Since the hydrogen derivative, $R.SH$, has been found to survive at the end of the few vulcanizations by derivatives of mercaptobenzothiazole for which information concerning end products is available, it may be provisionally deduced that the act causing acceleration consists in the removal of the required hydrogen atom from another body, *viz.*, the rubber, and this process in turn enables the rubber to combine with free sulfur. The first two stages of the acceleration process may then be:



and these may be followed presumably by:



It is necessary to suppose that the thermal decomposition of the delayed-action accelerators (especially of the lead and cadmium salts of dithiocarbamic acids and mercaptobenzothiazole) is considerably facilitated by admixture of the accelerator with rubber hydrocarbon or sulfur, or rubber impurities, otherwise the vulcanization of rubber by zinc, lead or cadmium salts in the course of about fifteen minutes would be out of the question. Signs of such facilitation have already been referred to above in connection with tetramethylthiuram disulfide, and can be observed to result from the mixing of piperidyl pentamethylenedithiocarbamate with other accelerators. Probably the effect is a very general one, resulting either from catalysis or the trigger action of easily decomposable components. Whether

or not any fragments of decomposed accelerators unite with rubber, as do fragments from dibenzoyl peroxide, remains to be determined by experiment.

Reference may be made to one other matter. Many simple bases of considerable thermal stability, such as piperidine and aniline, can function as accelerators, although they are not of very rapid type, and others are produced during vulcanization by the decomposition of more complex accelerators. Wherein does the accelerating action of these compounds reside? The only answer to this question at present discernible is that the simple organic bases either assist the removal of hydrogen atoms from rubber by "stretching" the dissociable C—H bonds, or form thermally unstable salts with mercaptan groups, which break down to generate the radical (or ion) >C.S— , in the manner discussed below in connection with the action of zinc oxide. It would be a mistake, however, to press theoretical deduction too far until a thorough examination of the fate of accelerators during vulcanization, the action of sulfur on rubber and the constitution of accelerated vulcanizates has been made.

6. *Effect of Zinc Oxide*

The inclusion of zinc oxide or some other basic oxide in rubber mixes is an accepted part of rubber technology, but the role of the oxide in the vulcanization process has never been determined, although much discussion has taken place on the subject. Like the part played by accelerators, the function of zinc oxide may not be quite a simple one. For the present purpose a distinction may be drawn between the employment of zinc oxide in conjunction with acidic or potentially acidic accelerators, and its employment with simple rubber-sulfur mixes or with rubber-sulfur together with simple basic accelerators.

The necessity for its use with mercaptobenzothiazole has already been referred to, but experience seems to show that few organic accelerators are active without zinc oxide or some other metallic oxide (15). The action of the accelerators is greatly improved if the oxide is rendered rubber-soluble by the addition of stearic or similar fatty acid (17, 68): thus, the addition of zinc laurate to a normal mercaptobenzothiazole-hexamethylenetetramine stock greatly increases the modulus, as though forming more cross bonds (14); also, it is a common experience that if zinc oxide is omitted the tensile strength is poor and the stock seems uncured. Busse (14) indeed has suggested that the function of zinc oxide used in conjunction with mercaptobenzothiazole does not consist merely in the formation of the zinc salt of the latter, for, if this zinc salt is used in the absence of added zinc

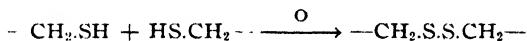
oxide the cures are not much better than when the free mercaptobenzo-thiazole is used. This suggestion means that, quite apart from the particular need for zinc oxide exhibited by acidic accelerators or those which yield acidic products by decomposition, the presence of the oxide is highly important in connection with the primary rubber-sulfur reaction if the best physical properties are to be attained.

Although there is little detailed information on the chemical side about the action of zinc oxide in simple rubber-sulfur mixes, it is clear that the incorporation of the oxide leads to higher vulcanizing efficiency than is obtained with sulfur alone. Thus, in an example described by Brown and Hauser (12), it is shown that addition of zinc oxide results in some decrease in the rate of combination of sulfur, and diminishes considerably the usual fall in the unsaturation of the rubber; at the same time it notably improves the tensile strength and modulus of the products. Several workers note the effect which zinc oxide has in restraining the combination of sulfur with rubber (39) and in greatly improving the rubber-sulfur vulcanizate (17, 60, 68); indeed, the latter effect is clearly illustrated by Dinsmore (17), who found that one volume of zinc oxide added to a rubber-sulfur mix increased the modulus almost twice as much as did one volume of channel gas black. Yet Park (60) has provided evidence showing that the marked stiffening effect of zinc oxide on rubber-sulfur mixes is not just a matter of powder reinforcement of the physical structure.

The result achieved by zinc oxide in the primary rubber-sulfur reactions seems fairly certainly to be one of controlling the *kind* of cross linking taking place, or the extent of cross linking occurring for the expenditure of a given amount of sulfur. It will be remembered that the employment of zinc oxide results in the production of vulcanizates which tend to resist dispersion by piperidine; and perhaps some significance may be attached to the observation that a rubber-sulfur-zinc oxide vulcanizate which had been heated to the stage at which it just remained dispersible (with difficulty) proved, when dispersed, and subsequently freed from uncombined zinc oxide by centrifuging and from organic base by precipitation, to possess a zinc content which was very nearly equivalent to the sulfur content, as though most of the sulfur at that stage of cure was present in the form of zinc mercaptide groups >C-S-Zn-S-C< . The nature of the zinc compound of course needs detailed examination, but since zinc oxide appears to be successful in promoting the formation of effective cross links, the possibility is considerable that it serves to neutralize the free mercaptan groups which become formed in the rubber molecules as the result of sulfur action, so yielding zinc salts which break down under heat, like the zinc

salts of accelerators, to give the radicals (or ions), >C—S— , which seem to be the most important intermediates in the cross-linking process. Normally but very little free hydrogen sulfide (an amount equivalent to a few units per cent of the combined sulfur) is liberated in the vulcanization process, which may well be due to the successful action of the zinc oxide. According to this view, the mechanism of zinc oxide action is of the same general character as that of *all* organic accelerators—a conclusion which is not inconsistent with the opinions concerning the effectiveness of zinc oxide action expressed by many workers.

In the field of synthetic elastomers, Patrick's very interesting vulcanization of ethylene polysulfide polymers (61) presents a problem of mechanism which has not yet been authoritatively solved. Several of the polysulfide polymers undergo a species of vulcanization when they are heated with suitable organic reagents (di- and trinitrobenzene, benzoyl peroxide, etc.) or with certain metallic oxides (*e. g.*, zinc oxide and copper oxide). Patrick suggests that oxidation is probably the cause of vulcanizations, and supposes that the quite effective action of zinc oxide may be confined to mercaptan groups at the ends of polymer chains, so causing the linking of polymer chains end to end, but no cross linking:



The marked increase in resistance to solvent penetration that occurs with increased cure would strongly suggest the possibility of a fairly compact union of the chains by cross links spaced along their lengths. Since the vulcanization proceeds with an ether disulfide polymer, $(\text{CH}_2\text{CH}_2\text{O}\cdot\text{CH}_2\text{CH}_2\text{S.S.})_n$, equally with an ethylene tetrasulfide polymer, $(\text{CH}_2\cdot\text{CH}_2\text{S.S.})_n$, the process does not appear to affect the coordinated sulfur



atoms along the chain. Thiokol A is severely attacked by cold piperidine, but the result of the action is not yet known.

VII. Conclusions

A survey of the numerous processes which have been used to vulcanize natural and synthetic elastomers indicates that genuine cross linking plays the principal part in many of them, although the proof of cross linking cannot usually be direct. The polyene constitution of all polymerized conjugated dienes, whether the polymers are natural or synthetic, confers an intrinsic tendency for the hydrogen atoms of the α -methylene groups to be relatively easily displaced, and this tendency is largely concerned in at

least some of the vulcanization procedures. A comparable tendency appears in carbonyl compounds, the α -methylenic hydrogen atoms here having a moderate degree of displaceability, owing to the carbonyl unsaturation, so that both saturated and unsaturated carbonyl compounds (especially the latter) become vulcanizable. The actual vulcanization process appears to depend on chain reactions initiated by reagents (*e. g.*, peroxides) which are radicals in nature or yield radicals by decomposition. Displacement of a hydrogen atom from a polymer molecule by the radical reagent leads to the union of the denuded molecule with a second molecule either through displacement of a hydrogen atom from the latter or by addition at a double bond. Vulcanization of rubber by light (photogelling) almost certainly follows a very similar course. Simple molecules can be proved to become cross linked, and when the process is applied to high-molecular polymers the products exhibit the characteristic properties of vulcanizates. It is a reasonable provisional deduction that cross linking in macromolecular materials confers quite definitely the special physical qualities of vulcanizates, although there is nothing at present to show that intermolecular secondary valences may not be auxiliary factors. Fragments of the reagent which brings about cross linking frequently become chemically incorporated in the vulcanized material.

The argument that the characteristic properties of the sulfur vulcanizates of natural rubber appear as the direct result of cross linking has been assailed on the ground that the vulcanizates are fairly readily dispersed by organic bases, and hence the polymer molecules are held not to be chemically joined. There are reasons for believing that the action of the organic bases is mainly a chemical one, such action serving to sever by specific chemical reactions many of the cross links on which the desirable vulcanized qualities depend. The question, however, of the character of the cross links in sulfur vulcanization is a difficult one owing to the great variability in vulcanized quality obtained by the use of different organic accelerators, zinc oxide, stearic acid, etc., and the liability of the vulcanizates to deteriorate by overvulcanization and reversion. Our present knowledge of the specific chemical action of sulfur on polyolefins, of the fate of accelerators during vulcanization and of the influence of zinc oxide on both is too scanty to permit final conclusions to be drawn concerning the precise chemical mechanisms of sulfur vulcanization. The information available, however, shows that sulfur definitely serves to link simple mono- and diolefins together, and therefore may be expected to link larger polyolefinic molecules; also, since the loss of olefinic unsaturation in the formation of low-sulfur rubber vulcanizates is but small there is good reason to believe

that many of the links are formed at α -methylenic carbon atoms. The links are probably largely sulfide and disulfide bridges with improbably any significant number of direct carbon-to-carbon bonds. The number of primary cross links between adjacent macromolecules that is required to confer adequate vulcanized properties is unknown, but may not be very large. The utility of organic chemical accelerators is probably due primarily to their thermal decomposability under the conditions of vulcanization, and secondarily to the coordinating powers of their nitrogen or nitrogen and sulfur atoms. The first of these properties may serve to provide radical fragments which detach hydrogen atoms from the rubber molecules, thereby initiating chain reactions between the polyolefin and sulfur; the second may provide activated sulfur capable of attacking the polyolefin. Zinc oxide plays an effective part which appears to be similar in mechanism to that of organic accelerator action. The phenomena of optimum curing, overcuring and reversion of vulcanizates are doubtless physical expressions of the number, kind and interconversion of cross links.

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RUBBER PHOTOGELS AND PHOTO-VULCANIZATES

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	PAGE
I. Introduction.....	363
II. Formation of Photogels in Inactive Solvents.....	364
III. Role of Oxygen.....	365
IV. Peroxidic Vulcanization.....	367
V. Carbonyl-Containing Activators.....	368
VI. Effect of Oxygen Inhibitors on Rate of Gelling.....	369
VII. Other Factors Influencing Rate of Gelling.....	369
VIII. Light Sources.....	371
IX. Properties of Photogels.....	372
X. Action of Light on Solid Rubber.....	373
XI. Properties of Dried Photogels and Irradiated Rubber.....	376
XII. Vulcanization—Thermal and Photochemical.....	378
XIII. Mechanism of Photovulcanization.....	381
XIV. Elastomers Other than Natural Rubber.....	384
XV. Photosynthesis of Rubber from Isoprene and Polymerization of Styrene.....	386
XVI. Summary.....	387

I. Introduction

The first recorded observation of a rubber sol setting to a gel on exposure to light was made by Porritt (14). This remained an isolated observation until the matter was taken up by Pummerer and Kehlen (15), whose work covers most aspects of the subject. Except for one or two isolated observations, the only other publications on the subject are those of Naunton (12) and Stevens (20-22).

It is perhaps surprising that photogelling of rubber sols was not noticed earlier and that, when recorded, attracted so little attention. This may have arisen from two circumstances. Gelling takes place only in the absence of oxygen or in the presence of a very limited amount; and the solvents commonly used by rubber chemists are either petroleum fractions or

coal-tar fractions and in neither of these does the gelling take place readily. The gels when obtained in these solvents tend to be weak and tenuous, unless after very long irradiation, and rapidly liquefy when exposed again to light and air. A portion of a gel formed in benzene and removed and placed in fresh benzene, does not dissolve in the dark, but dissolves rapidly on exposure to diffused light. Such solvents are therefore regarded as inactive. Stronger and tougher gels are easily obtained by means of "activators" or reagents added to the solvents or by means of "active solvents," mainly halogenated hydrocarbons. A large number of carbonyl compounds serve as sensitizers, including aldehydes, ketones, quinones and halogenated derivatives of these.

There are, however, marked differences between the physical properties and yield of gels obtained with inactive solvents and those obtained in active solvents with or without activating agents. Pummerer speaks of "sensitizing agents," but as these agents react with the rubber they are not strictly sensitizers; nor are they only catalysts. The term "activator" as used by Naunton has therefore been adopted.

II. Formation of Photogels in Inactive Solvents

The usual procedure consists in adding to the solvent the required amount, usually 0.5 to 5%, of the solid rubber under investigation and sealing off either *in vacuo* or in inert gas. The rubber is then brought into solution by agitation over a period in the dark before exposure to the source of light.

Take first the case of inactive solvents in which gelling is either very slow or does not take place even after very prolonged irradiation, for instance a whole summer's exposure to direct sunlight, or it may be longer according to the solvent employed. The presence of a sufficient quantity of oxygen (enclosed air) prevents gelling or greatly delays it. If, however, the air is removed by boiling off a little of the solvent under reduced pressure before sealing, gelling or partial gelling is obtainable, but only on very long exposure. Several experiments, to which reference will be made later, have been made by different investigators with the object of removing the whole of the oxygen by suitable precautions; but in no case could gelling be prevented. Nevertheless, recent experiments have shown that small quantities of molecular oxygen promote gelling in inactive solvents. The time taken to gel is dependent on the nature of the solvent; gelling takes place more rapidly with rubber in some solvents than in others and more slowly when the molecule of the solvent is large. With decimolar concentrations, *ca.* 5% of rubber on the solvent, the following times were taken

to form a gel, ascertained by inversion of the tube in which it was formed: petroleum ether (b. p., 60–80°), 16 days; benzene, 8 days; toluene, 9 days; cyclohexane, 14 days. No gelling could be obtained with tetralin or decalin, and only incipient gelling with cyclohexene and *m*-xylene. Gelling occurs readily in *o*- and *p*-xylene. All tubes were evacuated and exposed side by side to direct sunlight.

Sometimes gelling is accompanied by an initial stringiness. This seems to be usual where the rubber is not milled or only partly milled; and in consequence the dispersion is incomplete. Such solutions consist of swollen macroparticles of rubber suspended in a solution of a greater degree of dispersion and are thus lacking in homogeneity. Therefore the initial gelling is irregular. With well-milled solutions in benzene, a progressive increase in viscosity previous to gelling can be observed. There are also other differences in the recorded phenomena. Pummerer and Kehlen state that gelation starts on the surface. Porritt observed no preliminary increase in viscosity. Naunton also states that gelling is not attended by a uniform increase in viscosity. The writer has observed every type, *i. e.*, gel formation starting at the surface or below the surface on the exposed walls of the tube, irregularly with stringiness and progressively by increase in viscosity, depending on conditions. In some cases, *e. g.*, milled crêpe rubber in benzene, petroleum ether, or cyclohexene, partial separation may take place on the side wall, unaccountably above the surface of the liquid. The onset of gelling is, no doubt, partly conditioned by the elastic nature of the gel. A rubber sol treated with a weak sulfur chloride solution or with dithiocyanogen exhibits similar behavior; and as rubber sols are not homogeneous but are made up of molecules of a great variety of lengths it is to be expected that gelling will start at certain centers where the conditions are most favorable. Unless the rubber is well milled or consists of material separated by diffusion from the gel skeleton with which the protein is associated, it is likely to retain in suspension swollen particles of gel rubber which have not dispersed. This is invariably the case with unmilled crêpe and vigorous shaking of the solution in the tube is not sufficient to insure even dispersion. The presence of such gel particles may sometimes be seen on the walls of the tube when the solution is allowed to flow over them or may be detected by staining. Under such conditions, gelation cannot be expected to proceed uniformly.

III. Role of Oxygen

The rate of gelling in the presence of air depends on the amount of air present. If this exceeds a very small figure, the more air, the greater is the

delay. It has been shown (12) that the oxygen is absorbed by the rubber in the light; and not until the oxygen is completely removed does gelling set in. The process of oxygen absorption is accompanied by a fall in viscosity, but a corresponding increase after the oxygen has been absorbed is not always noticeable, as gelling with such solutions takes place rather suddenly. In the presence of sufficient oxygen, as when freely exposed to the air, gelling never takes place. The whole effect of the radiation from whatever source is concentrated on the oxidative disruption of the rubber molecules, and the viscosity falls to that of the solvent. The products of photolysis in air have not been studied.

The known catalytic effect of minute amounts of oxygen and of peroxides as gelling agents, and, incidentally, also vulcanizing agents, leads to the suggestion that oxygen plays a part in the process. There is, indeed, a general consensus that oxygen is necessary to initiate the reaction. But every attempt to show that gels are not formed in the complete absence of oxygen has failed. It is conjectured that traces of oxygen sufficient for the purpose are retained by the rubber in spite of most careful purification, boiling out of solvent and solution under reduced pressure (11, 15) and similar precautions, even to the extent of starting with the latex itself and carrying out the whole preparation of the rubber in an atmosphere of nitrogen (12). The only result of taking these precautions was a reduction in the time of gelling from sixteen to three hours. Naunton attributes gelling under these conditions to a few already existing oxygenated centers in the rubber molecules. If, however, in the oxygen-excluded experiments, there were still present a few oxygenated centers from which cross linking originated, one would anticipate still faster gelling where no special precautions had been taken to remove traces of oxygen before sealing, provided of course that insufficient air remained to delay gelling appreciably. The probable presence of oxygenated centers in rubber does not follow from parallel experiments on the polymerization of acrolein. Moureu and Dufraisse intentionally exposed acrolein to air to allow such centers to form and showed that such exposure was necessary to polymerization. The point of attack would no doubt be the CHO groups, so that there is no close analogy with rubber.

Recent work by the writer (22) has clarified the position without, however, affording an explanation of Naunton's failure to prevent gelling. In the first place, to assess the effect of oxygen it is necessary to avoid active solvents and similar agencies; otherwise the effect of oxygen, being relatively weak, is masked by that of the active solvent or activator present. If a series of tubes is prepared with 5% of milled rubber on the solvent

(inactive) and containing increasing proportions of air beginning with the equivalent of about 0.01% of oxygen on the rubber, the tube with the smallest proportion of oxygen gels first, followed by the remainder in the order of increasing proportions until the oxygen present reaches one or two per cent on the rubber. At this stage the rate of gelling is somewhere about the same order as in a tube from which the air has been removed as completely as possible by boiling off part of the solvent under reduced pressure. Further quantities of air cause still greater delay in gelling until no gelling takes place even after long exposures. It is noteworthy that, whereas the rubber sol in the exhausted tube gels slowly, changing gradually from a viscous to a ropy condition and sometimes failing to give a firm gel, the tubes with the larger proportions of air gel rather suddenly and completely. These relationships can obviously be attributed to the activating effect of the oxygen. The minute quantity in the evacuated tube, probably arising from the oxygen dissolved in the milled rubber, brings about slow and often incomplete gelation. A very small quantity of oxygen brings about fairly rapid gelling such as is effected by an exposure of six to eight hours in direct sunlight. As the proportion of oxygen is increased, there follows a delaying action caused by the time taken for the rubber to absorb the excess oxygen by photolytic degeneration; the larger the proportion, the greater is the delay. Eventually no gelling ensues, only oxidative splitting of the chains. This is apparent from a reduction in viscosity of the sol to approximately that of the solvent. The rapid gelling with moderate proportions of oxygen derives from the cross bonding which takes place rapidly when sufficient oxygen is present, in contrast to the slow gelling when only traces are there. The cross bonding may even proceed simultaneously with the chain splitting, so that gelling proceeds rapidly the moment the chain splitting comes to an end.

IV. Peroxidic Vulcanization

It has long been known that peroxides are efficient catalysts and vulcanizing agents. Van Rossem and coworkers (16) found that, for thermal reactions, 10% of dibenzoyl peroxide on the rubber was the optimum proportion, of which about two-thirds was recovered from the vulcanizate as benzoic acid, while one-third entered into combination with the rubber. No carbon dioxide was formed. The lowest temperature at which indications of vulcanization (insolubility in benzene) were obtained was 80° C., but the modulus under these conditions was so slight as to be of doubtful reality. Correspondingly, a carbon tetrachloride solution with 10% of dibenzoyl peroxide on the rubber gels in the dark without evolution of gas.

Also, a dry 10% mixture of rubber and the peroxide as used for vulcanizing becomes insoluble on putting aside for a year or two in the dark, although the product is soft and sticky and devoid of elasticity. No insolubilization is obtained by the thermal reaction in the dark at room temperature when the proportion of peroxide is low, say 1%, on the rubber although very much smaller amounts induce tackiness. These smaller amounts, however, promote photogelation. A peroxidized ether is also a very good gelling agent. The rubber peroxide reaction is therefore promoted either by heat or by light, the photochemical process being the more effective. Presumably, the mechanism of the reaction is much the same in both cases (5).

V. Carbonyl-Containing Activators

Activators other than peroxides, *i. e.*, carbonyl compounds, are very poor thermal vulcanizing agents, much inferior to the peroxides. It is, however, possible, given time, to obtain benzene-insoluble products by heating a mixture with rubber, although the tensile properties are extremely poor. They resemble the xerogels obtainable from rubber photogels with these reagents. On the other hand, carbonyl compounds are excellent gelling activators. Chloranil is one of the best, both thermally and photochemically. Anthraquinone and xanthone are extremely active. Benzoquinone behaves exceptionally, being moderately effective as a thermal vulcanizing or insolubilizing agent but of doubtful efficiency as a gelling agent. There are also active solvents, *i. e.*, rubber solvents which are also activating agents. These comprise halogenated hydrocarbons, of which carbon tetrachloride exceeds them all in efficiency with natural rubber, but appears to be ineffective with butadiene or chloroprene polymers. A carbonyl-containing activating agent may be combined with an active solvent to yield enhanced results.

Examples of activating agents are ketones (saturated), aldehydes such as benzaldehyde, quinones, substances of similar build such as anthraquinone, 1,4-naphthoquinone, phenanthrenequinone, benzanthrone and xanthone, chlorinated derivatives such as 1,5-dichloroanthraquinone, chlorobenzanthrone and chloranil. Another substance reported to be very efficient is eosin (15); other quinoid dyes like methylene blue and malachite green offer no advantage as they fade more quickly than eosin. As regards halogenated aliphatic hydrocarbons, no gelling could be obtained with either ethyl bromide or chloride without the addition of a sensitizer (acetone).

For comparative tests with activators, ligroin, benzene, cyclohexane and other inactive solvents are appropriate; but if a gel is required quickly

there is nothing better than a mixture of carbon tetrachloride and acetone. Experiments made with ethyl ether are difficult to interpret because a trace of peroxidation converts it into an active solvent of uncertain efficiency.

Photogels formed in inactive solvents show no increase in weight on that of the rubber taken; in the presence of an activator or active solvent, however, an increase is found which may be considerable if irradiation is prolonged. Where chlorinated activators or solvents are used, the product retains a considerable percentage of chlorine. A carbon tetrachloride sol may increase in weight by about 50%. Only a small part of this chlorine is removable by extraction with acetone or boiling with alcoholic potash, and is therefore firmly bound. Thus it seems that in addition to the primary vulcanizing effect, light brings about a secondary reaction or condensation of the activator with the rubber.

VI. Effect of Oxygen Inhibitors on Rate of Gelling

Hydroquinone is known to act as an inhibitor of some polymerizations and also retards gelling. Large proportions are required to prevent gelling or delay it appreciably. Much depends on the presence of oxygen during exposure. It has been observed to promote gelation in the presence of air; possibly it is itself oxidized to quinone, which may act as a feeble promoter. The effect of hydroquinone is also modified by the activator or solvent. When these promote gelling considerably, such as with carbon tetrachloride sols, the hydroquinone has only a small delaying action.

Naunton found that the phenylnaphthylamines and other antioxidants retard gelation; but again the effect is less marked in the presence of powerful activators or oxygen. On the other hand, substances which promote oxidation in the presence of air, like copper salts, also delay gelation or prevent it. Peptizing agents seem to vary in their action. Diethylamine and piperidine were found not to render a gel in ether soluble (15), while thionaphthols prevented gelling both in the presence and absence of oxygen. With every precaution to eliminate oxygen, no gel could be obtained in spite of prolonged irradiation (12). Since the thionaphthols are very powerful peptizing agents, this may explain the results obtained. Generally, it may be accepted that peptizing agents have a delaying or solvent action, just as they have on all vulcanized rubber; whether or not this is sufficient to prevent gelation depends on the conditions of the experiment.

VII. Other Factors Influencing Rate of Gelling

The physical condition of the rubber has some influence on the rate of gelling. Comparative tests must be made in the absence of air owing to the

delaying action of oxygen already referred to. It is found that milling retards gelation but not to a great extent, much less than would have been anticipated by taking into account the drastic reduction in molecule size so produced. If gelation were solely the result of cross linking, this would not harmonize with the facts. The explanation probably lies in the simultaneous formation of condensation products which are also insoluble and therefore tend to separate as a gel and augment the effect of cross linking.

If a lightly gelled rubber is dried and then remilled, it tends to become soluble again. In this respect it resembles any very lightly vulcanized soft rubber. The lowest ether-soluble fractions were found by Pummerer to be the first to gel of a series which were insolated alongside one another. This is plausibly attributed to the lower molecular weights of the first fractions, but parallel viscosity determinations were not given and recent research has thrown doubt on fractional extraction as a method of separating rubber of progressive molecular weights.

The iodine number of irradiated rubber has been quoted as 94 to 98% of the sol rubber from which it was made. This of itself does not convey very much information without an indication of the conditions of preparation, period of irradiation and so forth. It does, however, indicate that some small loss of unsaturation occurs which has been attributed to cyclization. Exactly the same effect is noted with thermal vulcanization, where good vulcanizates are obtainable with small loss of unsaturation, usually about 2 to 10%. This loss may have but little connection with cross bonding. It must not be forgotten that, in dealing with rubber, we are not handling a pure hydrocarbon but one with 6 or 7% of nonhydrocarbon constituents. The behavior of purified rubber is therefore of special interest.

Purification of the rubber may delay gelling but care must be taken to see that the rubber is not oxidized in the purification process. A number of experiments were made with a crêpe rubber purified by a combined enzyme digestion and fractional latex coagulation. After milling, this gelled faster under all conditions than ordinary crêpe similarly treated. Diffusion rubber fractions also gel faster but purification by acetone extraction or other methods may have no definite effect. Hydroquinone appears to be a more effective retarding agent with rubber which has been purified. The age of the specimen affects the rate of gelling. Milled rubber shows considerable increase in rate after a twelve months' storage in the dark. The change in rate is much greater than that caused by variation in degree of milling. Zinc oxide suspended in the sol has a considerable retarding action; barium sulfate and magnesium carbonate, a small ac-

celerating one. The delaying action of zinc oxide is unexpected, but may be caused by internal filter action. Zinc oxide is reported to be a photosensitizer but very opaque to a wide range of wave lengths. Zinc stearate accelerates gelling. Sulfur is of considerable interest as a gelling agent because of the parallel thermal action. Unfortunately, the records are contradictory. Far from promoting gelation, Porritt and Naunton found that it prevented gelation. The writer, on the other hand, found little or no inhibiting action. Naunton's results were complicated by the addition of benzophenone; but the absence of gelling is nevertheless surprising, particularly since sulfur acts as a powerful sensitizer when a dry rubber sheet surface-coated with sulfur is insolated. Recent work of the writer (22) has clarified the position, as in the case of oxygen discussed above. Earlier experiments with sulfur were carried out in the presence of powerful activators or active solvents which masked the action of the sulfur. Thus sulfur has been found to delay gelling in a carbon tetrachloride-acetone solution. This delay may arise from the opacity of the sulfur, if it is present in excess. But in an inactive solvent sulfur has a well-defined accelerating effect which is dependent on the proportion present. With three per cent of sulfur on the rubber a solution in benzene, toluene or cyclohexane gels in three or four hours in direct sunlight in the absence of oxygen. In petroleum ether it takes rather longer. Not much advantage results from a further increase in the proportion of sulfur. Smaller quantities result in slower gelling; 0.5% on the rubber decreases the time of gelling to thirty hours and still smaller proportions have little effect. A control would require at least one hundred hours. Oxygen is therefore a much more powerful gelling agent than sulfur, comparable to xanthone or anthraquinone in activity. Under conditions similar to the above, 0.1% of these latter activators on the rubber produced a firm gel in thirty minutes' exposure to direct sunlight. Experiments with the lowest limits of molecular oxygen are not yet completed. It may well be that it is the most powerful of any known activator. Trinitrotoluene, also a vulcanizing agent, inhibits gelling, as do copper oleate and cobalt linoleate, which are known to act as oxygen catalysts for rubber. The role of oxygen as an activator or catalyst is therefore complicated and confusing.

VIII. Light Sources

Any source of light may be employed, including sunlight, mercury-vapor lamps, and incandescent electric lamps. Pummerer carried out some experiments with light filters and a quartz mercury-vapor lamp. No

visible change occurred in a rubber solution in carbon tetrachloride with five filters: 5800, 4950-5800, 4950, 4200 and 3150-4000 Å. Apparently this indicates that light of less than 3150 Å. is effective. With benzophenone, wave lengths of 3150 to 4000 were effective and with benzanthrone up to 4200. Comparative experiments of the writer indicate that direct sunlight is as efficient as or more efficient than that from mercury-vapor lamps (15 cm. from a lamp of 4 amp. and 40 v.); and gels are obtained by a brief exposure to direct sunlight not only with carbon tetrachloride as a solvent but also in glass tubes (walls 0.5 mm. thick). Further, there is very little difference between the rate of gelling of sols contained in quartz and the rate of those in thin glass tubes, whether with mercury-vapor lamps or in sunlight. Although window glass delays gelation a little, the effect is small, indicating wave lengths greater than 2520 Å.; other experiments set the lower limit in excess of 2800 Å. A 5% carbon tetrachloride sol of well-milled crêpe gelled in less than a week when exposed to sunlight through four layers of window glass (about 1 cm. in all). These qualitative experiments indicate that the effective rays are either visible rays or those in the near ultraviolet. Confirmatory work is necessary, but this sensitivity to relatively long wave lengths and the relative inefficiency of the shorter ultraviolet rays would indicate that photogelation does not involve any radical disruption of the solvent or activator. Conditions of illumination, such as exposure to direct sunlight in glass tubes, which cause rapid gelling, are quite ineffective in breaking down an activator such as acetone to give the component radicals, so that, whereas one hour's sunlight is sufficient to gel a rubber sol in a mixture of carbon tetrachloride and acetone, a whole summer's exposure of either solvent under like conditions fails to bring about any appreciable change or evolution of gas.

IX. Properties of Photogels

Photogels are substantially colorless and become firmer on longer exposure; eventually syneresis sets in and the gel in a tube may contract to a compact cylinder, the greater part of the fluid being expelled. This usually takes place in the presence of activators or active solvents. Without them the gel is seldom stiff enough and does not arrive at the contractile stage for a long time. The fluid separated from the gel is almost, but not quite, free of rubber. These gels contract further on spontaneous evaporation. They vary in color, and some tend to darken with long exposure. Generally, they are pale yellow and resemble the yellow color of a sulfur vulcanizate. Like the latter, they exhibit increasing modulus and

hardness and eventually brittleness. The darkening is no doubt due to impurities in the rubber or solvent.

Experimental difficulties are responsible for the absence of numerical data but the general physical properties are apparent on handling the specimens. Compared with a sulfur vulcanizate the physical properties are very poor and in one respect may be markedly different. A xerogel from an exposure in an inactive solvent is extremely soft, generally softer than the original rubber or any sulfur vulcanizate however lightly vulcanized. Yet such xerogel may be partially insoluble in benzene if insolation is sufficiently prolonged. This applies also to gels obtained with the aid of dibenzoyl peroxide, whether by the light or dark reaction. Similar very soft xerogels can be obtained by spontaneous evaporation of rubber sols to which the peroxide has been added although insufficient in quantity to bring about gelling. This type of xerogel is so soft that it has the physical properties of one still retaining solvent. By insolubility in benzene is understood a maximum of 10 or 15% solubility as indicated below. Xerogels exhibit every stage of swelling and solubility, and as the irradiation is prolonged the swelling and the solubility lessen. The final products are hardly affected by prolonged immersion in benzene. The dried gels are stable and show no observable alteration with time when preserved in air in the dark.

A quantitative test for solubility may be conveniently combined with one for swelling. The solvent chosen is generally benzene; and to avoid errors resulting from the variation in solubility with concentration of solvent, the volume is chosen large, 100% of the specimen taken, which should be in one piece. The supernatant solvent is decanted and replaced after three days and again after one week. The swollen gel can then be weighed and the dry rubber residue ascertained, giving the volume increase and the amount dissolved. The increase should be calculated on the actual rubber it contains (swelling index). There is no close accordance between swelling index and the proportion soluble when comparison is made between a large number of gels prepared in different fashions, although a general proportionality is apparent.

X. Action of Light on Solid Rubber

At various times it has been observed that dry rubber without solvent or other addition becomes insoluble on exposure to light. It must not be forgotten that some forms of natural rubber are also largely insoluble even in benzene. The writer has specimens of smoked sheet in corked flasks in the dark, portions of which have remained undissolved for twenty-five

years (23). Therefore, in this, as in the study of gelation, it is advisable to start with a milled rubber or diffusion rubber which, before exposure, is readily soluble. The rubber should be irradiated *in vacuo* or in inert gas to avoid "disaggregation." Asano (1) and Garner (8) report insolubilization under these conditions without the development of tackiness. The in-

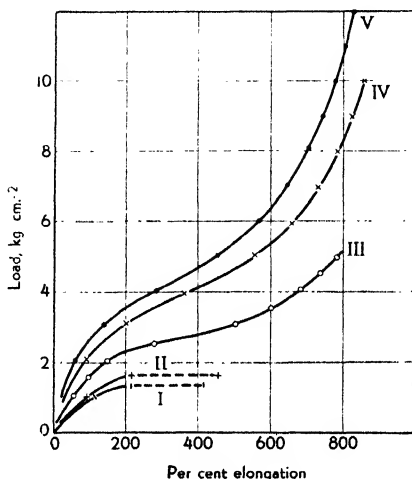


Fig. 1.—Stress-strain curves for dry rubber insolated *in vacuo*.

Curves I and II show a yield point at about 200% elongation. The specimens continue to elongate without further addition of load, as represented by the broken lines. Rate of loading, $0.1 \text{ kg.cm.}^{-2} \text{ sec.}^{-1}$

Curve	Identification	Stress at 600% elongation, kg.cm.^{-2}	Swelling index	Proportion soluble
I	Control, "cut sheet" untreated Irradiated 5 hrs. 15 cm. from lamp	1.3	Completely soluble	
II		1.6		
III	Insolated 3 months	3.5	49.7	0.41
IV	Insolated 1 yr.	5.4	23.5	0.18
V	Insolated 1 yr.	6.3	22.4	0.18

solubilization is comparable with that obtained by drying photogels (20); and the products behave in all respects like slightly vulcanized rubber. They do not harden or become opaque at 0°C. , but are not immune to surface oxidation in air and light and consequent stickiness when exposed for some time to direct sunlight, though they are less sensitive in this respect than the original rubber. As in the case of gels formed in inactive solvents without activator, the susceptibility to subsequent oxidation in light and

air depends on the time and intensity of exposure in the absence of oxygen. The longer the exposure under these latter conditions, the more resistant is the product both to solvents and oxidizing influences and the better are the tensile properties. The stress-strain curves for such irradiated rubber are of the type usual for vulcanized rubber (21) (Fig. 1). It is probable that the tensile properties of dry rubber from photogels are of the same

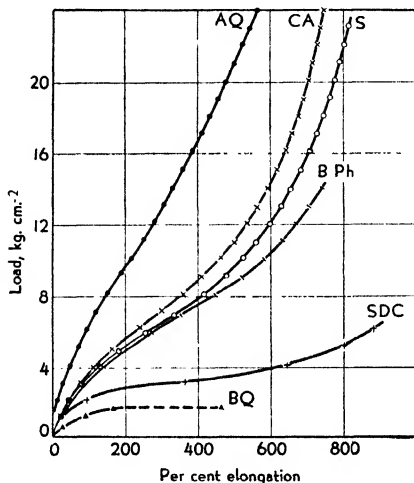


Fig. 2.—Stress-strain curves for dry rubber insulated *in vacuo* with undersurface dusted with powdered reagent.

Rate of loading, $0.1 \text{ kg.cm.}^{-2} \text{ sec.}^{-1}$

Curve	Compound	Load at 600% elongation, kg.cm.^{-2}	Swelling index	Proportion soluble
BQ	Benzoquinone	(1.6)	46.3	0.46
SDC	Sodium diethyldithiocarbamate	3.8	37.2	0.32
BPh	Benzophenone	10.2	10.5	0.03
S	Sulfur	12.1	14.5	0.10
CA	Chloranil	14.2	10.3	0.06
AQ	Anthraquinone	25.0	6.6	0.04

order. Further, if the surface of the milled rubber in sheet form is treated with photogelling agents, a much improved product is obtained which gives stress-strain curves more nearly approaching those of a sulfur-vulcanized rubber (Fig. 2). This improvement in physical properties in the presence of an activator or vulcanizing agent is often obtainable in the presence of air (Fig. 3). It would seem, therefore, that photogelation is merely the insolubilization of rubber caused by vulcanization or some other

form of polymerization engendered photochemically. If this is so, photogelling would be expected to take place in all rubber solvents unless they proved to have greater solvent action on vulcanized rubber than typically good ones such as benzene. As has been stated, photogelling does not take place in some hydrocarbon solvents. An examination of the rubber

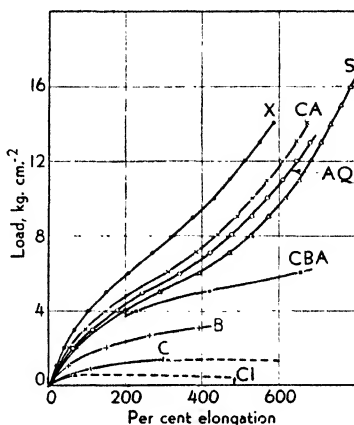


Fig. 3.—Stress-strain curves for dry rubber insolated in air with undersurface dusted with powdered reagent.

Rate of loading, $0.1 \text{ kg.cm.}^{-2} \text{ sec.}^{-1}$

Curve	Compound	Stress at 600% elongation, kg.cm.^{-2}	Swelling index	Proportion soluble
C	Control as used	(1.3)	Completely soluble	Completely soluble
CI	Control irradiated	(0.6)		
BQ	Benzoquinone	(3.5)	101.2	0.63
CBA	Chlorobenzanthrone	5.8	91.0	0.56
S	Sulfur	9.8	44.0	0.28*
AQ	Anthraquinone	10.7	12.2	0.14
CA	Chloranil	11.9	29.8	0.31
X	Xanthone	14.4	13.4	0.15

* 0.35% combined sulfur.

recovered by precipitation from the exposed sols is found to have undergone no change. These solvents therefore inhibit the formation of insoluble products. No separation of gel takes place because none is formed, not because the gel failed to separate.

XI. Properties of Dried Photogels and Irradiated Rubber

It has been stated that the vulcanizing action of light is only slight and that this is obtained at an early stage of irradiation; also that there is a

limiting degree of gelation and that it is not possible to obtain products comparable with rubber vulcanized in the ordinary way (12). While it is true that the physical properties are poor compared with an ordinary sulfur vulcanizate, prolonged exposure with the aid of activators produces a progressive change, although this may not take the form of fully vulcanized rubber. The first tenuous gel stiffens; syneresis sets in; and the greater part of the solvent is expelled. The dried photogels exhibit a gradual change from a soft, weak, but elastic solid to harder, tough masses which inclined to brittleness and in some instances may be powdered. This is the final stage. It seems clear that, with inactive solvents, a weak vulcanizate results, and this is certainly improved by longer irradiation. But, where active substances are present, the initial vulcanization is masked by reactions between the rubber and the "activator" which are more of the type produced by such energetic reagents as halogens or hydrohalides, stannic chloride and sulfuric acid. The reactants or "activators" condense with the rubber in the course of the reaction and form part of the reaction product. Irradiation of dry rubber *in vacuo* is also progressive, possibly through the agency of oxygen dissolved in rubber. There seems no reason to doubt that sufficiently prolonged irradiation of rubber in an inert solvent would similarly yield a more substantially vulcanized product, but it is not yet possible to state the maximum vulcanizing effect obtainable in an inert solvent because very long periods of irradiation have not yet been tried. No limit has been reached for the improvement of the physical properties of dry sheet rubber insulated *in vacuo*. As no active chemical reagent is present, the hardening without improved tensile properties, characteristic of rubber which is irradiated in the presence of activators, does not eventuate. The photochemical vulcanization of rubber from this view is substantially the same process as thermal vulcanization, but the acceleration in the presence of activators is accompanied by a secondary chemical reaction, indistinguishable as far as the products are concerned, from any other reaction between rubber and a chemical reagent, whether thermally induced or taking place at room temperature.

The products obtained with dibenzoyl peroxide are similar whether obtained photochemically or by the "dark" reaction. Here again we may presume a vulcanizing action in the early stage, followed by a series of reactions in which substitution of the rubber molecule by a benzoyl or phenyl group sets in (5). The formation of such products, *e. g.*, that isolated by Bock (2) does not imply the properties of vulcanized rubber. Although Ostromislensky has sponsored Bock's reaction product (a brittle, insoluble substance), he apparently attributes the vulcanization to a

“partial cyclization” (13). Farmer and Michael (7), having separated a large number of reaction products in the parallel treatment of cyclohexene with dibenzoyl peroxide, regard Ostromislensky’s view of the reaction as an oversimplification. But whatever products are obtained, and these include carbon dioxide which is not formed when the peroxide acts on the rubber, they do not of themselves elucidate the process responsible for the properties of a vulcanizate. This Farmer and Michael attribute to the free radicals from the decomposing peroxide which initiates cross linking and can be continued by chain reactions. Naunton (12) believes the vulcanization in photogelation to be brought about by the oxygen bridging of centers already oxygenated. We do not propose to discuss the mechanism of the vulcanization process in detail, as this is a subject in itself, but it is desired at this stage to emphasize the independence of the vulcanization mechanism from other secondary reactions which yield oxidized or condensation products of rubber. The products obtained with dibenzoyl peroxide may be expected to resemble physically those obtained with ketones and other carbonyl-containing activators. Under suitable conditions thermal vulcanizates may be obtained with dibenzoyl peroxide which have fair tensile properties, about half the value of that obtained with sulfur and accelerators, but the products are unstable. Dibenzoyl peroxide also causes softening of the rubber with which it is mixed and changes set in so that any delay in heating the mixture results in poor vulcanizates. It is therefore not surprising that a long drawn out process of irradiation gives time for reactions to proceed which obscure any improvement in physical properties resulting from simultaneous vulcanization.

XII. Vulcanization—Thermal and Photochemical

Perhaps some definition of this latter term is necessary from the point of view of the photoprocess, or, at least, a formulation of those changes which can be grouped together as characteristic of soft rubber vulcanization, since there appears to be some difference of opinion regarding the criteria to be applied in defining vulcanization. These criteria are: (1) insolubilization of the rubber, (2) indifference to a wider range of temperature changes, and (3) an all-round improvement in physical properties. This assumes that milled rubber, which is substantially plastic, is taken as the starting point for comparative purposes. Clearly (1) and (2) can be conferred by many chemical changes; thus, rubber hydrochloride fulfills both conditions but cannot be described as a vulcanized rubber. This term can be applied only where characteristic high-elastic properties are conferred on the material. The change, presumably cross linking, which is generally held to

lead to a vulcanizate, is to be regarded as the primary reaction; and the reagents and conditions which promote this cross linking to the maximum extent, whatever the mechanism, while suppressing substitution or saturation of the isoprene unit, will result in the best vulcanized rubber, *i. e.*, with the highest tensile, modulus, recovery, etc. By means of accelerators in thermal vulcanization, an improved product is obtained, for the conditions appear to favor cross linking with a minimum of sulfur substitution or addition. If the heating is continued so that the latter reactions progress, the excellent physical properties are submerged in those of a sulfur reaction product (which results with 5 to 10% of combined sulfur). This latter is soft, harsh, weak, and brittle. High elasticity is absent. Similarly, with a photovulcanization, the initial improvement is soon lost in the inferior physical properties of the chemical reaction products when active solvents or activators are employed. For this reason, the degree of milling has relatively little effect on the rate of gelling or physical properties of the dried gel, the predominant reaction being a substitution or saturation and not a vulcanization.

When rubber is vulcanized thermally with sulfur and no other ingredient, maximum physical properties are attained with a combined sulfur of 3 to 4%; and the properties, *e. g.*, modulus, vary with the proportion of sulfur bound. By introducing accelerators, the optimum results, which are higher than those obtained with sulfur alone, are given with a combined sulfur of 1 to 2%. By using the most efficient ultra-accelerators, *e. g.*, a tetra-alkylthiuram disulfide without free sulfur, or a mixture of mercapto-benzothiazole with a smaller amount of the thiuram disulfide, still better vulcanizates are obtained with only 0.3 to 0.5% of combined sulfur (18). The latter are remarkable for their resistance to oxidation by oxygen or air at raised temperatures, confirming the conclusions of Boggs and Blake (3) that all combined sulfur in excess of 0.5% is detrimental to soft rubber, causing it to age more rapidly. The concomitant variation in combined sulfur and degree of vulcanization, as determined by physical properties for a simple rubber-sulfur mix, naturally led to the conclusion that vulcanization was a result of the combination of the rubber with sulfur. This view survived the advent of ultra-accelerators because the same relationship held, although at a different level, as regards vulcanizates obtained with them and because no perceptible degree of vulcanization is obtainable without some combined sulfur. A consideration of these facts raises once more the question of whether sulfur combination is necessary to vulcanization. If it is not necessary, then combination with sulfur is a side reaction and has no direct cross-linking action (as judged by enhance-

ment of physical properties). It corresponds to the condensation reactions taking place during photogelation. In any case, the facts given above indicate that sulfur bridges cannot be regarded as a satisfactory explanation of vulcanization because the smaller the proportion of combined sulfur (within limits) which may be reasonably interpreted as indicating a smaller proportion of sulfur bridges, the better the effects obtained, especially in regard to tensile properties and resistance to oxidation. If sulfur bridging is excluded as the mechanism of vulcanization, then oxygen bridging must likewise be ruled out, and the cross bonding must be direct without other elements in the link. From this standpoint, such elements, although they function as reactants, must also act as catalysts. The detrimental effect of sulfur or oxygen entering the chain on the efficiency of the catalysts in promoting cross linking is easily understood, as will be shown later. This view of vulcanization has been presented since it appears to obtain confirmation from the behavior of photogels and provides a theory on which the insolubilization of rubber under varying conditions can be simply explained.

The broad conclusion to be drawn from the study of photogelation may be stated, therefore, as that the products represent nothing more than a system in which a catalyzed cross bonding or vulcanization exists with which condensation products are associated. The effect of illumination of rubber, whether in inactive solvent or in dry mass form, is to render the molecule photochemically active, a state still further enhanced by the presence of a catalyst or sensitizer. As a result, some cross linking, *i. e.*, direct binding through the opening of adjacent double bonds, ensues with gelling, *i. e.*, insolubilization of the rubber. Without activator, incipient vulcanization is easily detected but the amount of cross linking is small. The physical change is also small and is sometimes confined to little more than insolubilization: tensile properties are only a little in advance of those of raw rubber (milled) taken initially. The products are also readily oxidized and rendered soluble again by air in light. This initial vulcanization progresses slowly with prolongation of light exposure, its physical character becoming more definite. With a long exposure, the rubber stoutly resists the solvent action of benzene and the swelling is moderate. Stress-strain curves obtained from insolated rubber show improvement in modulus obtained with prolongation of insolation; but figures for breaking load have not exceeded 18 to 20 kg.cm.⁻² The curves (Fig. 1, page 374) have the pronounced S shape of vulcanized rubber and do not differ materially from rubber vulcanized to this small degree by ordinary thermal methods (21).

In the presence of an activator or reactant (ketone, quinone, chlorinated

hydrocarbon, etc.), which also acts as a catalyst, the system becomes more complex. Parallel with a slow improvement of the vulcanizing characteristics due to cross linking there intervenes a condensation product formed between the rubber and the activator, which now becomes the major resultant and on which the properties of the final product in the main depend, including insolubility and stiffness of the gel.

An examination of a progressive series, whether obtained by photogelation as a series of xerogels or alternatively by direct exposure of the dry rubber, shows that the product gradually loses or appears to lose its initial soft-vulcanized rubber character, becoming leathery and eventually hard and brittle. The change is closely paralleled by the thermal vulcanization of soft rubber as already outlined. As in the case of thermal vulcanization, the physical properties are largely dependent on experimental conditions. In the presence of sufficient air, a gel is not obtainable because oxidation and splitting of the chains predominate. Similarly, a rubber-sulfur mixture cannot be thermally vulcanized unless enclosed in a mould which excludes air. By vulcanizing with the aid of ultra-accelerators, particularly at low temperatures, exclusion of air is not necessary to the formation of a physically satisfactory vulcanizate. Similarly, satisfactory photovulcanization can be obtained with a sufficiently powerful sensitizer by insolation of dry rubber in the presence of air. Chloranil, benzophenone, anthraquinone, sulfur, and several other substances give products with breaking loads of the order of 30 to 35 kg.cm.⁻² and extension of 700 to 800% (21) (Fig. 2, page 375), and, where sulfur is used, a combined sulfur figure of about 0.5%. Although this figure for breaking load is little more than 10% of the maximum obtainable with thermally vulcanized soft rubber, it is an improvement on the best figures for the insolation of rubber alone.

XIII. Mechanism of Photovulcanization

At first sight, the photoexcitation of such large molecules as that of rubber appears unlikely, but the special modifying features due to the long chains comprising the molecules must be taken into account. As Bunn has pointed out (4), the melting point of rubber is no higher than that of a normal paraffin containing 14 to 15 carbon atoms, so that short lengths of the chain can vibrate independently. The increased frequency of vibration of parts of neighboring chains may well bring them into a favorable enough position to permit intermolecular bonding to take place. Further evidence in favor of this view may be drawn from the behavior of other elastomers (see next section), the more heavily substituted the chain

the less is the movement and consequently the tendency to gel formation, and the more readily the gel, when formed, is oxidized in light and air. This also applies to the addition or substitution of sulfur or oxygen in the chain, as in vulcanizates obtained with sulfur and dibenzoyl peroxide, and explains why these secondary reactions hinder the cross linking at the initial stages and prevent the formation of a vulcanizate with good physical properties. This is a further reason why cross bonding should be direct.

It has been stated (9) that vulcanized rubber differs from raw rubber essentially in that it possesses a structure which cannot be broken down completely by any solvent; the material therefore swells but cannot be dispersed unchanged. This may be accepted, as far as it goes, as a characteristic of a vulcanizate. All vulcanized rubbers tend toward insolubilization; but since so many other reaction products of rubber do likewise it follows that insolubilization of raw rubber is not the only change or the most critical of the changes produced by vulcanization. Great caution is necessary in interpreting insolubilization of a sol or the swelling and insolubility of a gel as a criterion of vulcanization. For example, if a rubber sol is treated with 10% of dibenzoyl peroxide in substantial absence of air in the dark, and the rubber is then recovered by evaporation at a low temperature, the product is soft and sticky; it even softens and tends to flow at 100° C., yet it is insoluble in benzene in the dark over a long period. This is an instance of insolubilization with vulcanization (enhancement of physical properties) entirely absent, softening having set in. As a contrast, a photogel from a benzene sol without activator after long exposure, *e. g.*, 2 or 3 weeks to direct sunlight, yields on spontaneous evaporation, a pale rubber which shows no signs of stickiness, and except for its slightly greater tenacity and rubberlike elasticity resembles the plastic milled rubber from which it was produced. This product swells, and in the course of 1 to 2 days is completely dispersed in benzene in the dark. Here we have, judged by physical properties, a slightly vulcanized rubber which is solvent-soluble and in contrast an apparently almost unvulcanized rubber which is solvent-insoluble. Similarly, insolubilization may result from cyclization. The product obtained with boron trichloride is insoluble but its properties are not those of vulcanized rubber; the progressive change effected with this reagent is reminiscent of that produced by photogelling in the presence of activators and active solvents.

It has been suggested that the mechanism of photogelation arises from excitation, not of the rubber itself as in the author's view, but of the activator or reactant. On this hypothesis (6, 19), the fragments of the solvents and/or sensitizers, *i. e.*, products of short life periods resulting

from photolysis, react with the rubber, which functions as an acceptor for the fragments. If the formation of activator fragments were a necessary first step in the formation of a photogel, gelling would not occur in the absence of an activator. Yet rubber sols gel in inactive solvents and dry rubber (protected from oxidation) becomes insoluble when exposed to light. So far as data are available, this takes place with various purified rubber specimens as readily as with the commercial product (milled crêpe). Further, activators (*e. g.*, acetone) require energetic attack to break them into fragments. They are not resolved into radicals by radiation of wave lengths longer than 3300 Å. Carbon tetrachloride, the most active solvent sensitizer, is not resolved at all by visible or ultraviolet radiation. Neither acetone nor carbon tetrachloride was found to undergo photolysis when exposed for a whole summer to direct sunlight in sealed, thin-walled, glass vessels. Under the same conditions, rubber gels in an acetone-carbon tetrachloride mixture in one or two hours. It may be suggested that the presence of the rubber as acceptor permits the reaction to proceed by exposure to radiation of longer wave lengths and less intensity than are required to break up the activator itself. This is a possible interpretation of the secondary reaction but throws no light on the vulcanization (cross-linking) process which, in the author's opinion, proceeds independently of the reaction. From another circumstance this viewpoint is less probable since insolation by direct sunlight in glass vessels results in gelling efficiency at least as great as that from exposure to an ultraviolet radiation of intensity sufficient to break up acetone into its radicals.

Neither hypothesis affords an explanation of the absence of gelling (without sensitizers) in certain hydrocarbons of relatively larger molecular size than those in which it takes place readily, as, for example, in tetralin and decalin. It is not a matter of solubility, for a photogel shows approximately the same degree of solubility in the larger molecule solvents as in the smaller ones, such as benzene, and, as already stated, the rubber recovered by precipitation from the irradiated solutions of the above-mentioned solvents is readily benzene-soluble and shows no sign of the exposure it has undergone. If it is suggested that the radiation has been preferentially absorbed by the solvent, then benzene should also have given a negative result. It is well known that the solvent medium generally has an effect on photochemical reaction velocity; the meager data available are in conformity with the behavior of rubber sols; thus, in the photopolymerization of anthracene, the rate of reaction was greatest in benzene and decreased with other solvents in the order: toluene, xylene, anisole, and phenetole (10). Or, again, the photopolymerization of vinyl chloride took

place in (rubber) solvents in the following order: carbon tetrachloride, ethyl ether, toluene, and carbon disulfide. It has been suggested that the rubber molecule takes up different configurations in different solvents in conformity with a variation in viscosity, the lower viscosity corresponding to a more compact molecule. The latter would be expected to be less responsive to radiation. However, the influence of solvent on reaction velocity is not confined to photoprocesses but is also common in thermal processes and presumably has an origin common to both.

XIV. Elastomers Other than Natural Rubber

We are indebted to Naunton (12) for a preliminary examination of some photogels from synthetic elastomers.* Solutions of these gel with a varying degree of ease and the xerogels obtained from them vary in solubility. The most sensitive to light are the simpler butadiene polymers which gel even more readily than rubber. The gels formed are more resistant to oxygen. It is stated that they do not revert in contact with oxygen, but this no doubt is a matter of degree, and gels obtained by very short exposures would presumably tend to be more soluble, as in the case of rubber. Similarly, the butadiene xerogels show better physical properties.

Next come the chloroprene polymers, whose solutions gel less readily than rubber sols. In conformity with this, the gels are more susceptible to oxygen, so that rubber appears to hold a position intermediate between butadiene and chloroprene polymers. All these show the same tendency to syneresis on further irradiation of the gel. The least reactive to light are the butadiene interpolymers. They do not readily form solutions [benzene-methyl ketone mixture (3:7) was used]. Twenty-five times as much "activator" is required as with the straight polymers. Incomplete solution, as is the case with some raw crêpes, does not hinder photogelation, so that the difficult solubility of butadiene interpolymers is not likely to be the cause of delayed gelation. When formed, the gels are resistant to oxygen and behave like those from the straight polymer. All three synthetic elastomers differ from rubber in that photogels could not be obtained with them in carbon tetrachloride solutions. Benzophenone was a suitable activator.

It seems clear that the greater resistance to oxygen of the straight

* In this article, the term "rubber" has been restricted to natural rubber, and rubber-like synthetics are termed "synthetic elastomers" in accordance with the suggestion of H. L. Fisher.

butadiene polymers is in line with the greater readiness to form gels. Experience with rubber indicates that the more rapid the gel formation and the more the irradiation is prolonged, the greater is the resistance of the resultant gel to oxidation and reversion to a soluble product. This resistance to oxygen cleavage cannot be assumed to be directly associated with the cross bonding (vulcanizing). It may rather be with the secondary reactions resulting in condensation products built up of hydrocarbon and elements of the solvent and/or activator, or by cyclization, all of which tend to insolubilization. Naunton's data indicate that gel formation takes place most readily with a straight diene chain without substituents, that the presence of methyl groups, as in rubber, retards gelation and that the replacement of these methyl groups by chlorine retards gelation still further. The presence of sulfur in the chloroprene chain (as in Neoprene GN) prevents gelation (12) altogether. This behavior supports the view that cross linking is the result of photoinduced vibration of parts of the hydrocarbon chain. The butadiene chain is the least encumbered with substituents and consequently requires less energy input to induce vibration. Vulcanization as indicated by gelling therefore takes place most readily. The introduction of substituents, the methyl groups in rubber, somewhat hinders vibration and gelling is slower. Chlorine has still greater retarding action while sulfur and chlorine in the chain so immobilize it that no cross linking and consequently no gelling take place. It is generally agreed that some sort of bond must come into existence between adjacent molecules in order to explain the insolubility of the vulcanizate. It has been assumed in this article that the cross linking is by primary valencies. There is, however, no proof of the existence of such valencies, and it may be that the chains become attached by some other agency. The photovulcanization and photogelling of rubber by mere exposure to sunlight and the rapid resolution of a freshly formed photogel necessitate a type of linkage readily formed and readily broken. It will be recalled that peptizing agents (thionaphthols) prevent gel formation both in the presence and absence of oxygen (12). Also, Whitby noted that fully vulcanized rubber gradually disperses in many swelling agents (24), and Williams has shown that vulcanizates giving good tensile figures can be more or less completely peptized with piperidine and ethyl sulfide and that the process does not require oxygen but must involve the breaking of primary bonds if they exist. Further, a film from a soluble fraction gave fair tensile figures, yet presumably cross bonding was practically absent (25). It seems, therefore, that the type of linkage is still open to question.

XV. Photosynthesis of Rubber from Isoprene and Polymerization of Styrene

Pummerer and Kehlen (15) have investigated the photosynthesis of rubber from isoprene and the photopolymerization of styrene. In the former, the nature of the product varied with the experimental details. Using eosin as a sensitizer, a white, very firm, elastic rubber was formed with the solubility of an ether-sol rubber. With styrene alone, a thickening to a syrup was obtained in a few hours; and, with a sensitizer under similar conditions, a solid resin resulted. Like the photopolymerized isoprene, this also was readily soluble in organic solvents, indicating absence of cross bonding. If, therefore, monomers can yield long-chain polymers as a result of irradiation, it would seem to follow that photogelation may also result, at least partially, from the lengthening of hydrocarbon chains, and the insolubilization may be a consequence of increase in length of molecule. Pummerer holds that the complete analogy in the behavior of rubber, isoprene, and styrene and the properties of the products formed from the latter two indicate the manner in which rubber polymerizes. If this is so, such products would have the nature of gel rubber obtainable from unmilled raw rubber rather than of a vulcanized rubber. It is worth recalling that the gel rubber of Smith and Saylor (17), obtained by dialysis of latex followed by tryptic digestion to remove protein and separated by means of ether, dissolved slowly in the presence of minute quantities of oxygen. Presumably, diffused light was not excluded; and in that case the behavior of this gel or ether-soluble fraction (25% of the whole) corresponds exactly with the behavior of photogels formed in inactive solvents at the initial stages. Smith and Saylor believe this relationship is superficial but do not give their reasons.

The writer has recently carried out a series of insolutions of rubber sols in inert solvents enclosing varying amounts of air (22). Alongside were insulated control tubes from which the air was exhausted as completely as possible. As the proportion of oxygen to rubber was reduced, the time taken to gel correspondingly fell until only small quantities of oxygen, about 0.2 to 0.3% on the rubber, remained. Still further reduction in the amount of oxygen had no appreciable effect on rate of gelation, and tubes containing 0.0013% gelled in almost the same time (10 to 20 hours) as larger quantities. In the latter cases, gelling took place suddenly after a preliminary loss of viscosity. On the other hand, the controls showed no preliminary loss of viscosity, but a gradual increase which, however, stopped short of a firm gel, producing only a ropy or semigelled mass.

It is concluded, therefore, that oxygen is the catalyst responsible for

initiating gelation and that there was not enough in the control tubes to bring about formation of a firm gel.

On the assumption that two atoms of oxygen are sufficient to link two molecules of rubber (degree of polymerization, 370), only one molecule in every 64 need be cross linked to gel by insolation a 5% sol of milled rubber.

XVI. Summary

To recapitulate, the formation of photogels results from the insolubilization of the rubber, and similar light effects may be obtained with dry rubber. The activators, sometimes termed sensitizers, are reactants which condense with the rubber to yield insoluble products, as shown by a considerable increase in weight. These products are not necessarily vulcanized but, being insoluble, may under some circumstances account for gelation. The same reactants condense with dry rubber, when irradiated, to give similar products. The condensations are side or secondary reactions and do not contribute to the vulcanized character of the product. This results from the capacity of the reactants to exert a simultaneous catalytic action on the rubber, promoting cross linking. Without the catalyst, cross linking and the development of the properties of a vulcanizate take place very slowly or not at all. The effect of the radiation in this regard is to incite the free sections of the rubber chains or elements of the same to approach under conditions enabling the cross linking between two neighboring chains to take place. This assumes great freedom of movement between adjacent chains. Any weighting of the chains, by substituents such as methyl groups, chlorine, sulfur, etc., or by condensation with activators, reduces the energy of vibration and consequently reduces the probability of an approach that will enable cross linking to take place by the opening up of the double bonds, assuming that primary cross linkages are essential for the development of the properties characteristic of vulcanization. The properties of the final product will vary with the relative extent of the manner of action of the activator, *i. e.*, whether predominantly an intermolecular cross linking or other form of attachment of individual rubber molecules catalytically promoted, or a condensation, with or without cyclization.

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REINFORCING AND OTHER PROPERTIES OF COMPOUNDING INGREDIENTS

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	PAGE
I. Introduction.....	389
II. Physical Characteristics of Fillers.....	390
1. Particle Size.....	390
2. Particle Shape and Structure.....	392
III. Behavior of Fillers in Vulcanized Rubber.....	393
1. Reinforcement.....	393
2. Tensile Strength.....	394
3. Stiffness.....	396
4. Hardness.....	397
5. Tear Resistance.....	397
6. Abrasion Resistance.....	398
7. Work of Extension.....	399
8. Work of Retraction and Static Hysteresis.....	400
9. Dynamic Hysteresis and Rebound Resilience.....	401
10. Electrical Resistance.....	403
11. Mixtures of Fillers.....	404
IV. Fillers in Synthetic Rubber.....	404
V. Criteria of Reinforcement.....	406
VI. Dispersion and Flocculation.....	408
VII. Dispersing Agents for Carbon Black.....	413
VIII. Causes of Reinforcement.....	414
1. Particle Size and Specific Surface.....	414
2. Particle Shape and Structure.....	415
3. Flocculation of Particles.....	416
4. Particle Surface.....	416
IX. Mechanism of Reinforcement.....	417
X. Effect of Carbon Black on Hysteresis.....	426
XI. Conclusions.....	427
Bibliography.....	428

I. Introduction

Finely divided powders, and particularly carbon blacks, have long been known to impart desirable properties to rubber. Dawson (17) mentions

that, from 1830 onward, the files of British patents contain references to the high quality of rubber compounded with carbon black. The scientific study of the application of fillers to rubber compounding, however, received scant attention before the publication of Wiegand's work in 1920 (62). Since that time, considerable research has been conducted on various aspects of the rubber-filler problem, and in 1937 a comprehensive and critical review of the existing data was published by Shepard, Street and Park (52). The present contribution, while discussing critically some of the work, and more particularly some of the more recent work on the subject, does not attempt to give an exhaustive review of the literature. Carbon blacks will receive more consideration than other fine powders primarily because they are the most valuable reinforcing agents, and in consequence have been studied, both in themselves and in rubber, in greater detail than have other types of filler.

II. Physical Characteristics of Fillers

1. Particle Size

A new tool for the examination of solids in a fine state of subdivision has been provided by the electron microscope. Particle size measurements by means of this instrument of a standard rubber-grade channel (gas or impingement) black (Micronex) reported by the Columbian Carbon Company in 1940 (14) showed this material to possess a mean particle diameter of 28 $m\mu$. In the same year, results were published of an investigation (43) by a centrifugal method which indicated that the great majority of the particles of a standard rubber channel black have particles ranging in diameter from 25 to 35 $m\mu$. The low-temperature nitrogen isotherm method developed by Emmett and Brunauer was used by Emmett and De Witt (20) and Smith, Thornhill and Bray (53) to determine the surface area and hence, by calculation, assuming the particles to be spherical, the mean diameter of a number of fine carbons. Values for channel black were reported which agreed well with those obtained by the electron microscope. The adsorption technique seems capable of differentiating between the rubber-grade impingement blacks. It places the acetylene and semireinforcing blacks in the right order of particle size. This method seems to depend on the type of surface activity as well as on surface area. It has not hitherto proved successful in the case of the thermal and high-volatile blacks (15).

In view of the agreement of the above three methods of determination, it would appear that the average particle diameter of a standard medium-

grade channel black used in rubber compounding is established as of the order of 28–30 $m\mu$. The method of the electron microscope seems to be the most reliable; and it ought to be possible, as the technique improves, to measure mean diameter of carbon particles with a sufficient degree of accuracy for the different rubber-grade channel blacks to be distinguished from each other.

In 1941, Wiegand (65) and Wiegand and Ladd (66) published the results of an investigation made by the electron microscope of a wide range of carbon blacks. The values of mean particle diameter and specific surface found by these authors are given in Table I. A fuller account of this

TABLE I
MEAN PARTICLE DIAMETER AND SURFACE AREA OF VARIOUS CARBON BLACKS

Carbon	Mean diameter, $m\mu$	Surface area	
		Acres per lb.	Sq. meters per gram
Medium thermal (Thermax)	274	1.1	10
Lampblack (Rubber Velvet)	97	2.6	23
Semireinforcing furnace (Furnex)	83	3.4	31
Fine thermal (P33)	74	4.1	36.5
Acetylene (Shawinigan)	43	7.3	65
Fine furnace (Statex)	34	8.4	75
Medium channel (Micronex)	28	10.6	94.5
Color carbon (Super Spectra)	13	22.2	198

investigation appeared later (15). This Columbian Carbon publication supplements the earlier one (14) in comprehensively reviewing previous work on the subjects of particle size, shape and structure of carbon blacks.

Assuming the values of particle diameter in Table I to be correct, indirect methods are available for the determination of unknown particle sizes. One such method which has recently been described (44) depends on the relationship existing between the particle size of any given carbon black and the rebound (impact) resilience of the rubber in which it is incorporated. The method is sufficiently sensitive to distinguish between carbon blacks differing from each other by less than $\pm 5\%$, *e. g.*, the easy-processing and medium-processing channel blacks. It has given values of particle diameter of high-modulus furnace black (Kosmos 40), coarse (easy-processing) channel (Spheron 9) and fine channel (Spheron 1) of 41, 30 and 24 $m\mu$, respectively. Its application is dependent on the assumption that the blacks being compared have spherical or spheroidal particles existing in the rubber in a similar state of dispersion and structural arrangement. The method, therefore, has its limitations.

Another method of comparing particle sizes of black dispersed in rubber is sometimes applicable (44). Thin microsections of carbon black loaded compounds (58) transmit a color which depends, within certain limits, on the size of the carbon particles. These limits are determined by the proportion of light scattered and appear to be approximately within the range of 30 and 80 $m\mu$. Above this range, where scattering is inappreciable, the color of the transmitted light is blue-grey. Below it, where scattering has reached a maximum, it is reddish brown. Between the limits mentioned as the particle diameter becomes smaller compared with the wave length of the incident light, and scattering increases, there is a progressive change in color, which appears to be quite sensitive to small differences in diameter provided the structural arrangement of the particles is unaltered. It is possible that this principle could be used to compare particle sizes of blacks suspended in liquid media.

The question of the particle diameter of fillers other than blacks usually involves a consideration of shape as well as size, and is discussed below.

2. *Particle Shape and Structure*

The investigations of Wiegand and Ladd show all carbon black particles to be spherical or spheroidal in shape. In 1941, Schoon and Koch (51) examined a number of blacks by means of the electron microscope and concluded from stereoscopic photographs that the particles consisted of hexagonal or circular platelets. It would appear that these authors have based their conclusions on a misinterpretation of the photographs (15). The view that carbon black particles are approximately spherical is confirmed by the surface area measurements made by the low-temperature adsorption technique (53).

Electron diffraction (61) and x-ray diffraction studies indicate that carbon blacks are two dimensionally crystalline, consisting of graphite layers arranged roughly parallel, but otherwise in random orientation. Biscoe and Warren (6), after providing convincing evidence of such a structure for carbon blacks, suggest that the term "turbostratic" (unordered layers) might be applied to this particular class of mesomorphic solids. These authors further show by small-angle scattering that carbon black particles consist of clusters of such parallel unordered layers. Their results indicate that a single channel black cluster is a few hundred angstroms in diameter, which is the same order of magnitude as determined by the electron microscope.

By making use of the x-ray data of Biscoe and Warren on three types of carbon black and determining the densities by helium displacement, Ross-

man and Smith (49) evaluated the free space within the particles. They found that the separation between the parallel layer groups in Shawinigan acetylene black particles may be as much as 6 Å. compared with 0.8 Å. for rubber channel black (Grade 6). They note that acetylene black, although possessing larger particles than channel black, has only about 1000 parallel layer groups in each particle compared with 3000 for Grade 6 black. The third black examined, Carbolac 1 (a paint black with particles as small as 5 $m\mu$) was found to have no more than 10 to 15 parallel layer groups in each particle.

The authors suggest that the porous nature of acetylene black may be reflected in residual forces at the surface of the particles, and that these forces may induce a secondary association of particles, which in turn accounts for the high electrical conductivity of this material. Electron micrographs of acetylene black (15) do in fact show chains of aggregated or flocculated particles.

Among the fillers other than carbon blacks, Mapico 297 iron oxide, which is manufactured by a calcination process, has spheroidal particles of 60 $m\mu$ diameter. Another red iron oxide, pigment Mapico 516-M, made by a precipitation (plus calcination) process, is shown by the electron microscope to consist of acicular crystals approximately 30 $m\mu$ in width and 150 to 300 $m\mu$ in length. The difference in shape and crystal habit of these two powders presumably results from their different methods of production (45).

Electron micrographs of zinc oxide show prismatic crystals, most of which vary in length between 0.5 and 1.0 μ . The variation in thickness is much greater. Some of the crystals are dendritic, and consist of four needles, often less than 10 $m\mu$ in diameter and united in the center of the dendrite.

Among the other reinforcing fillers, magnesium carbonate and china clay possess crystals of elongated habit, the exact size and shape of which do not appear to have been determined. Mica flakes are usually present as an impurity in clay.

III. Behavior of Fillers in Vulcanized Rubber

1. Reinforcement

The term "reinforcement" as applied to vulcanized rubber has been defined in various ways. According partly to the criterion chosen, partly to the type of test and partly to the magnitude of the experimental errors involved, different investigators have arrived at different conclusions as

to the reinforcing value, if any, of a particular compounding ingredient. Some fillers increase tensile strength without having much effect on other desirable properties such as abrasion or tearing resistance; some have a stiffening effect with relatively small increase in tensile strength. Others, and notably channel gas black, enhance most of the desirable properties of rubber vulcanizates. Naunton and Waring (38) have defined a reinforcing filler as one "which tends to move the rubber from the rubbery state to the solid state even at low concentrations." By the solid state is meant the completely crystalline state.

On any assessment of reinforcement, channel black ranks first in reinforcing power; but the channel blacks cover a range of particle sizes, and different properties appear to reach an optimum value at different particle sizes. The problem is further complicated by other factors which modify the effects of particle size.

At the other end of the scale are the coarse-grained fillers such as naturally occurring barytes and whiting which either do not reinforce at all or which show negligible reinforcement. The methods of evaluation of reinforcement employed by different investigators with the conclusions on a number of fillers are tabulated by Shepard, Street and Park (52).

The effect of various powders on certain properties of vulcanized rubber will now be considered. The question as to whether any particular property should or should not be regarded as indicative of reinforcement is deferred to a later page (page 406).

2. *Tensile Strength*

For various reasons which need not be discussed in detail, tensile strength values of similar and even of identical rubber compounds show considerable variability. Until recently, the data of different authors agreed in assigning higher tensile values to vulcanizates loaded with rubber-grade channel blacks than to those containing other ingredients, either of the carbon or noncarbon type. Within recent years, new types of furnace carbon (*e. g.*, Statex and Kosmos 40) have been produced which approach the channel blacks in fineness of subdivision and which give to vulcanized rubber an almost equal tensile strength at equivalent concentrations.

The tensile strength imparted to rubber by a reinforcing filler in general increases with increasing volume to an optimum and then declines. The maximum tensile strength promoted by different fillers varies with the concentration of filler. Because of the influence of fortuitous break and errors of testing it is often difficult to find the optimum; in fact this may not vary sensibly over a moderate change in concentration.

The results of an investigation recently published (44) relate particle size and specific surface of a number of carbon blacks to certain properties of rubber. The blacks were mixed at various concentrations in a base compound having the following formula (parts by weight): rubber, 100; sulfur, 3; mercaptobenzothiazole, 0.85; stearic acid, 3; and zinc oxide, 5. Wiegand's values of particle diameter and specific surface as given in Table I were employed in the case of the blacks studied by him. The resilience method described above was used to determine the particle size of the other blacks. Figures 1 to 8 are all reproduced from this paper (44).

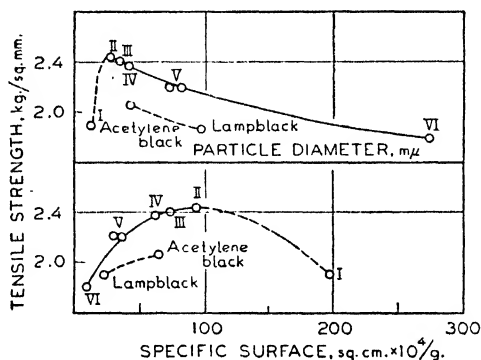


Fig. 1.—Relationship of tensile strength to specific surface and particle diameter of various carbon blacks (44). I, Super Spectra; II, Micronex; III, Statex; IV, Dixie 40; V, Gastex, Furnex; VI, thermatomic black.

The data on tensile strength show that, if the highest values irrespective of carbon concentration are plotted against particle diameter or specific surface, the points, with two exceptions, namely those representing lamp and acetylene blacks, lie on approximately smooth curves which have peaks corresponding to a particle diameter of 25–30 $\text{m}\mu$. These curves (Fig. 1) indicate the existence of an optimum particle size for best tensile strength at the position occupied by the rubber-grade channel blacks, but it should be noted that evidence is lacking in the region between these blacks and the extremely fine grained Super Spectra. It will be evident that certain carbon blacks for some reason or reasons have properties which modify the effect of particle size. Since all carbon smokes apparently possess approximately spherical particles, we are not concerned here with differences in shape (see pages 413, 415, 416, 424, and 425).

Until more is known of the size distribution and precise shape of rein-

forcing fillers other than carbon blacks, an analysis such as the one referred to above cannot be made. Because of the great diversity in crystalline shape and structure of such fillers the problem is more complicated than that of the blacks. These remarks apply not only to tensile strength but also to other properties of rubber vulcanizates.

3. Stiffness

This term is used to denote either elongation at a given stress or stress at a given elongation. The latter means of expressing the stiffness of a vulcanizate is commonly but incorrectly referred to as "modulus." Probably any filler, whether reinforcing or otherwise, has the property in some

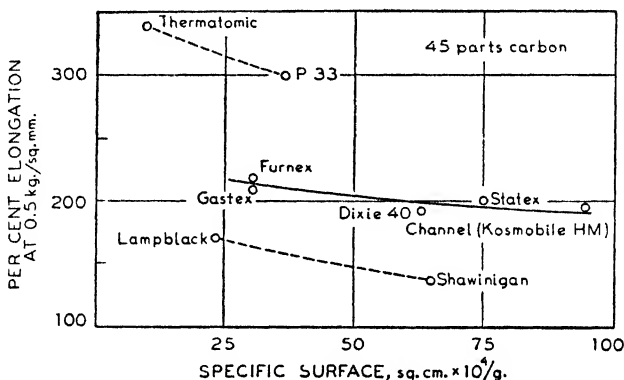


Fig. 2.—Dependence of the stiffness of carbon black loaded vulcanizates on specific surface (44).

degree of displacing the stress-strain curve toward the stress axis, and increased filler loading gives a progressive increase in stiffness up to very high concentrations. Figure 2 shows that the stiffness of carbon black loaded vulcanizates is dependent on specific surface (or particle size, since the particles are spherical) only on the assumption that carbon blacks can be divided into different series—or classes as they have been termed (44). Thus, lamp and acetylene blacks show a much greater stiffening effect in respect to their particle size than do blacks in the normal class, which includes the furnace and channel blacks. The thermal carbons, on the other hand, show a correspondingly reduced stiffening. Within the normal class there is an increased stiffening effect, or the modulus increases, as the specific surface increases.

Some reinforcing clays stiffen rubber to a degree almost equal to that

given by the semireinforcing blacks, but the stiffening effect of most non-carbon fillers is less even than that of the thermal blacks.

4. Hardness

This property is a measure of the indentation produced in a rubber product or test specimen by the application of a constant load. In the case of carbon blacks, the order of hardness is not necessarily the same as

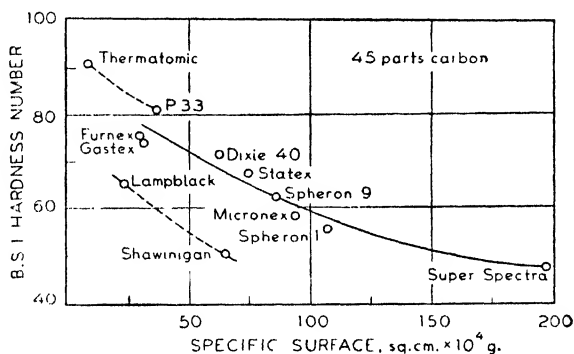


Fig. 3.—Dependence of the hardness of carbon black loaded vulcanizates on specific surface (44).

that of stiffness, except within the same class (Figs. 2 and 3). These tests were made on an improved form of British Standards Institution hardness tester developed by Hickman (32).

5. Tear Resistance

Resistance to tearing is a property which is difficult to measure accurately, and the results obtained depend to some extent on the form of test employed. The indications are that all types of carbon black except thermatomic increase the tear resistance of rubber and that the improvement approximately follows the order of particle size from thermatomic to channel. As in the case of tensile strength, resistance to tear decreases somewhere in the region between the rubber-grade blacks and Super Spectra. The latter, with particles of 13μ diameter, promote tearing properties of the same order as those of the semireinforcing blacks with particles about 83μ in diameter. Iron oxide, zinc oxide and specially treated calcium carbonate would appear to give tearing resistance of the same order as that given by the semireinforcing blacks.

6. Abrasion Resistance

For certain types of rubber compounds and particularly for tire treads, resistance to abrasive wear is one of the most important of all properties. High abrasion resistance is achieved only by incorporation into the rubber of a substantial volume of a finely divided carbon black. No other class of filler has any real value as a means of providing the necessary toughness

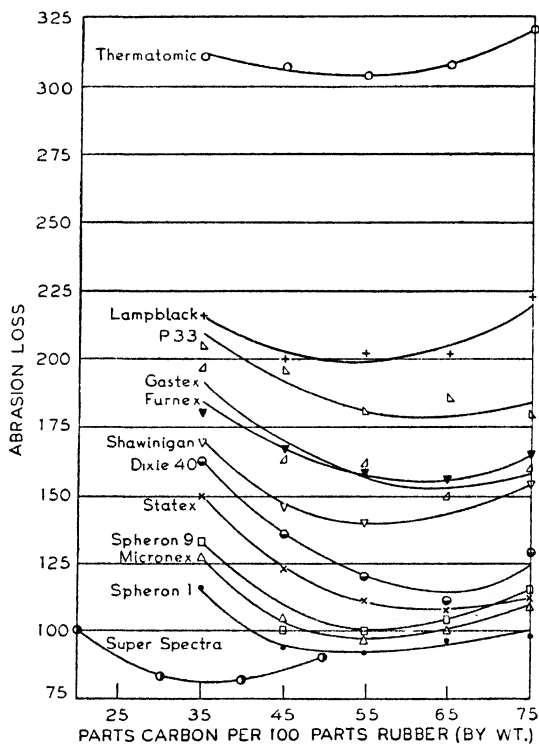


Fig. 4.—Relation of volume loss on abrasion resistance to loadings (44).

to resist rapid tread wear on the road. Lambourn (36) and others have adduced evidence that laboratory abrasion machines can be constructed which produce results showing a reasonable degree of correlation with the results of road testing. An improved form of the Lambourn machine, which takes account of transmitted energy in addition to slip, has been used for several years in the Fort Dunlop laboratories for evaluating tire treads, and has provided results which with most types of compound have agreed

with road testing data. A linear relationship with some spreading of the points has been found between road and abrasion-machine testing.

The effect of abrasion resistance of the various types of carbon black as measured on the Dunlop machine (44) is illustrated in Figure 4, which shows that the volume loss on abrasion decreases with increasing carbon concentration down to a minimum and then increases. The curves show that the maximum abrasion resistance (minimum abrasion loss) tends to occur at lower loadings as the particle size decreases and that its value in general increases with diminishing particle size. Figure 5 illustrates the

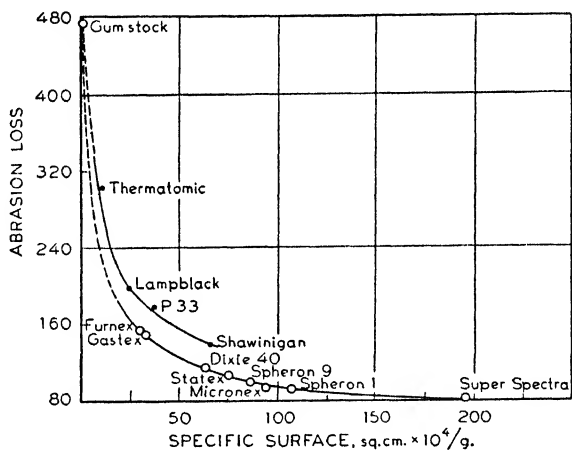


Fig. 5.—Relation between abrasion loss and specific surface (44).

relation between abrasion loss and specific surface, and shows that the blacks sort themselves out into two distinct curves. One of these consists of the normal class of blacks. In regard to the other blacks, it is probable that the cause of the anomalous abrasion properties of the thermal blacks is not the same as that of lamp and acetylene blacks, although these four carbons are represented by points on a smooth curve.

7. Work of Extension

This function is represented graphically by the area enclosed between the stress-strain curve and the elongation axis. The total energy input when the rubber is stressed to rupture has been termed its "proof resilience" by Wiegand. The term "resilient energy" has been employed in the same sense as proof resilience, and also to denote work of extension to points

below the breaking stress. As Wiegand first showed (62), the energy input to rupture of vulcanizates containing reinforcing fillers increased with filler concentration to a maximum and then diminished with further additions of filler. Wiegand further showed that this energy input had its highest value in compounds containing channel blacks, and suggested a correlation with abrasion resistance. The area obtained by plotting proof resilience as ordinate against filler concentration as abscissa was defined by Wiegand as the A function. The ordinate for no concentration gives the value of the proof resilience of the base compound, and the area between the curve and the horizontal line passing through this ordinate is the ΔA function which Wiegand used as an index of reinforcement of the filler (63).

8. *Work of Retraction and Static Hysteresis*

The work done by a specimen of rubber undergoing retraction after stretching is represented by the area between the retraction curve and the elongation axis. Hysteresis is a measure of the energy lost as internal heat when rubber is stressed, and is represented by the area of the loop enclosed between the extension and retraction curves. Conover (16) has adduced evidence which is claimed to show that, when rubber compounds containing different concentrations of different fillers are stretched at slow speeds to points approaching the breaking stress, the work of retraction is the same for all compounds. This is a surprising conclusion which has been challenged by Barron and Cotton (4), who contend that it is contrary to experience. The conclusion of the latter authors, however, that "with any rubber vulcanized to optimum tensile properties, hysteresis loss and work of retraction are proportional to the work required to extend to that elongation" is almost equally surprising, since it means that, unless static conditions of stressing are fundamentally different from dynamic, the capacity of any compound to generate heat can be calculated from its stress-strain properties. Such a conclusion is certainly contrary to experience under dynamic stressing conditions, and it is important that the evidence for its truth under slow-speed conditions should be scrutinized closely before it can be accepted. For this reason the Barron and Cotton data, which are published in full in the paper under consideration, have been submitted to a statistical examination. This analysis shows that the data in question, except at stresses near the breaking load, conform to general experience to the extent that the ratio of energy loss to energy input depends on the compound (that is, on the nature and quantity of the filler). The results also show that this ratio depends on the applied stress and is much more influenced by the stress than by the compound. In the case of loads at

or near the breaking point, the ratio is approximately constant for the fillers tested, *i. e.*, channel black, china clay, whiting and two grades of zinc oxide, over a range of concentration.

The conclusion of Barron and Cotton, therefore, does not seem to express a general truth. It may, however, be tentatively accepted in so far as it applies to stressing conditions near the breaking load, but it needs confirmation by an independent investigation covering a wider range of fillers. It would appear that the influence of the filler on hysteresis increases as the applied stress decreases, that is, as the operating conditions more nearly approximate those of most rubber products in service. If this is true, it has certain implications which will be considered later.

9. Dynamic Hysteresis and Rebound Resilience

Hysteresis loops on rubber compounds at frequencies up to 1000 cycles per minute have been obtained by Roelig (47), who used an optical method.

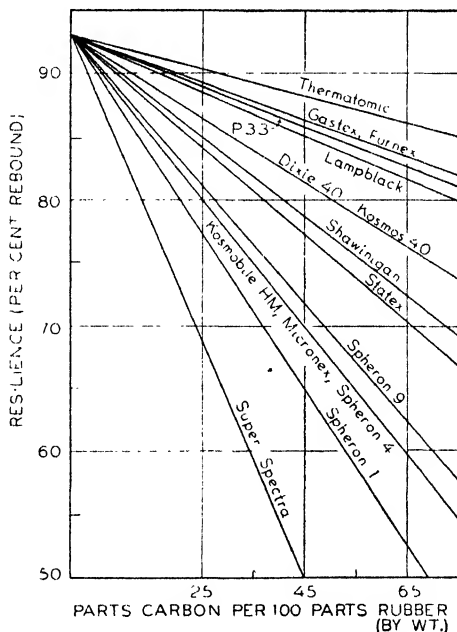


Fig. 6.—Relation of resilience to loadings at 50° C. (44).

The effect of filler loading was reported on one series of compounds only, it being shown that the percentage hysteresis increased almost linearly

with increased concentration of P33 black. The speed of testing was not given.

The most convenient, and probably the most accurate, method of determining hysteresis at speeds of distortion comparable with those of tires running in service is that of the impact pendulum (21, 31, 34). This is a compound pendulum carrying a steel ball which strikes a rubber block when allowed to fall under gravity. The percentage rebound of the pendulum after striking the rubber sample, that is, the percentage energy returned to it, is a measure of the resilience of the rubber. It is the equivalent in static testing of the work of retraction expressed as a percentage

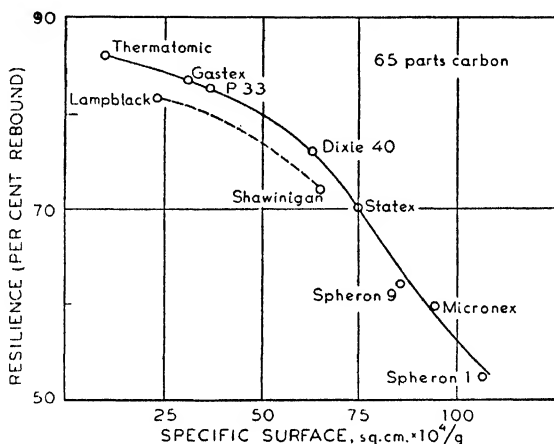


Fig. 7.—Relation of resilience to specific surface at 50° C. (44).

of the work of extension (or compression) and it is equal to 100 minus the percentage hysteresis. Except at temperatures approaching the freezing point, the resilience of vulcanized rubber increases with temperature increase to 120° C. and higher according to the type of compound and state of vulcanization. It then falls with further temperature increase.

As a result of recent work by Bulgin (10) in increasing the accuracy of rebound testing, it can now be shown that resilience decreases linearly with increasing carbon concentration throughout the range of normal compounding practice. At a given black concentration, rebound in general decreases with decreasing particle size or increasing specific surface. Figures 6 and 7 illustrate these points. The resilience was determined at a temperature of 50° C. It is seen that, as in the case of other properties,

the lamp and acetylene black compounds occupy anomalous positions on the rebound-specific surface graph.

By the use of a method involving the attachment of rubber specimens to a moving-coil loud-speaker unit and the measurement of the amplitude and frequency at resonance, Naunton and Waring (38) have calculated modulus and resilience at frequencies varying from 80 to more than 1000 cycles per second. They reach the surprising conclusion that, at frequencies above 150 cycles per second, channel black compounds have a higher resilience than any others tested and that increasing the gas black loading increases the resilience.

In an investigation on the dynamic properties of rubber, Gehman, Woodford and Stambaugh (24) used an apparatus based on the same principle as that employed by Naunton and Waring. They figure resilience-loading curves illustrating tests at a frequency of 60 cycles per second which resemble closely previously published curves (43) relating rebound to filler loading.

10. Electrical Resistance

The electrical resistance of rubber compounds containing any form of carbon decreases as the carbon content increases. In general, the decrease follows the decrease in particle size of the black, but there are exceptions to this rule. As in the properties already considered, acetylene and lamp-blacks are anomalous, these blacks producing a lower resistivity than might be expected from particle size considerations. The change in resistance can be enormous with even small differences in particle size; and other factors such as milling treatment have a profound effect on the electrical properties. It is generally agreed (25, 30, 35) that channel black particles are so arranged in tire tread compounds that continuous conducting paths are formed throughout the mass and that these paths are more complete when the black is well dispersed. The probability that such an arrangement of channel black particles results from a submicroscopic flocculation of dispersed black is discussed later (page 408). Other factors being equal, it is to be expected that, since the number of particles in a given volume varies inversely as the cube of the diameter, the number of conducting paths will presumably increase very rapidly with decrease in particle size. The data of Cohan and Mackey (13) conform to this view.

The electrical conductance of acetylene black compounds is ordinarily considerably higher than that of similarly loaded channel black compounds, although acetylene black particles are larger than channel black particles. This behavior of acetylene black as compared with gas black is generally

ascribed to a more complete development of conducting paths through the rubber. A possible reason for this enhanced tendency to flocculation of acetylene black put forward by Rossman and Smith (49) has been referred to on page 393.

11. Mixtures of Fillers

Shepard, Street and Park (52) mention that the data available at the time they discussed the effect of the blending of pigments on the stress-strain relations of rubber are insufficient for a definite conclusion to be formed as to whether such blending causes any deviation from values to be expected from the mixture law. Recent work (44) indicates that mixtures

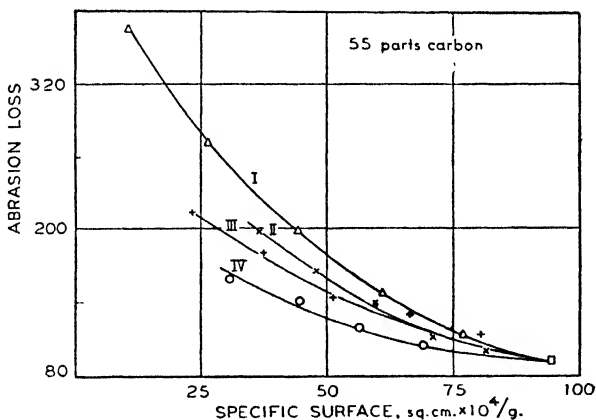


Fig. 8.—Relation of abrasion loss of mixtures of carbon blacks to specific surface at a total loading of 55 parts carbon to 100 parts rubber (by weight) (44). Micronex plus thermatomic black (I), P 33 (II), lampblack (III) and Gastex (IV).

of carbon blacks give resilient and abrasive properties which show no appreciable departure from those anticipated from the mixture law. Figure 8 relates abrasion loss of mixtures of carbon blacks to specific surface area at a total loading of 55 parts carbon by weight to 100 parts rubber.

IV. Fillers in Synthetic Rubber

Space does not permit a discussion of the influence of carbon black and other fillers on the different types of synthetic rubber. In fact, because of the present state of knowledge of some of them, such a discussion here would not be profitable. In general, it can be said that the effect of rein-

forcing pigments on chloroprene polymers such as Neoprene E and Neoprene GN, on interpolymers such as butadiene-styrene (Buna S and GR-S) and olefins with a little diolefin (Butyl rubber) is similar to that in natural rubber; but there are differences in detail. A complete understanding of the mechanism of filler reinforcement will no doubt be greatly helped by a knowledge of the interactions between fillers and the various types of synthetic rubber; and it is important, though axiomatic, that any anomalies which might be formed should be closely studied in view of their possible bearing on the problem.

In some ways, the effect of reinforcing powders in GR-S is more striking than in natural rubber. The necessary reinforcement for adequate properties of those types of compound (other than low-grade compounds) which with natural rubber do not require the addition of reinforcing fillers can only be attained by the employment of fully reinforcing, or at least semi-reinforcing, blacks. This is because the properties—particularly tensile strength—of the unloaded stocks are so poor that only the more powerful reinforcing fillers can provide the necessary degree of improvement.

The tensile strength of a pure gum GR-S stock is of the order of one-sixth to one-eighth that of an unreinforced natural rubber stock. The addition of 50 parts by weight of channel black increases the tensile strength tenfold and the same volume of semireinforcing furnace blacks about sixfold, which means that the influence of the blacks is to raise the tensile strength to a level not far below that of similarly loaded natural rubber compounds.

Another weakness of GR-S is its poor tear resistance, particularly at high temperatures. At ordinary temperatures, the effect of channel black is to impart tear resistance almost equal to that of a similarly loaded natural rubber stock, but at 100° C. the resistance to tear of GR-S tread stocks is considerably lower than that of natural rubber treads. The effect on tearing of other blacks approximately follows the order of particle size.

The resistance to wear of GR-S tread compounds as judged by the results of road testing is little inferior to that of natural rubber treads. Abrasion test comparisons on the Dunlop machine show all types of black to have an effect on abrasion resistance similar to that exerted on natural rubber.

The effect of carbon blacks on the rebound resilience of GR-S (itself having lower resilience at all temperatures than has natural rubber) is similar to that on the resilience of rubber, but the rate of decrease with increased loading is less. The linear relationship with loading probably holds for all blacks up to moderately high concentrations. Channel black seems

to show a departure from it at high loadings where higher rebound has been noted than is anticipated from the linear law. The resilience of lamp-black-GR-S compounds is higher, relative to particle size than that of lampblack-natural rubber compounds. This filler also gives softer vulcanizates of GR-S than of natural rubber.

V. Criteria of Reinforcement

Among the properties of powder-reinforced vulcanized rubber which have been discussed above, tensile strength, tearing resistance and abrasion resistance pass through an optimum value at some concentration of the filler, the concentration varying with the filler and with the property. Each of these properties might be classed as reinforcing, though the possession of any one of them except abrasion resistance does not necessarily mean that the compound is reinforced. There are other means of achieving high tensile strength and high tear resistance than that of the addition of finely divided powders. Thus, pure gum vulcanizates can be produced directly from latex having very high tensile strength and under certain conditions of preparation extremely high resistance to tearing, but such compounds have poor resistance to abrasive wear. (The remarks on tensile strength probably do not apply to GR-S which, without substantial additions of carbon black, possesses in all known types of compound extremely low tensile strength.) High abrasion resistance can only be attained on known compounding technique by incorporation into the compound of finely divided powders.

Among the other properties of rubber which have been considered in the foregoing pages, hardness, stiffness (modulus) and resilience do not pass through a maximum or minimum value at some concentration of filler, but increase or decrease progressively with successive increments of filler. In this respect they are unlike tensile strength, tearing and abrasion resistance, which seems a sufficient reason for their not being placed in the category of reinforcing properties. Other reasons support this view. The action of fillers on, for instance, resilience is generally to reduce it; and thus low resilience, an undesirable property for most purposes, normally accompanies high reinforcement. Low resilience, of course, can equally well be possessed by compounds in which the rubber has been diluted by nonreinforcing ingredients. Similarly, a high modulus is no necessary criterion of quality, the degree of stiffness arrived at depending on the properties required. It has been shown that moderately reinforcing acetylene black (Fig. 2) enhances modulus to a greater degree than does fully reinforcing channel black. In this connection the term "improved

modulus" so frequently met with in rubber technical literature has, as usually employed, little meaning.

As an index of the reinforcing effect of a filler, Wiegand's concept of the ΔA function is useful; but its application is limited since, in the case of certain fillers, it does not correlate with abrasion and tear resistance. As Wiegand showed, the rubber-grade channel blacks give a greater value for this function than do other fillers (except possibly the fine furnace blacks), partly because at optimum concentration they give higher proof resilience than other pigments and partly because they maintain a higher proof resilience than that of the base mix over a wider range of concentration. Magnesium carbonate and, in particular, some refined china clays, produce at optimum concentration energy input values at the breaking point not far below those of channel black, but these values are not maintained over as long a range of loading.

It has been shown (44) that, in the case of carbon black stocks (Super Spectra compounds excepted), there is a rough relationship between maximum energy input and maximum abrasion resistance. It will be evident that no correlation can be expected between proof resilience and abrasion resistance of compounds loaded to the optimum with nonblack fillers. The wear resistance values of magnesium carbonate, zinc oxide and refined clay, whether determined by road or laboratory testing, are small compared even with that of the semireinforcing black. It follows that energy input to rupture and the ΔA function cannot be universally applied as an indication of abrasion resistance. It is suggested that, to be fully satisfactory, any index of reinforcement should show reasonable correlation with abrasion resistance which, whatever its theoretical significance, is a property of supreme practical importance. There is similarly no necessary correlation between the stress-strain properties of rubber and its resistance to tearing, since magnesium carbonate and the finer clays give high resilient energy but poor tear resistance.

The reinforcing effect of four fillers, namely channel black, thermatomic black, zinc oxide and precipitated barium sulfate, was determined by Lunn (37) from resilient energy relationships at successive elongations up to breaking point. The energy attributable to the filler was separated from that of the base mix for each increment of loading. This method showed that the energy input value per unit volume of filler at any particular elongation increased to a greater degree, as the concentration increased, in the case of gas black than in that of the other fillers. Next in order came thermatomic black, followed by zinc oxide. All the curves tended toward zero value as the concentration increased, suggesting that the pigment

energy does not fall below zero and that at zero energy the filler acts as a simple diluent.

It should be mentioned that Lunn did not include either of the high modulus blacks, lamp and acetylene, in his investigation. Among the fillers tested, gas black, as anticipated, easily gave the highest energy values. Lampblack might have been expected to produce energy input values of the same order as those of gas black at moderate elongations, and Shawinigan black because of its great stiffening power would have given higher energy values than gas black up to quite high elongations. It would appear, therefore, that even if energy considerations at the breaking point are valid as indicating reinforcement they do not serve when compared at lower points on the stress-strain curve.

The trend of the above argument has been toward the conception that abrasion resistance itself is the most satisfactory index of reinforcement, and indeed such a view was recently put forward (44). There are, of course, objections to it. Some abrasion testers are of little value and the best of them are likely to give fictitious results with certain types of vulcanizate. Another objection which may be raised is that abrasion resistance is a composite property, that it is a complicated function of certain more fundamental properties. What those simpler properties are no one has yet been able to say, though there has been much speculation on the subject. To sum up, we may say that, for a complete evaluation of reinforcement, not only the stress-strain properties but also tearing and abrasion resistance should be taken into consideration.

VI. Dispersion and Flocculation

Most dry powders if added to rubber in sufficient quantity on a mixing mill or in an internal mixer have a pronounced stiffening effect. This stiffening is particularly marked with channel black which, volume for volume, probably reduces the plasticity of unvulcanized stocks to a greater degree than does any other filler (52), with the possible exception of acetylene black.

Some reinforcing fillers, notably carbon black and zinc oxide of fine particle size, reduce the "solubility" of the unvulcanized mixtures. Twiss (59) described the effect of carbon blacks on the solvation of rubber. He mentioned that, when a mixture of unmasticated rubber and gas black was immersed in petroleum naphtha, it retained its shape, although becoming softer and swollen. He detected the presence of a little dissolved rubber in the clear solvent and suggested that the carbon black was retained in an

adsorbed condition by the major portion of the rubber which remained undissolved.

Goodwin and Park (26) studied the effect of various volume loadings of five different blacks on the solution of the unvulcanized stocks in benzene. In every case but one (thermatomic) there was a limiting value beyond which the stock would not disperse in the solvent. The data of Goodwin and Park are reproduced in Table II.

TABLE II
EFFECT OF VOLUME LOADING OF CARBON BLACKS ON THE SOLUTION
OF UNVULCANIZED STOCKS IN BENZENE

Black	Volume at which solution no longer occurred
Charlton.....	45
Micronex.....	25
Super Spectra.....	10
Thermatomic.....	(154)
Goodwin.....	32

It is interesting to note that, although precise information of the particle size of Charlton lampblack and Goodwin black is lacking, the values in Table II are apparently in order of particle size. The authors attribute this behavior to complete inhibition of dispersion, and state that samples have shown no sign of dispersion after eighteen months, the rubber being extracted from the lump and making a perfectly clear solution in the benzene. They show that complete removal of the rubber by the benzene would be a matter of excessively long extraction.

Depew (18) studied in particular the solubilities in benzene of rubber-zinc oxide and rubber-channel black stocks and showed that fine zinc oxide passed into the solvent much more slowly than ordinary zinc oxide. He showed further that, when stearic acid was added to the compounds, the solubility of the stock containing fine zinc oxide was greatly increased, but that the carbon black stock remained insoluble. Depew attributed this lack of solubility to flocculation of the pigment, and the change in solubility induced by the addition of stearic acid to a change in the interfacial energy between the rubber and the pigment.

Stamberger (55) and Blow (8) found that the solubility of rubber-gas black stocks depends not only on the black concentration but also on the period of standing between mixing and dissolving in the solvent. Blow showed that an overmasticated mix containing 10% channel black would

still go into solution after 30 days' standing, but that a mix containing 15% black swelled to a homogeneous jelly after this period. The change in solubility is accompanied by a change in viscosity of the solutions. Blow showed that there is an increase in viscosity with increasing black content as well as with time of standing of the undissolved stocks.

Both Stamberger and Blow explained these phenomena on the assumption that the rubber is adsorbed on carbon black. Further work by Stamberger (56) designed to test the adsorption hypothesis did not definitely establish an adsorption of rubber from solution by gas black. He did not accept Depew's explanation that the changes on standing of the black-rubber mix were the result of flocculation of the black particles, arguing that, in such a highly viscous medium, changes in the dispersion of the gas black could hardly be expected.

It has been claimed by Carson and Sebrell (11) that the extreme difficulty of centrifuging channel black from dispersion in a very dilute rubber cement indicates a powerful union between rubber and black. But it has been shown (43) that impingement black dispersed in a rubber cement of very low viscosity is removed by centrifuging at a rate of the same order as is to be expected from its small particle size, assuming that the particles move freely in the liquid under the operation of Stokes' law. Unless the centrifugal field is very powerful, the rate of sedimentation is exceedingly slow and the smaller particles are difficult to remove from suspension. This, of course, does not prove conclusively that no force, adsorptive or otherwise, exists between black and rubber, since surface films of rubber, held tenaciously to the carbon particles, might be expected to be sedimented with the black. Such layers of rubber hydrocarbon if only a few angstroms thick would not greatly change the effective particle size of the black and, in consequence, the rate of sedimentation. It is at least as likely, however, that the black particles are suspended in the rubber cement quite freed from union with the rubber. Further experiments on the centrifugation of rubber-black cements under very carefully controlled conditions might throw more light on this question.

It has been found that the structural changes which take place in unvulcanized rubber-channel black mixtures are greatly accelerated and carried much further if the stocks are subjected to heat treatment for times and at temperatures which can vary within fairly wide limits. Temperatures preferably between 149° and 188° C. are recommended in a U. S. Patent Specification (25) by Gerke, Ganzhorn, Howland and Smallwood, who show that the action of the high temperature is to stiffen the stock greatly and to reduce very considerably its electrical resistivity.

This effect is attributed to a severe flocculation of the black. The mix is then remilled and the flocculated structure broken down to such a degree that it is not built up again during the vulcanization of the completed mixing, the final resistivity being many times greater than that of a conventionally mixed stock. These changes are illustrated in Figure 9. The authors claim that vulcanizates treated in this way have considerably lower torsional hysteresis and higher abrasion resistance than have normally mixed stocks, and attribute these improved properties to a more complete

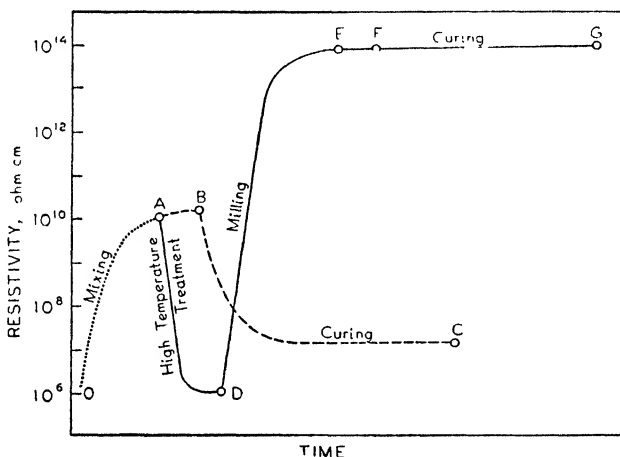


Fig. 9.—Changes in resistivity of heat-treated mixtures of unvulcanized rubber and channel black (25). Unbroken line is new process; broken curve is conventional process; dotted line is common to both.

dispersion of the carbon black particles. They suggest that the hysteresis of ordinary high carbon black compounds is largely caused by friction between aggregates of particles submicroscopic in size, or between particles in a flocculated state which form a network, giving a rigid structure providing continuous paths of relatively low resistance for the conduction of electricity through the rubber. The heat treatment is claimed to break down this structure to such an extent that the particles are more or less completely dispersed and the torsional hysteresis is reduced to a value approximating that of a pure gum compound.

The general conclusions of Gerke *et al.* have been confirmed (43) qualitatively and quantitatively as regards the specific resistance changes. Hysteresis as determined by the Dunlop-Healey pendulum is substantially

reduced by the heat treatment, but apparently not to anywhere near the same extent as is indicated by torsional pendulum measurements. [It should be noted here that hysteresis data as determined on the Dunlop fatigue machine (27) are in reasonable agreement with those of the impact pendulum.] The heat treatment has indicated that abrasion resistance, as measured by the Dunlop machine and by road testing of a number of tires, is improved by a small amount—about 4%—as compared with 30% claimed by Gerke *et al.*

The evidence considered above indicates strongly that, as suggested by Depew (18), the structures built up by black-rubber unvulcanized stocks are the result of a submicroscopic flocculation of the carbon particles, such flocculation taking the form of a network of strings and chains disposed throughout the rubber matrix. Despite the difficulty referred to by Stamberger (56) of movement through such a highly viscous medium as rubber, rearrangements of the particles do, in fact, appear to take place; otherwise it is difficult to account for the profound changes in electrical conductivity following the successive processing operations. The more rapid flocculation at the higher temperatures is to be expected because of the decreased viscosity of the rubber and possibly the greater thermal movement. The more complete breaking down of the flocculated structure on remilling the heated as compared with the unheated rubber may be a consequence of the greater shearing action on the stiffer structure.

A study of the effects of heat upon the structure of carbon black-rubber mixtures has also been made by Park and McClellan (40), who heated the stocks in nitrogen for eight hours at 132° C. These authors show that the stiffening action of heat is not confined to channel black mixings, and that it is shown to a less degree with a master batch containing 67 parts of a semireinforcing furnace black (Gastex). They also showed that, if a channel black master batch of this composition is heated and later milled into a final batch having a greatly reduced percentage of black, the heated stock is merely torn apart and distributed in the form of discrete lumps, whereas a portion of the same master batch which was not heated blended uniformly with the rest of the rubber.

Park and McClellan suggest that, if the stiffening effect is the result of flocculation, it is probable that a similar structural effect takes place to some extent during the early stages of vulcanization of an ordinarily milled tread stock, and state that their data support the view of Depew and Ruby (19) and of Green (28) that flocculation is related to the reinforcing effect in vulcanized rubber.

It has been argued (44) that the anomalous behavior of lamp and

acetylene blacks in vulcanized rubber is explained, at any rate partly, by the formation of carbon to carbon structures, or "complexes" as Wiegand has termed them (66), in the rubber. In other words, these blacks occur in vulcanized rubber in a higher state of flocculation, as this term is used above, than do the channel, furnace and thermal blacks. Electron micrographs of dry mountings (15) show well the irregular networks of contacting particles assumed by lamp and acetylene blacks; and it may be presumed that there is a tendency for such structures to persist in rubber, particularly as the electrical conductivity of compounds loaded with these two blacks is higher than expected from particle size consideration alone.

Unvulcanized acetylene (Shawinigan) and lampblack stocks do not stiffen up to anywhere nearly the same extent as gas black stocks, and when such stocks are covered with petroleum naphtha or benzene the carbon particles diffuse with the rubber into the solvent. A possible explanation is that the black particles remain in their original chainlike arrangement on entering the rubber and thus there is no tendency for them to come still closer together when the stock is allowed to stand or is heated. The fact that freshly milled acetylene black stocks in particular are stiff and difficult to work may be significant in this connection. But it would seem that the flocculated state of lamp and acetylene black does not prevent these blacks from diffusing out of the mix when the latter is immersed in a solvent. Following heat treatment of the uncured stocks, moreover, there is no increase in rebound resilience of lamp and acetylene black vulcanizates.

VII. Dispersing Agents for Carbon Black

So-called softeners or emollients, which are of several types, are added to rubber during the mixing operation as an aid to subsequent processing and to promote even distribution of the powder in the stock. We are here concerned primarily with softeners of the fatty acid type and notably with stearic acid. This substance is important as an activator of certain accelerators of vulcanization; as a softener, it is also valuable, provided it is not used in excess. Its value as a dispersing agent for carbon black has been the subject of much controversy. Blake (7) advanced the hypothesis that the natural fatty acids in the rubber wet the black by forming an adsorbed layer in which the carboxyl groups are attached to the surface of the carbon particles. His calculation that there is just about enough fatty acid in the rubber to form a monomolecular film around each channel black particle at a concentration of 30 volumes of black in 100 volumes of rubber is based on the assumption of a particle diameter of 0.2μ , which is

now known to be seven times too large. A rather crude attempt was made (42) to test Blake's theory by mixing two channel black stocks, the rubber in one of them having the fatty acid removed by acetone extraction. The black dispersion of the two stocks as judged by macroscopic and microscopic examination was about equal. It seems certain, however, as was suggested by Park and Morris (41), that the extraction in the experiment under consideration was not complete. Park and Morris showed by macroscopic examination and the microscopic methods of Allen (1) and Roniger (48) that 1% stearic acid was effective as a dispersing agent in acetone-extracted rubber. Other types of softener, notably pine tar and Degras, also reduced black agglomeration in acetone-extracted rubber, but not to the same extent as fatty acids. Experience over a number of years with the Dunlop microscopic technique (58) on normal tread compounds indicates that stearic acid is effective in breaking down black agglomerates. These methods of examination by means of the optical microscope are, of course, incapable of enabling the actual channel black particles to be viewed and tell us little of their ultimate dispersion in rubber. The fact that the methods show that stearic acid reduces the larger black aggregates does not justify the assumption that it is the fatty acid and not the rubber which wets the black. Channel black does not readily disperse in stearic acid alone; and it appears, as mentioned above (18), that stearic acid will not deflocculate black, though it does seem to deflocculate zinc oxide. That there is a limited adsorption of stearic acid by channel black in rubber has, however, been shown by Gehman and Field (23) from x-ray diffraction observations on black-rubber master batches.

A study of the behavior in solution of black-acetone-extracted rubber stocks, heated and unheated, and of the effect on electrical resistivity of the unvulcanized and vulcanized compounds might throw further light on this problem.

VIII. Causes of Reinforcement

1. Particle Size and Specific Surface

We have seen that the properties of stiffness, hardness, rebound resilience and abrasion resistance are related in a regular manner to particle diameter and its reciprocal specific surface throughout the range of blacks—semi-reinforcing furnace, high-modulus furnace (Kosmos 40), fine furnace (Statex), coarse, medium and fine channel and color black (Super Spectra)—that is, as the particle diameter is reduced from about 83 to about 13 $m\mu$. We have seen, further, that the tensile strength and tear resistance increase

as particle diameter decreases to about 30–25 $m\mu$ and then fall with further reduction of diameter.

Lamp and acetylene blacks, as has been noted, invariably impart anomalous properties to natural rubber in relation to their particle size. In certain other properties not associated with rubber, such as water absorption and oil absorption, they are also anomalous with respect to particle size (15). Evidently some factor or factors are operating in the case of these blacks which modify the effects of particle size; and reasons have been given above that such a factor is the presence of carbon networks.

The thermal blacks, unlike acetylene black and lampblack, give softer vulcanizates than do the normal class, but like lamp and acetylene they result in poorer abrasion resistance than is expected from their state of subdivision. Again, factors are operating tending to modify the influence of particle size. Of the fillers other than carbon blacks, one form of iron oxide (Mapico 297), as mentioned on page 393, has spheroidal particles about 60 $m\mu$ in diameter (45). This imparts rather higher tensile strength and, up to 10 volumes' loading, rather higher tearing resistance than semireinforcing furnace carbons, in keeping with its smaller state of subdivision. It also gives lower rebound resilience than do the furnace blacks.

2. *Particle Shape and Structure*

All carbon black smokes appear to have spherical or spheroidal particles. The anomalies mentioned above, therefore, are not a result of differences in particle shape. Mineral (and some precipitated) powders are composed of crystalline particles of varying shapes; and it would seem that, in some instances at least, the geometrical shape, which is not necessarily related to crystalline structure, affects the properties of rubber in an adverse manner. There is no reason to suppose that straight-sided crystals, whether equidimensional, acicular or platelike, are equal in reinforcing action to spherical particles of similar specific surface. As yet no accurate information such as might be obtained by means of the electron microscope has been reported on the surface areas developed by powders such as zinc oxide, magnesium carbonate and china clay; but it is evident that the surface developed by finely divided zinc oxide must be high because the crystallites include a large proportion of excessively thin spicules. As judged by abrasion resistance, zinc oxide has reinforcing properties no stronger than those of the medium thermal blacks, although it must possess a much larger specific surface area. As judged by stress-strain and tearing properties, it has resemblances to both the fine thermal and the semireinforcing carbons.

3. *Flocculation of Particles*

A study of the literature, some of which has been reviewed in the foregoing pages, reveals the existence of two schools of thought with regard to the influence of flocculation on reinforcing fillers. One view is that flocculation increases reinforcement; the other, that it reduces it. There seems little evidence in support of the first view beyond the microscopic observations of Depew and Ruby (19), Green (28), Grenquist (29), Park and Morris (41) and Park and McClellan (40) which suggest that carbon black exists in vulcanized rubber to some extent in a flocculated condition, and that since flocculation produces stiffer structures it is therefore a factor in reinforcement. Any structures built up by channel black particles in rubber which can be viewed in an optical microscope are on a large scale compared with the ultimate state of division, and are not necessarily of the same kind as the submicroscopic structures discussed above which are inferred from resistivity measurements. Highly compounded channel black stocks when examined under high power do, however, suggest an impression that the black forms some sort of structure. Grenquist (29) states that the particles "seem to float through the rubber in an orientated network which possibly is a measure of the reinforcement of the system." This appearance may be illusory, but whether it is or not, the evidence now available does not on the whole support the hypothesis that flocculation is a positive factor in reinforcement; on the other hand, the evidence tends to show that it operates in the opposite direction. Thus, although the "structure-forming" carbons, acetylene and lamp, produce very stiff vulcanizates in relation to their state of subdivision, such vulcanizates have poorer tensile strength, tearing and abrasion resistance than would be anticipated from particle size considerations. Moreover, the abrasion resistance of vulcanizates produced from deflocculated, heat-treated, channel black stocks is somewhat higher than that produced from similar stocks not subjected to the preliminary heating and remilling.

In summary, we may say that flocculation of fillers is a phenomenon normally present in vulcanized rubber compounds which contain the filler in a sufficiently high concentration, but that on present evidence its relationship to reinforcement is a secondary one which tends toward reducing the reinforcing effect of the filler.

4. *Particle Surface*

It has been suggested (44) that the low reinforcing effect of fine thermal black (P33) in relation to the size of its particles might result from its low surface activity (15, 53). The question of surface forces is considered below.

IX. Mechanism of Reinforcement

The foregoing argument indicates that particle size, for some reason or reasons not yet clear, is the primary factor influencing the reinforcing action of a filler in rubber. It also indicates that spherical particles are likely to be more strongly reinforcing than those of other shapes giving similar specific surface area, although precise information on this point is lacking. It has further led to the tentative conclusion that the degree of flocculation of the particles should be as small as possible, or, in other words, that the particles should be uniformly dispersed in the rubber matrix.

The question now arises as to what mechanism, chemical or physical, or both, causes small particles to reinforce. Certainly until a few years ago (and possibly at the present day) the most favored hypothesis was that the phenomena were concerned with surface energy changes at the interface between the filler and the rubber matrix. The views expressed on the surface energy concept were largely speculative and, as pointed out by Wiegand in 1937, even contradictory (64). Some of the confusion of thought seems to have arisen from a wrong interpretation of the term "interfacial tension." This of course does not prove that energy changes which might take place at the rubber-filler interface are of no consequence in reinforcement, but that they have not as yet led to a satisfactory explanation of its action.

Surface energy changes are by definition reversible. If they are invoked to explain reinforcement, the implication according to Wiegand is that an energy change which takes place at the rubber-filler interface when the filler is incorporated in rubber is reversed when the rubber is stretched to rupture and that the break should occur at the rubber-filler boundary. Wiegand mentioned that reinforcement had been attributed to both increase in and decrease in free surface energy. He stated that the increased free energy concept implied a progressive increase in rubber-pigment surface boundary as a specimen is stretched to breaking point and explained that "such a condition has never been demonstrated, never suggested and can scarcely even be imagined." In regard to the decreased free energy concept, he pointed out that there was no evidence for the assumption previously made by himself "first that failure occurs at the rubber-pigment boundary, and second that the increased proof resilience (work of rupture) is measured by the increase in surface energy required to separate rubber from pigment."

It might be argued that, although no evidence has been adduced that progressive changes and finally rupture occur at the rubber-filler interface

when a specimen is stretched, it does not necessarily follow that surface energy itself bears no relation to reinforcement. It is conceivable that the adhesion tension (*i. e.*, the difference between the surface tension of the filler and the interfacial tension between filler and rubber) might be so high in a properly mixed compound that the rubber fractures entirely in the matrix; in other words, Blake's theory (7) that a reinforcing filler is one which forms a bond with the rubber matrix that is stronger than the matrix itself might offer an explanation of reinforcement. Blake pointed out that it follows from his hypothesis that the tensile strength, calculated on the cross section at break, is a measure of the tensile strength of the matrix and should be constant for all reinforced compounds. Although he argued from Wiegand's data that this was generally true, the results of subsequent work (52) do not seem to support his contention.

Whether or not reinforcement itself is a result of surface forces of a reversible character, it will be evident that if, as is usually assumed, rubber can be regarded as behaving like a liquid when it acts as a dispersion medium for colloidal particles, surface energy changes will of necessity take place when the particles are immersed in the medium. As mentioned by Shepard, Street and Park (52), the addition of fine powders to rubber is a case of immersion wetting as this term is defined by Osterhof and Bartell (39). The following considerations show that there can be no doubt that during an ordinary mill mixing operation there is wetting of the filler particles by the rubber.

If channel black is mixed with natural rubber latex and the crumb which forms on coagulation is pressed up and vulcanized, it is found that the black has merely acted as an inert filler. Microscopic examination of a thin section of the vulcanizate reveals a mosaic of opaque and clear transparent areas. If the latex-black crumb stock is worked for a minute or two on a mixing mill, the black as judged by microscopic examination disperses completely, the section having the uniform reddish-brown color characteristic of normally mixed gas black stocks. It may be assumed that until the latex globules are broken up there is no possibility of intimate contact between black and rubber.

It seems evident, therefore, that, if we still assume that rubber behaves as a liquid, there is some degree of immersion wetting when channel black is incorporated into masticated rubber. If the degree of wetting were high, it might be expected that, since the surface developed between channel black and rubber is enormous—about 170 square meters per cubic centimeter of carbon, assuming complete dispersion, there would be a very pronounced effect on those properties of rubber which collectively

give reinforcement. There would also not be expected to be much migration or flocculation of the wetted particles in the highly viscous medium. Bartell and Hershberger (5) show that in systems in which the liquid forms a zero contact angle with the solid the degree of wetting is high and there is no evidence of incomplete dispersion, but that in systems in which the liquid forms a finite contact angle with the solid the degree of wetting is low and there is evidence of flocculation. As shown above, there seems ample evidence that in unvulcanized channel black-rubber stocks the degree of wetting of the black by the rubber is not high enough to overcome the tendency to flocculation. It should be added that the work of Hock and others (33) on the heat of wetting of fillers in rubber has not led to any convincing evidence of a relationship between surface energy changes and reinforcement.

The above reasoning justifies Wiegand's contention of the need for a new theoretical approach to the problem of reinforcement; and this brings us to a consideration of Wiegand's own "discrete rubber" theory which was propounded in 1937 (64). This theory assumes that: (1) the rubber does not form a continuous phase, but is discrete, and consists of structural units larger in general than the individual particles of reinforcing carbon; (2) the reinforcing particles are associated with the rubber macromolecules in a new molecular complex; (3) single layers of carbon black surround each rubber unit and function as bonds between adjacent units; (4) an additional number of carbon particles fills the "voids" between the rubber macromolecules; and (5) additional carbon black after the voids are filled will wedge the rubber units apart with progressively diminishing reinforcement.

This hypothesis has some attractive features. In particular, it offers a possible explanation as to why the high theoretical proportions of black loading based on tetrahedral piling have never even been remotely approached, and why maximum reinforcement might be expected to occur at moderate concentrations. It also offers a better explanation of conducting rubber than that which assumes the rubber to form a continuous phase, since those carbon blacks which promote electrical conductivity are presumed to be flocculated into a structure whereby the particles are virtually in contact with each other throughout the mass of rubber.

The x-ray work of Gehman and Field does not fully support this theory. These authors point out that x-ray diffraction patterns of rubber-black stocks show a continuous change as black loading is increased, and conclude there is no evidence that rubber exists as the dispersed phase as suggested by Boiry (9) and elaborated by Wiegand. They point out that,

if individual rubber macromolecules are surrounded by carbon black particles, crystallization should be hindered or at least the lattice should be distorted. Their work, however, does not seem to disprove entirely the possibility that the rubber itself can exist as discrete units, particularly as they state that the rubber crystallites responsible for the x-ray diagrams are of the same order of magnitude as the particles of channel black.

The view that, in a reinforced mixing, the filler constitutes the continuous phase and acts as a bond between the individual rubber molecules and aggregates has received support from Naunton and Waring (38) for the reason that reinforcing fillers decrease the resilience of rubber.

On the whole, the evidence seems to support the hypothesis that the rubber forms a discrete phase but that Wiegand's theory needs some modification in order to explain all the phenomena. In this respect, mention might be made of the property of rebound resilience, the linear relation of which with loading is difficult to account for, on the assumption that at relatively low concentrations substantially all the black is bound to the rubber molecules while at higher loadings only a portion of it is so bound.

This brings us again to the question of the mode of attachment of the carbon or other fillers to the rubber molecules. It has been argued above that surface forces of a reversible character are inadequate to explain reinforcement, since there is little evidence that such forces are developed to any great extent. Naunton and Waring (38) regard reinforcement as a type of vulcanization, and suggest that the "strong bond between the rubber and reinforcing particles acts like the sulphur bridge in vulcanization with sulphur." Gehman and Field (23), in discussing this hypothesis, point out that, although the x-ray patterns do not show any evidence that the black acts as a primary valence cross linkage, they bear out the analogy of reinforcement to vulcanization to the extent that black assists crystallization of the rubber (the diffraction spots appear at lower elongations with reinforced than with unreinforced compounds) in the way that vulcanization assists the crystallization of milled rubber upon stretching by the reduction in plasticity.

Thornhill and Smith (57), in testing the chemical linkage hypothesis, worked on the assumption that, if primary valence linkages between carbon and rubber are formed, the ethylenic bonds of the rubber molecule would be involved and a specific loss in unsaturation of the rubber by hydrocarbon should occur. They detected no such loss in unsaturation that could be attributed to association of channel black at the double bonds of the rubber hydrocarbon, but pointed out that lack of reinforcing action of fillers in

saturated polymers such as polyisobutylene is an argument in favor of the view that unsaturation is essential for reinforcement. They further point out the possibility that only a few chemical bonds are essential for reinforcement; and, making the assumption that only those ethylenic linkages within 3 Å. of the black particles (of 300 Å. diameter) are able to form a true bond with the particle, they show by calculation that the maximum loss in unsaturation due to carbon black cannot exceed 1.5% in the compounds studied. The authors conclude from their data that, if a chemical combination of the type suggested does occur, it cannot involve more than one or two double bonds out of every hundred.

The conclusion of Thornhill and Smith that the mechanism of rubber-sulfur combination during vulcanization appears to be altered by the presence of a reinforcing filler leads them to the suggestion that such changes may be due in part to the initiation of some particular type of sulfur-rubber linkage at positions other than those involved in unreinforced stocks. In support of this view, they mention that the demonstration by Gehman and Field of an orientation of rubber molecules in the presence of reinforcing pigment might mean that certain portions of such molecules are no longer available for reaction with sulfur. This new type of linkage, Thornhill and Smith suggest, may account for some of the characteristic properties of reinforced stocks. It does not, of course, account for the reinforcing effect of channel black in unvulcanized rubber, nor does it seem in itself adequate to explain the fourfold increase in abrasion resistance of vulcanized compounds which is achieved by incorporation of channel black in the mixing. It is difficult, further, to see why the blacks sort themselves out into different groups in relation to their properties in rubber if they themselves are not the direct reinforcing agents. But such a type of rubber-sulfur linkage might well exist as a contributory factor in reinforcement.

Sedimentation experiments (43) made some years ago showed that lamp-black could be recovered from a solid tire tread with unchanged particle size. Amon, Smith and Thornhill (2) have shown that channel black can be recovered quantitatively and with unchanged surface area from vulcanized rubber stocks. This implies, as was recognized by the authors, that carbon black reinforcement is a physical phenomenon, though they point out that unaltered surface area need not necessarily be interpreted as evidence of complete lack of surface reactions. Clark and Rhodes (12) showed that x-ray diffraction patterns of carbon black loaded compounds could be duplicated by superposing on the same film the patterns of rubber alone and black alone. They concluded that the mix is a physical disper-

sion, although admitting that adsorptive forces may be powerful. Weiss (60) in a theoretical treatment of reinforcement, remarks that, according to modern valence concepts, there is a continuous change from the (physical) van der Waals' forces to the true valence forces, and consequently no sharp distinction can be made between physical and chemical effects in the action of surface forces of finely divided particles.

The above evidence points to the probability that the forces between the carbon particle surfaces and the rubber molecules are for the most part neither purely physical, in the sense that they are fully reversible, nor purely chemical. They may therefore be supposed, in the absence of evidence to the contrary, to be van der Waals' forces of intermediate and mainly nonreversible type. But the factors producing reinforcement, one would imagine, must be presumed to result in a strong bond between filler and rubber, whereas it has been argued above that the degree of wetting of the black as a whole by the rubber is of a low order. This line of reasoning leads to the suggestion that, if there is anything in the nature of a strong bond between rubber and filler, it is confined to a small proportion of the filler particles. Such a view has also been offered in an attempt to explain why some properties (the reinforcing properties) of vulcanized compounds pass through an optimum at a certain filler concentration while others do not (44). The property of impact resilience is of particular interest in this respect, since the fact that it diminishes linearly up to very high filler loadings seems to mean that the carbon is in a similar state of dispersion throughout the whole range of concentration. Electrical resistance considerations support this view; and it would appear that in the case of a particular filler, the mere increase in surface area between rubber and reinforcing filler by increasing the concentration has no necessary relationship to reinforcement because, at the higher loadings, as reinforcement diminishes the effective surface area continues to increase.

To account for these difficulties, it has been suggested (44) that carbon black exists in rubber in four states: (1) aggregated in compact clusters; (2) flocculated into chainlike structures; (3) dispersed, but not firmly attached to the rubber molecules; and (4) dispersed and strongly bonded to the rubber molecules and constituting the primary factor in reinforcement. It will be noted that such a concept is not fundamentally opposed to Wiegand's more elaborate hypothesis. In common with Wiegand's theory, it specifies both strongly bonded and weakly bonded particles but leaves open the question of the nature of the rubber phase and the actual structural arrangement of the carbon particles. From the foregoing con-

siderations it has been seen that serious difficulties arise when it is assumed that the black as a whole or in greater part is strongly linked to the rubber molecules either as an adsorptive or chemisorptive bond or as a true valence linkage. However, the fact of reinforcement itself seems to demand the attachment of black particles to rubber molecules, and hence it is assumed that a fraction only of the particles is so attached. It would appear that, if such a picture is to accord with the known facts, the proportion of black forming a strong linkage to the rubber must be sufficiently small as not seriously to modify the linearity of the rebound-loading curves, since a high proportion of carbon in such a relation to the rubber molecules would probably tend to modify the effects of hysteresis at the low and moderate loadings. It is, of course, assumed that there is no further increase of firmly linked carbon beyond the concentration for maximum reinforcement. If the proportion of strongly bound carbon particles were sufficiently small, it would escape detection by the known experimental methods (57). Thus, there seems to be no good reason why primary valence linkages should not, after all, be present to a limited extent.

In the above analysis, no mention was made of the so-called plastic solid film theory which was one of the earliest attempts to explain reinforcement. Spear (54) pointed out that, if rubber is adsorbed on the carbon particles, the portion on the immediate surface ought to have less extensibility than the rubber, and that, according to the plastic film theory, the films between the particles of carbon are much more resistant to distortion than the matrix would be in the absence of a filler. This hypothesis is useful in helping to explain the stiffening action of fillers; in fact, Gehman and Field (23) have interpreted their x-ray diagrams (which show that the effect of carbon black is to spread the spots into arcs) in terms of a field of enhanced stress in the vicinity of the carbon particles. We have seen, however, that, although increased stress or stiffness always accompanies reinforcement, the blacks promoting the highest stresses at a given elongation are not necessarily the most powerful reinforcing agents, and also that the stress continues to increase with increased concentration of filler beyond optimum concentration for reinforcement.

Two recent theories of reinforcement have subjected to mathematical treatment the question of stresses in the vicinity of spherical particles in a rubber medium. Weiss (60), while accepting the view that surface energy is an important factor in reinforcement, considers also the elastic energy on the assumption that a particle embedded in the rubber will in general have a different volume from the actual space in the material available for it, and will either expand or compress the surrounding medium depending on

whether its size is smaller or larger than the hole available for it. He deduces that, if there is no mutual interaction of the particles, the shear stress is independent of their size and depends only in the number; and also that the total elastic energy is independent of the particle size.

The more general theory of Rehner (46) was developed by determining the stresses in the region of a spherical particle embedded in a rubberlike medium subjected to an applied tension. Rehner deduces expressions for the average stress where the particles are sufficiently far apart to avoid the effect of particle interactions (which as he admits will not be the case in a tire tread compound), and shows that "the filler concentration required to give a maximum value to the average tensile stress will not in general coincide with that giving the maximum shear stress." He also deduces the average radial and shear stresses to be independent of the size of the particle and to depend only on their concentration. The conclusion that stresses near particles are independent of particle size is not in agreement with the results of Schippel (50) and of Barnett (3), who conclude that stresses are greater at the surfaces of large than of small particles.

While the validity of the assumption that a consideration of stresses in the vicinity of small particles forms an adequate basis on which to formulate a theory of reinforcement might be questioned, it may be significant that the calculations both of Weiss and of Rehner and the experiments of Gehman and Field have indicated the importance of the number or concentration of particles in respect to their behavior in rubber. Gehman and Field (23) attribute the fact that the fiber diagrams appear at lower elongations as the particle size diminishes to the greater number of particles present per unit volume loading, which more than offsets the decrease in stress due to reduction in particle size.

If the conclusions of the above authors are right, an important factor in the stiffening action (but not necessarily the reinforcing action) of a rubber vulcanizate is the number of particles per unit volume, which varies inversely as the cube of the particle diameter. We have still to explain why some blacks, notably lamp and acetylene, give stiffer vulcanizates than is expected from their particle concentration, and why the thermal blacks give more stretchy vulcanizates. The dominance of chain structure of the former blacks may be sufficient to account for their greater stiffening power. It has been mentioned in the case of the thermal blacks that they possess a low adsorptive activity per unit area of surface compared with other blacks, which probably means that, when incorporated into rubber, their wetting power is lower even than that of other types of carbon. The low degree of wetting of channel black has been deduced partly from the

mobility and flocculating tendency of the black particles. The still lower degree of wetting of the thermal blacks cannot be ascribed to such mobility, and it can only be suggested that movement is prevented because of the larger size of the particles.

It seems possible that the concept of particle concentration can be usefully applied to the case of a truly reinforcing property such as abrasion resistance. To the extent that, like specific surface, the number of particles per unit volume is a function of particle size it has obviously a regular relation with abrasion resistance. The term "particle concentration" in regard to abrasion resistance is applied here to those particles presumed to be firmly linked to the rubber molecules. If particle concentration is paramount in abrasion resistance, it is implied that the strength of bond between particle and rubber molecule is the same for all particles and that the improvement given by the smaller particles results purely from their greater number. This means that, in the case of the thermal carbons, those particles which are held to the rubber molecules have the same bond strength as that of the other carbons, which may be doubted in view of the low surface activity of the thermal carbons.

Finally, a comment should be made on one or two features of synthetic rubber that might be expected to throw further light on reinforcement and related phenomena. It is noteworthy that, like natural rubber, some synthetic polymers produce fiber diagrams on stretching while others do not. Neoprene, which crystallizes on stretching, has a tensile strength similar to that of natural rubber, whereas GR-S, which does not produce a fiber diagram, has very low tensile strength when unreinforced and it is necessary to strengthen it by the use of a reinforcing black. Fielding (22) remarks that natural rubber "is already well bound together and the possible increase in tensile is not so great as it is with GR-S." The action of colloidal carbon in enormously increasing the tensile strength of GR-S is not such as to induce crystallization of the polymer. Whether the mechanism whereby tensile strength is increased is the same in GR-S as in natural rubber is not clear.

It is interesting to note that, throughout the range of loading with all blacks, GR-S has roughly equivalent abrasion resistance to natural rubber. There is no suggestion here that the lack of the capacity of GR-S to form fiber diagrams has had a pronounced effect on its resistance to wear. Since abrasive wear proceeds at distortions lower than those giving diffraction patterns this result might be expected, but it emphasizes the point made earlier that stress-strain properties in themselves are inadequate criteria of reinforcement.

X. Effect of Carbon Black on Hysteresis

The energy which is lost as frictional heat when a rubber vulcanizate is stressed in general depends, not only on the nature of the compound and on the state of vulcanization, but also on the stressing conditions. The results of Barron and Cotton (4) which have been discussed above indicate that, at the breaking point, under conditions of slow-speed stretching, the ratio of the returned to the input energy is constant for all compounds tested. Under such testing conditions, the actual energy returned is low and the hysteresis is high. Under comparatively easy conditions of stressing such as are used in impact pendulum testing, the hysteresis is much lower and changes with slight changes in the compound; in fact, some pure gum stocks at optimum cure are almost 100% resilient as judged by rebound tests at 100° C. Whether or not it is legitimate to divide the hysteresis of reinforced compounds into two parts, one due to the rubber and the other to the filler, may be questioned, but it is convenient to do so. Looked at in this way, it is seen from Figure 6 (page 401) that, in a typical tire tread compound containing 50% channel black and tested at 50° C., about five-sixths of the hysteresis is due to the black. The same compound, when stretched slowly to rupture, though developing a higher percentage hysteresis would not, according to the data of Barron and Cotton, undergo a percentage hysteresis loss appreciably greater than that of an unloaded compound. The *actual* hysteresis loss would, of course, be greater because of the greater energy input or proof resilience.

A possible partial if somewhat crude explanation of this behavior is suggested from considerations which have been outlined above. On the assumption that a large proportion of the carbon particles dispersed in the mix are not firmly attached to the rubber molecules, it is to be expected that, under comparatively low stresses, they will exhibit movement, and that friction will develop between particles and rubber and between the particles themselves. At such low stresses, provided the rubber itself is correctly vulcanized, the plastic properties of the rubber molecules will be small compared with their elasticity, and most of the internal heat development will be concerned with the carbon particles. (The Gough-Joule effect, which is reversible, can be ignored in this connection.) As the stresses are increased, plastic flow begins to be important, particularly under static stressing conditions. The nearer to the breaking point, the greater is the hysteresis resulting from the inelasticity of the rubber molecules.

A complete explanation would probably have to consider the effect of

carbon in varying degrees of attachment to rubber on the thermal energy as well as on the elastic and plastic properties of the molecules.

XI. Conclusions

This review will have shown that, although substantial progress has been made during recent years in our understanding of the action of reinforcing fillers in rubber, knowledge has not yet reached the stage at which the subject can be discussed in terms of modern scientific theory.

Attempts to explain the action of reinforcing agents in rubber based on present-day knowledge, which includes a large body of facts, some of an apparently contradictory nature, have led to the following largely hypothetical and fragmentary picture of the present state of the problem. It is hoped that it may help to form the basis of a unified theory. The controversial nature of some of the views expressed is fully recognized.

(1) Reinforcing action is distinguished from stiffening action. A filler should not be regarded as a reinforcing agent unless it substantially increases abrasion and tear resistance.

(2) Particle size is indirectly the major factor in reinforcement. (Number of particles per unit volume is probably of more direct significance than actual size of particles.)

(3) Spherical particles give a higher degree of reinforcement than other particles of equal specific surface.

(4) The effect of particle size on reinforcement is somewhat reduced by flocculation of the particles.

(5) Flocculation of particles and surface activity are factors of equal importance to particle size (or particle concentration) in the stiffening action. Modulus is increased by flocculation and decreased by a reduced activity per unit area of particle surface.

(6) Wetting of fillers by rubber is generally of a comparatively low order, and surface energy changes are probably not important in reinforcement. A limited number of particles are firmly bonded to the rubber molecules. This view is purely hypothetical, since neither adsorptive forces nor true chemical linkage between rubber and carbon have definitely been proved to exist.

(7) Stresses at the particle surfaces help to explain stiffening action.

(8) A subsidiary factor in reinforcement might be the formation of a new type of rubber-sulfur linkage.

(9) The effective dispersion of fillers increases to loadings considerably in excess of that giving maximum reinforcement.

(10) Rubber may exist as a discrete phase in the carbon-rubber system.

(11) Carbon black increases the abrasion resistance of GR-S and of natural rubber by the same mechanism, but possibly increases the tensile strength of GR-S by a different mechanism from that operating in natural rubber.

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APPENDIX

H. MARK

Because of wartime conditions and restrictions it was, unfortunately, not possible to issue this volume as early as the publishers and editors would have wished. In order to bring the references to the literature up to date, we shall list and very briefly review articles which are pertinent to the content of the various chapters of this book, but which could not be included in the text proper.

R. F. Boyer and R. S. Spencer

A comprehensive paper on the structure and properties of polyethylene (Polythene), by F. C. Hahn, M. L. Macht and D. A. Fletcher, *Ind. Eng. Chem.*, **37**, 526 (1945), contains a complete collection of thermal and mechanical data for the various types of this polymer and discusses thoroughly the various transition phenomena observed with it. Compare also the publication of S. N. Zhurkov and R. I. Lerman, *Compt. rend. acad. sci. U. R. S. S.* **47**, 106-109 (1945), on the influence of the volume sorption of vapors on the solidification temperature of polymers (polybutadiene, Buna N, polymethyl methacrylate, and polyisobutylene).

L. A. Wood

A careful experimental study of the influence of high pressures (up to 1150 atmospheres) in raising the melting point of crystalline rubber was published by L. A. Wood, N. Bekkedahl and R. E. Gibson, *J. Chem. Phys.*, **13**, 475 (1945), together with a discussion of the significance of this phenomenon.

C. W. Bunn

No x-ray investigation of typically rubberlike materials has been reported recently, but L. K. Frevel, *J. Am. Chem. Soc.*, **67**, 2275 (1945), cites very interesting details about a silicone of low molecular weight which may prove to be the key to structure of the silicone rubbers.

G. Gee

Attention may be drawn here to two more recent publications of W. Kuhn and F. Grün, *Kolloid-Z.*, **101**, 248 (1942), and W. and H. Kuhn, *Helv. Chim. Acta*, **26**, 1394 (1943), in which a very thorough analysis of high-polymer molecules in streaming liquid is carried out.

R. H. Ewart

Applying Flory's well-known fundamental theory of gel structure and gel swelling, R. F. Boyer, *J. Chem. Phys.*, **13**, 363 (1945), has carried out the deswelling of cross-linked polystyrene gels using the osmotic pressure of a polystyrene solution. He has used this phenomenon to measure in a novel way the molecular weight of polymers in solution. The practical importance of the gel fractions of GR-S is emphasized in an article by L. M. White, E. S. Ebers, G. E. Shriver and S. Breck, *Ind. Eng. Chem.*, **37**, 770 (1945); and a review by L. F. C. Parker of rubber swelling appeared in *J. Soc. Chem. Ind.*, **64**, 651 (1945).

E. Guth, H. M. James and H. Mark

A very important expansion of the kinetic theory of rubber elasticity was recently made by M. L. Huggins, *J. Polymer Science*, **1**, 1 (1946), who considers the influence of the van der Waals' attraction between long flexible molecules on their statistical behavior. New experimental data of considerable interest for the kinetic theory were recently contributed by S. L. Dart and E. Guth, *J. Chem. Phys.*, **13**, 28 (1945), who measured the temperature increase during the rapid stretching of Butyl rubber.

E. H. Farmer

N. Sheppard and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **41**, 261 (1945), have carried out an extensive study of rubber vulcanizates by infrared absorption spectroscopy and have been able to draw specific conclusions about the presence and relative frequency of such bonds as C—S—C, S—S and C—S—H. New and expeditive analytical methods for the determination of double bonds and peroxides in elastomers have been reported by J. Rehner and P. Gray, *Ind. Eng. Chem., Anal. Ed.*, **17**, 367 (1945), and R. F. Robey and H. K. Wiese, *ibid.*, 425. D. F. Twiss, *India-Rubber J.*, **108**, 731, and **109**, 14 (1945), discusses the significance of oxygen as a chemical plasticizer for rubber.

H. P. Stevens

The most important recent progress in our understanding of the action of light and radical-forming substances (oxygen, peroxides) on the softening and hardening of polymers seems to be reported in the recent work of A. V. Tobolsky and his collaborators (P. J. Blatz and A. V. Tobolsky, *J. Phys. Chem.*, **49**, 77, 1945), who are studying the effect of the superposition of simultaneous chain scission and chain cross linking.

D. Parkinson

A simple and interesting theory of the reinforcement of elastomers by nonspecific fillers has been developed independently by H. M. Smallwood, *J. Applied Phys.*, **15**, 758 (1944), and E. Guth, *ibid.*, **16**, 20 (1945).

Finally, attention should be drawn to a series of excellent review articles in 1945 by G. Gee and L. R. G. Treloar in *India-Rubber J.*, **108**, 289, 319, 349 and 375.

AUTHOR INDEX*

A

- Acken, M. F., 78 (ref. 1), 88
 Adams, L. H., 13, 51
 Alekseeva, E. N., xxxiv, xxxv, xxxix
 Alexander, J., 13 (ref. 121), 53, 55, 258
 (ref. 15a), 265 (ref. 15a), 268 (ref. 15a),
 297
 Alexandrov, A. P., 38, 39, 43, 51
 Alfrey, T., 4, 5, 22, 51, 77, 85-87, 88, 89,
 132 (ref. 1), 141, 210 (ref. 2), 211, 215
 (ref. 2), 235, 236 (ref. 2), 244, 245 (ref.
 1), 249, 262 (ref. 1), 297
 Allen, M. T., xxiii
 Allen, R. P., 414, 428
 Amon, F. H., 421, 428
 Anthony, R. L., 60 (ref. 33), 75 (ref. 33),
 90, 279 (ref. 7), 287 (ref. 2, 5, 41), 289,
 290 (ref. 2, 5), 291 (ref. 41), 297, 298
 Arnold, R. T., 326 (ref. 1), 359
 Arvin, J. A., 128 (ref. 18), 141
 Asano, M., 374, 387
 Astbury, W. T., 131, 141
 Aston, J. G., 135 (ref. 74), 143
 Auluck, F. C., 248, 249
 Avrami, M., 83-85, 89

B

- Bailey, E. D., xv, xxii
 Baird, W., 353 (ref. 58), 360
 Baker, W. O., xxvii, xxxix, 3 (ref. 5), 4,
 5 (ref. 7), 27, 47, 51, 52, 83 (ref. 6, 7,
 46), 89, 90, 130, 142, 201, 218, 230, 249
 Ball, J. M., 75 (ref. 26, 27), 89, 140 (ref.
 24, 25), 142, 189, 194
 Barnes, N. F., 15 (ref. 7a), 51
 Barnes, W. H., 59 (ref. 8), 74 (ref. 8), 78
 (ref. 8), 89, 132 (ref. 3), 141
 Barnett, C. E., 424, 428
 Barron, H., 125, 141, 400, 401, 426, 428
 Bartell, F. E., xxiv, 418, 419, 428, 429
 Bartovico, A., 210 (ref. 2), 211, 215 (ref.
 2, 6), 235, 236, 245, 249
 Bateman, L., 110 (ref. 5), 111 (ref. 5), 141
 Bateman, L. C., 311 (ref. 2), 322, 359
 Baum, A. A., 318 (ref. 84), 361
 Beach, J. Y., 107 (ref. 9), 141
 Beaver, D. J., 351 (ref. 10), 359
 Beck, C., 5, 6 (ref. 8), 51
 Becker, R., 84 (ref. 9), 89
 Bedford, C. W., 351 (ref. 71), 361
 Bekkedahl, N., 2 (ref. 9-11), 6-8, 17, 51,
 55, 59, 60, 62, 63, 64 (ref. 10), 65 (ref.
 10, 145), 68, 69 (ref. 13), 70 (ref. 146),
 71 (ref. 14), 74, 75 (ref. 14), 76 (ref. 14),
 78 (ref. 146), 80, 85 (ref. 10), 89, 93, 431
 Belitzkaya, R. M., xxxiv, xxxix
 Berg, R. M., 28, 32, 44, 47, 52
 Bernal, J. D., 99, 141
 Biggs, B. S., xxvii (ref. 5), xxxix, 316
 (ref. 26), 360
 Bilmes, L., 46 (ref. 12), 47, 48, 51
 Bing, K., 60 (ref. 82), 91
 Bingham, E. C., 205, 249
 Biscoc, J., 392, 428
 Bishop, W. S., 338 (ref. 41), 360
 Blake, J. T., 6 (ref. 74), 53, 59 (ref. 140),
 68 (ref. 140), 70 (ref. 140), 74 (ref. 140),
 78 (ref. 140), 93, 316 (ref. 59), 317, 321
 (ref. 4), 338, 339, 359, 360, 378 (ref.
 13), 379, 387, 388, 390 (ref. 52), 394
 (ref. 52), 404 (ref. 52), 408 (ref. 52),
 413, 414, 418, 428, 429
 Blaker, E., 75 (ref. 26), 89, 140 (ref. 24),
 142
 Blakers, A. L., xxvi (ref. 19), xxxix
 Blaschke, F., 209, 250
 Blatz, P. J., 432
 Blodgett, K., 124 (ref. 7), 141
 Bloomfield, G. F., 192, 194, 310 (ref. 5),
 316 (ref. 7), 318 (ref. 6), 327 (ref. 7),
 328 (ref. 7), 331 (ref. 7), 332 (ref. 7),
 333 (ref. 7), 334 (ref. 7), 339 (ref. 7),
 342 (ref. 7), 343 (ref. 7), 344 (ref. 7),
 346 (ref. 6), 347 (ref. 7), 359
 Blow, C. M., 409, 410, 428
 Bock, W., 377, 387
 Böeseken, J., 332 (ref. 8), 359
 Boggs, C. R., 379, 387
 Boiry, F., 419, 428
 Boissonnas, C. G., 149 (ref. 2), 151, 152,
 156 (ref. 34), 166 (ref. 2), 171 (ref. 34),
 194, 195, 219, 250
 Bolland, J. L., 303 (ref. 9), 359
 Booth, E. W., 351 (ref. 10), 359
 Booyis, J. de, 203, 249
 Bostroem, S., 60 (ref. 70), 91
 Boyer, R. F., 2 (ref. 13), 3 (ref. 13), 10

* *Italic numerals refer to the bibliographies of the different papers.*

- (ref. 13), 13 (ref. 13), 21 (ref. 14), 22 (ref. 14a), 25 (ref. 14a), 26 (ref. 14), 28 (ref. 14), 30 (ref. 14), 52, 59 (ref. 15), 74 (ref. 15), 89, 431, 432
- Braendle, H. A., xxviii, xxxix
- Braucker, E., 2 (ref. 50), 24 (ref. 50), 53
- Braun, J. v., 347 (ref. 11), 359
- Bray, R. I., 390, 392 (ref. 53), 416 (ref. 53), 429
- Breck, S., 432
- Bredée, H. L., 203, 249
- Breuer, F. W., xxvii (ref. 7), xxxix
- Bridgman, P. W., 14, 15, 52
- Briegleb, K., 345 (ref. 25), 360
- Brill, R., 80 (ref. 1), 89, 125, 141
- Brønsted, J. N., 175, 176, 178, 190, 194
- Brockway, L. O., 107 (ref. 9), 141
- Brown, J. R., 338 (ref. 33), 339 (ref. 12, 33), 340 (ref. 12, 33), 343, 356, 359, 360
- Bruce, P. L., 317, 321 (ref. 4), 338, 339, 359
- Brunauer, S., 390
- Bruni, G., 79 (ref. 17), 89
- Buizov, B. V., 317, 334, 359
- Bulgin, D., 402, 428
- Bunbury, H. M., 137 (ref. 45), 142, 353 (ref. 58), 360
- Bunn, C. W., 4, 52, 78 (ref. 19), 79, 81, 87, 88, 89, 99 (ref. 12), 100 (ref. 10), 101 (ref. 13, 15), 102 (ref. 10), 104 (ref. 10), 105 (ref. 12), 106 (ref. 12), 107-109, 110 (ref. 12), 112, 113, 114 (ref. 12), 115 (ref. 12), 116, 117 (ref. 12), 118, 119 (ref. 15), 120, 133 (ref. 11), 135 (ref. 13), 136 (ref. 14, 15), 137 (ref. 14), 141, 263, 297, 381, 387, 431
- Bunschoten, E., 59, 74 (ref. 22), 89
- Burk, R. E., 61 (ref. 92), 82 (ref. 92), 91, 267, 298
- Busse, W. F., 28, 29, 48, 52, 258, 297, 355, 359
- C**
- Cambron, A., 353 (ref. 88), 361
- Carman, F. H., 180, 194
- Carothers, W. H., xiii, 79 (ref. 23), 89, 98 (ref. 19a), 116, 128, 141, 300
- Carson, C. M., 65 (ref. 24), 89, 410, 428
- Carter, S. R., 151 (ref. 6), 194
- Caspari, W. A., 107 (ref. 21), 141, 238, 249
- Caston, R. H., 287 (ref. 2, 5), 289, 290 (ref. 2, 5), 297
- Cattoir, F. R., 10, 17 (ref. 87), 54
- Chang, T. S., 10, 49 (ref. 17), 52
- Church, H. F., 8 (ref. 17a, 17b), 52
- Clark, C. R., 87 (ref. 109), 92
- Clark, G. L., 59 (ref. 25, 28), 66 (ref. 25, 28), 75 (ref. 26, 27), 89, 132 (ref. 23), 139, 140, 141, 142, 189, 194, 421, 428
- Clash, R. F., Jr., 2 (ref. 20), 11, 28, 32, 44, 47, 52, 59 (ref. 29), 81 (ref. 29), 89
- Clews, C. J. B., 79, 90, 116, 142
- Coffman, D. D., xxvii (ref. 9), xxxix
- Cohan, L. H., 403, 428
- Cole, K. S., 19, 52
- Cole, R. H., 19, 52
- Collins, A. M., 79 (ref. 23), 89, 116 (ref. 20), 141
- Collins, C. J., 326 (ref. 1), 359
- Conant, F. S., 47, 52, 62 (ref. 31), 71, 90
- Conover, F. S., 400, 428
- Cotton, F. H., 65, 90, 355 (ref. 15), 359, 400, 401, 426, 428
- Coumoulos, G. D., 124, 125, 142
- Crawford, B. L., 262 (ref. 6), 297
- Criegee, R., 326 (ref. 16), 359
- Cummings, A. D., 8 (ref. 75), 16, 17, 53
- Curtis, H. L., 18, 52, 54
- D**
- Daniel, W., xxvii (ref. 20), xxxix
- Daniels, H. E., 248, 249
- Dart, S. L., 60 (ref. 33, 34), 75 (ref. 33), 80, 90, 279 (ref. 7, 8), 287, 291, 297, 432
- Davey, W. P., 65, 78 (ref. 1, 87), 88, 91
- Davies, B. L., 317, 318 (ref. 19), 361
- Davies, J. M., 28, 29, 48, 52
- Davis, C. C., 6 (ref. 74), 53, 59 (ref. 140), 68 (ref. 140), 70 (ref. 140), 74 (ref. 140), 78 (ref. 140), 93, 316 (ref. 59), 360, 378 (ref. 13), 388, 390 (ref. 52), 394 (ref. 52), 404 (ref. 52), 408 (ref. 52), 418, 429
- Dawson, T. R., 389, 428
- Daynes, H. A., 8 (ref. 17a, 17b), 52
- Dean, J. N., 79 (ref. 35), 90
- Debye, P., 226, 227, 249
- Dekker, P., 367 (ref. 16), 388
- Depew, H. A., 409, 412, 414 (ref. 18), 416, 428
- De Witt, T., 390, 428
- Dexter, S. T., xxi
- Dinglinger, A., 231, 250
- Dinsmore, R. P., 82 (ref. 121), 92, 118, 142, 355 (ref. 17), 356, 359
- Dorinson, A., 17 (ref. 25, 26), 52
- Dornie, R. W., 17 (ref. 27), 52
- Dostal, H., 86, 90
- Doty, P. M., 227, 228, 249, 251
- Dow, R. B., 65, 90
- Dufraisse, C., 366
- E**
- Ebers, E. S., 432
- Ehrenfest, P., 2, 52
- Eilers, H., 203, 223, 224, 245, 246, 247 (ref. 16), 249

- Einstein, A., 202, 204, 240, 249
 Eisenschitz, R., 243, 249
 Eley, D. D., 25, 30, 38, 39, 43, 44 (ref. 29), 52
 Emmett, P. H., 390, 428
 Engel, E. W., 18 (ref. 106), 54
 Erickson, C. L., 128 (ref. 34), 142
 Evans, A. B. A., 180, 195, 374 (ref. 23), 388
 Evans, A. G., 137 (ref. 30), 142
 Evans, H. C., 177 (ref. 8), 194, 212, 249
 Ewart, R. H., 206 (ref. 70), 250, 432
 Exner, F., 15, 52
 Bymers, J. G., 61 (ref. 49, 102), 90, 92
 Eyring, H., 3 (ref. 30), 4, 14, 22, 23, 24 (ref. 53), 25 (ref. 53), 52-54, 87 (ref. 109), 92, 202, 248, 249, 250, 258, 265 (ref. 43), 267 (ref. 9, 43), 297, 298
- F**
- Fanselow, J. R., xxi
 Faraday, M., xx
 Farmer, E. H., 192, 194, 302 (ref. 20, 22), 303 (ref. 19), 315 (ref. 21), 316 (ref. 7), 318 (ref. 22), 319 (ref. 18, 21), 327 (ref. 7), 328 (ref. 7), 331 (ref. 7), 332 (ref. 7), 333 (ref. 7), 334 (ref. 7), 339 (ref. 7), 342 (ref. 7), 343 (ref. 7), 344 (ref. 7), 347 (ref. 7), 348, 359, 368 (ref. 5), 377 (ref. 5), 378, 382 (ref. 6), 388, 432
 Ferguson, W. J., 2 (ref. 92), 8, 9, 54, 60 (ref. 112), 92
 Ferri, C., 16, 54, 72 (ref. 96), 92, 289, 298, 306, 320, 359, 360, 366 (ref. 11), 388
 Ferry, J. D., 2 (ref. 31), 10, 12 (ref. 31), 52, 318, 320, 361
 Feuchter, H., 68, 71, 74 (ref. 38), 78 (ref. 38), 90
 Field, J. E., 60 (ref. 51), 63, 65, 66, 72-74, 75 (ref. 40), 76 (ref. 40, 52), 77, 78, 90, 99 (ref. 40), 118, 139, 140, 142, 227, 249, 307 (ref. 30), 360, 414, 419-421, 423, 424, 428
 Field, R. F., 19, 52
 Fielding, J. H., 73, 90, 402 (ref. 21), 425, 428
 Fikentscher, H., 244, 249
 Fischer, H. J. v., 61 (ref. 150), 93
 Fischer, K., 170 (ref. 51), 171 (ref. 51), 172 (ref. 51), 174 (ref. 51), 195, 238, 250
 Fisher, C. H., 34 (ref. 33), 52
 Fisher, H. L., xxv, xxix, 317 (ref. 24), 359, 384
 Fletcher, D. A., 81 (ref. 60), 91, 431
 Flory, P. J., 22, 24, 28, 30, 38, 39, 52, 151 (ref. 10), 157-161, 170 (ref. 10), 172, 174, 181, 191, 192, 194, 206, 215, 217, 219, 221, 223, 230, 231 (ref. 27), 233, 234, 239, 240, 244, 245, 249, 258, 274, 280 (ref. 11), 297, 432
 Föhrenbach, E., 345 (ref. 25), 360
 Fordyce, R., 229, 249
 Forman, D. B., 62, 71 (ref. 42), 79 (ref. 42), 90, 347 (ref. 28), 360
 Fowler, R. H., 5 (ref. 37), 52, 159 (ref. 11c), 162 (ref. 11b), 194
 Frazer, D. F., 62, 72 (ref. 149), 79 (ref. 149), 93
 Frenkel, J., 5, 15, 52
 Freundlich, H., xvii
 Frevell, L. K., 431
 Friedman, L., xxi
 Frith, E. M., 28, 52, 85, 90
 Fritsch, J., 313, 361
 Frölich, H., 11, 52
 Fröhlich, P. K., 314, (ref. 74), 361
 Fromm, E., 345 (ref. 25), 360
 Frosch, C. J., 80 (ref. 47), 83 (ref. 48), 90, 125-129, 131, 137, 142
 Fuller, C. S., xxvii, xxxix, 4, 27, 51, 52, 61, 79 (ref. 44), 80, 83 (ref. 6, 7, 46, 48), 89, 90, 107, 125-131, 137, 142, 201, 218, 230, 249, 316 (ref. 26), 360
 Fuoss, R. M., 4, 18, 20 (ref. 40), 28, 50, 52, 54, 151 (ref. 12), 152, 194, 201, 210-212, 219, 231, 249, 250
- G**
- Gallay, W., 27 (ref. 41), 52
 Ganzhorn, G. H., 403 (ref. 25), 410, 411 (ref. 25), 428
 Garner, C. S., 262 (ref. 40, 55), 298
 Garner, E. V., 101 (ref. 15), 118, 141
 Garner, T. L., 374, 388
 Garner, W. E., 11, 53
 Garvey, B. S., 306, 347, 350, 360
 Gee, G., 147 (ref. 21), 148-150, 151 (ref. 14, 21), 152 (ref. 14), 153 (ref. 16), 154, 156 (ref. 21), 165, 166 (ref. 21), 167, 170 (ref. 21), 171 (ref. 15, 21), 172, 173 (ref. 16), 174, 175, 176 (ref. 18), 178 (ref. 20a), 180 (ref. 13), 181 (ref. 19), 183 (ref. 20), 190 (ref. 17), 191 (ref. 13, 21), 192 (ref. 15), 194, 212, 238, 245, 249, 382 (ref. 9), 388, 431, 433
 Geel, W. C. van, 61 (ref. 49), 90
 Gehman, S. D., 60 (ref. 51), 61, 65, 74, 75 (ref. 50), 76 (ref. 52), 77, 78, 90, 99 (ref. 40), 118, 139 (ref. 39), 140, 142, 227, 249, 403, 414, 419-421, 423, 424, 428
 Gelissen, H., 315, 360
 Gerke, R. H., 71, 76 (ref. 54), 90, 403 (ref. 25), 410-412, 428
 Germer, L. H., 392 (ref. 61), 429
 Gethman, S. D., 307 (ref. 30), 360
 Giaque, W. F., 12 (ref. 43), 53
 Gibbons, W. A., 71, 76 (ref. 54), 90

- Gibson, C. S., 335 (ref. 31), 360
 Gibson, R. E., 13, 51, 65 (ref. 145), 68, 93, 431
 Gilbert, C. B., 28 (ref. 44), 53
 Gladstone, M. T., 316 (ref. 42), 360
 Glasstone, S. M., xix
 Gleichenheil, S., 60 (ref. 55), 75 (ref. 55), 90
 Gloor, W. E., 28 (ref. 44), 53
 Go, Y., 131 (ref. 62), 142
 Göler, F. v., 83 (ref. 56), 90
 Goetz, A., 83 (ref. 56), 90
 Goetz, S. S., 83 (ref. 56), 90
 Goggin, W. C., 81 (ref. 57), 90
 Gold, O., 203, 249
 Goldfinger, G., 5, 22, 51
 Goodwin, N., 409, 428
 Gottlob, K., 63 (ref. 59), 90
 Gough, J., 257, 297
 Gough, V. E., 412 (ref. 27), 428
 Gralén, N., 225 (ref. 31a), 249
 Gray, P., 432
 Green, H., 412, 416, 428
 Greene, E. S., 15, 53
 Greene, H. E., 46, 53
 Grenquist, E. A., 416, 428
 Grew, E. L., 303 (ref. 19), 359
 Grimm, H., xxxvi (ref. 25), xl
 Gross, H., 225, 244, 250
 Gross, S. T., 59 (ref. 25), 66 (ref. 25), 89, 132 (ref. 23), 140, 141 (ref. 23), 141
 Grün, F., 431
 Grummitt, O., 61 (ref. 92), 82 (ref. 92), 91
 Guggenheim, E. A., 159 (ref. 11c), 162, 194
 Guth, E., 21, 38, 53, 60 (ref. 33, 34), 75 (ref. 33), 80, 90, 203, 249, 258, 259, 265 (ref. 13, 14, 15a, 16), 266, 267 (ref. 16), 268, 269, 270 (ref. 24, 27), 271, 272, 274 (ref. 24), 275, 277-279, 285 (ref. 15b), 287 (ref. 2, 5, 7, 8, 24, 41), 288 (ref. 24), 289, 290 (ref. 2, 5), 291, 292 (ref. 24, 41), 293 (ref. 24), 294-296, 297, 298, 432, 433
- H**
- Habgood, B. J., xxvii (ref. 12), xxxix, 403 (ref. 30), 428
 Hahn, F. C., 81 (ref. 60), 91, 431
 Halle, F., 80 (ref. 16), 89, 122, 125, 141, 142
 Haller, W., 258, 298
 Hanna, N. P., 59 (ref. 122), 74 (ref. 122), 92
 Hardman, A. F., 337 (ref. 32), 352, 360
 Harman, R. A., 248, 250
 Harris, C. W., 46, 53
 Harris, M., 215, 250
 Hartshorne, N. H., 389 (ref. 17), 428
 Hauk, V., 63, 72, 91
 Hauser, E. A., 60 (ref. 62-64), 68, 71, 79 (ref. 65), 90, 91, 105 (ref. 44), 106, 111, 139 (ref. 43), 142, 338 (ref. 33), 339 (ref. 12, 33), 340 (ref. 12, 33), 343, 356, 359, 360
 Healey, A., 402 (ref. 31), 428
 Heilbron, I. M., 137 (ref. 45), 142, 304 (ref. 34), 360
 Heiss, J. H., 201, 218, 230, 249
 Hengstenberg, J., 77, 91, 120 (ref. 46), 140, 142
 Henne, A. L., 192, 195, 335 (ref. 54), 336 (ref. 55), 360
 Hermans, P. H., 315, 360
 Herrman, D. B., 403 (ref. 35), 428
 Hershberger, A., 419, 428
 Herzog, R. O., 219, 249
 Hess, H., 209, 249
 Hey, D. H., 315 (ref. 35), 317 (ref. 35), 360
 Hibbert, H., 229, 249
 Hickman, J. C., 397, 428
 Hildebrand, J. H., 157 (ref. 22), 162 (ref. 22), 189, 194, 213, 222, 249
 Hill, J. W., 98 (ref. 19a), 128 (ref. 19b), 141
 Hill, R., xxvii (ref. 12), xxxi-xxxiii, xxxix
 Hinsberg, O., 346 (ref. 36), 360
 Hintenberger, H., 63, 72, 91
 Hock, L., 60, 74 (ref. 69), 91, 155, 194, 419, 428
 Hofmann, W., 122, 142
 Hohenemser, W., 326, 360
 Holt, W. L., 59, 65, 74, 75 (ref. 71), 78, 91, 280 (ref. 20), 298
 Hopff, H., xxvii (ref. 15), xxxix, 105 (ref. 48), 142
 Houwink, R., 21 (ref. 82), 54, 233, 239, 249, 272 (ref. 21), 298
 Howard, J. B., 34 (ref. 55), 53
 Howland, L. H., 403 (ref. 25), 410, 411 (ref. 25), 428
 Huffman, H. M., 10, 17 (ref. 87), 54
 Huggins, M. L., 22 (ref. 45), 53, 157, 159-161, 164 (ref. 24), 166, 167, 194, 211, 221-223, 240-242, 249, 250, 432
 Hulburt, H. M., 248, 250
 Hunemorder, M., 60 (ref. 62), 91
 Hunter, E., 2 (ref. 20), 11 (ref. 20), 52, 59 (ref. 72), 62 (ref. 72), 81 (ref. 72), 91
 Husemann, E., 24, 54
- I**
- .
- Ingmanson, J. H., 34 (ref. 55), 53
- .
- J**
- James, H. M., 21, 38, 53, 258, 259, 266, 268, 269, 270 (ref. 24, 27), 271, 272,

- 274 (ref. 24), 275, 277-280, 287 (ref. 24), 288 (ref. 24), 291, 292 (ref. 24), 293 (ref. 24), 294-296, 297, 298, 432
- James, R. R., 32, 54
- Jeffrey, G. A., 79, 91, 102 (ref. 49a), 109, 110 (ref. 5), 111 (ref. 5), 141, 142
- Jenckel, E., 2 (ref. 48-50), 3, 4, 22, 23, 24 (ref. 50), 25, 26, 41, 53, 83 (ref. 129), 93
- Jeziarski, T. W., 335 (ref. 37), 360
- Jilk, L. T., 151, 195, 219 (ref. 69), 250
- Johnson, W. A., 83 (ref. 74), 91
- Jones, F. A., 353 (ref. 85), 361
- Jones, F. B., 402 (ref. 34), 428
- Jones, H. C., 59 (ref. 75), 91
- Jones, M., 79 (ref. 76), 91
- Jones, S. O., 326, 332, 360
- Jordan, C. B., 82 (ref. 101), 92
- Joule, J. P., 257, 258, 292, 298
- Jullander, I., 221, 225 (ref. 46a), 250
- K**
- Kabler, M., 75 (ref. 26), 89, 140 (ref. 24), 142
- Kahlenberg, L., xvii
- Kamm, E. D., 304 (ref. 34), 360
- Karrer, E., 258, 298
- Katz, I. R., 257
- Katz, J. R., 60, 65, 80, 91, 98 (ref. 50), 111, 131 (ref. 51), 142
- Kauzmann, W., 4, 5, 19, 22, 24 (ref. 53), 25 (ref. 53), 29, 30, 53, 248, 250
- Kaysar, E., 345 (ref. 25), 360
- Keays, J. L., 11, 54
- Kehlen, H., 320, 360, 363, 365, 366 (ref. 15), 368 (ref. 15), 369 (ref. 15), 386, 388
- Kelly, W. J., 356 (ref. 39), 360
- (Lord) Kelvin, (Thomson, W.), 257, 298
- Kemp, A. R., xxvi, xxxix, 31, 32, 33 (ref. 98), 34 (ref. 55, 98), 36, 41-45, 53, 54, 153, 177, 178, 188 (ref. 27), 191, 192, 194, 195, 212, 214, 218, 226, 234, 238, 250, 334, 338, 339, 344, 345 (ref. 72), 360, 361, 403 (ref. 35), 428
- Kemp, J. D., 264 (ref. 32), 298
- Kharasch, M. S., 316 (ref. 42), 360
- Kimura, S., 6, 8 (ref. 57), 53
- Kincaid, J. F., 14, 53
- King, A. M., 11, 53
- King, G. E., 32, 33 (ref. 59), 34 (ref. 59), 41, 44-46, 53
- Kirby, J. E., 79 (ref. 23), 89, 116 (ref. 20), 141
- Kirchhof, F., 74 (ref. 83), 91
- Kirkpatrick, A., 28 (ref. 60), 53
- Kirkwood, J. G., 4, 49 (ref. 61), 53
- Kirsch, W., 61 (ref. 84), 65, 67, 72, 75 (ref. 84), 76 (ref. 84), 78, 91, 93
- Kistiakowsky, G. B., 135 (ref. 52), 142, 262 (ref. 33), 298, 432
- Kistler, S. S., xxiv
- Kitchin, D. W., 18, 53
- Klebsattel, C. A., 314 (ref. 74), 361
- Klenck, J. v., 27 (ref. 111), 55
- Koch, E. A., 32, 33 (ref. 63), 46 (ref. 63), 53
- Koch, H. P., 302 (ref. 20), 359
- Koch, H. W., 392, 429
- Kohman, G. T., 31, 33 (ref. 64), 36, 53
- Kothari, D. S., 248, 249
- Kraemer, E. O., xiii-xxiv, 173, 195, 209, 216, 218, 224 (ref. 53, 55), 225, 226 (ref. 55), 230, 238, 250
- Krejci, L. E., xxiii, xxiv
- Kroger, M., 61 (ref. 85), 91
- Krylov, H. I., 116, 142
- Kuhn, H., 431
- Kuhn, W., 37, 233, 244, 248, 250, 258, 265 (ref. 34a, 34b), 267 (ref. 34a), 295, 296, 298, 431
- Kurtz, S. S., 17 (ref. 65), 53
- L**
- Lacher, J. R., 135 (ref. 52), 142
- Lackner, J., 338 (ref. 41), 360
- Ladd, W. A., 391, 392, 429
- Lambourn, L. J., 398, 429
- Lange, J. J. de, 115 (ref. 29), 142
- Langenbeck, W., 351 (ref. 43), 360
- Lansing, W. D., xv, xvi, xxii, 173, 195, 216, 225, 250
- Laskowski, L., 267, 298
- Lauffer, Max A., 199, 203, 250
- Lawson, A. W., 5, 12 (ref. 66), 53
- Lazurkin, I. U. S., 38, 39, 43, 51
- Lecher, H., 346 (ref. 44), 360
- Lee, S. C., 178 (ref. 32), 195
- Lenher, V., xvii
- Lens, J., 149 (ref. 33), 154 (ref. 33), 195
- Lerman, R. I., 431
- LeTourneau, R. L., 75 (ref. 27), 89, 140 (ref. 25), 141, 142, 189, 194
- Leupold, E. O., 302, 361
- Levi, T. G., 317, 360
- Lewis, J. R., xxxi, xxxiii, xxxix
- Lewis, W. K., 351, 360
- Lightbown, I. E., 314 (ref. 74), 315 (ref. 47), 360, 361
- Lillie, H. R., 22 (ref. 67), 53
- Linde, N. v. d., 332 (ref. 8), 359
- Lindemann, F. A., 133, 142
- Liska, J. W., 32, 44, 46 (ref. 68), 47, 52, 53, 62 (ref. 31, 86), 71, 79 (ref. 86), 90, 91
- Long, J. D., 65 (ref. 87), 78 (ref. 87), 91
- Lonsdale, K., 105 (ref. 56), 121 (ref. 55), 142
- Lotichius, J., 60, 62, 72 (ref. 115), 74 (ref. 115), 92

- Lotmar, W., 106, 111, 112, 131 (ref. 63),
132 (ref. 63), 142, 305 (ref. 48), 360
- Loughborough, T. L., 46, 53
- Lowry, R. D., 81 (ref. 57), 90
- Lunn, R. W., 407, 408, 429
- Luther, R., 383 (ref. 10), 388
- M**
- McClellan, P. P., 412, 416, 429
- McCorkle, M. R., 17 (ref. 25), 52
- Macht, M. L., 81 (ref. 60), 91
- Mack, E., 135, 142
- Mackey, J. F., 403, 428
- McPherson, A. T., 6 (ref. 74), 8 (ref. 75),
16, 18, 52-54, 59, 61, 65, 74, 75 (ref.
71), 78, 91, 93, 280 (ref. 20), 298
- Magat, M., 178, 195
- Malm, F. S., 31, 32, 41, 42 (ref. 56), 53,
188 (ref. 27), 194
- Marder, M., 83 (ref. 139), 93
- Mark, H., 4, 5, 22, 37, 51, 53, 60 (ref.
63), 61, 74, 77, 80 (ref. 91), 81 (ref. 80),
82, 85-87, 88, 89, 91, 92, 99 (ref. 59),
105 (ref. 59), 106, 111, 132 (ref. 1), 139
(ref. 43), 140, 141-143, 170, 195, 210,
211, 215, 222, 227, 233, 235, 236, 244,
245, 249, 250, 258, 262 (ref. 1), 265
(ref. 16), 267 (ref. 16), 297, 298, 305
(ref. 49, 52), 335 (ref. 53), 360, 432
- Martin, S. M., 32, 53
- Marvel, C. S., 123, 142
- Matheson, H., 2 (ref. 10), 8, 51, 60, 74, 89
- Matthes, A., 218, 236, 237, 250
- Mayer, J. E., 2, 10 (ref. 73), 53
- Mead, D. J., 28 (ref. 76), 54, 151 (ref. 12),
152, 194, 201, 210-212, 219, 231, 249,
250
- Mehl, R. F., 83 (ref. 74), 91
- Memmler, K., 60 (ref. 68), 91
- duMesnil de Rochemont, R., 258 (ref.
54), 298
- Messenger, T. H., 62, 92
- Meyer, K. H., 16, 54, 68, 72 (ref. 96), 74,
77 (ref. 97), 79 (ref. 95), 82, 87 (ref.
98), 92, 106, 111, 112, 116, 122 (ref. 61),
131, 132 (ref. 63), 142, 143, 151, 152, 156
(ref. 34), 170, 171 (ref. 34), 195, 219,
222 (ref. 66), 232, 238, 250, 258, 289,
298, 305 (ref. 48, 52), 320, 326, 335
ref. 53), 360, 366 (ref. 11), 388
- Michael, S. E., 315 (ref. 21), 319 (ref. 21),
348, 359, 378, 388
- Michalek, J. C., xxvii (ref. 17), xxxix
- Midgley, T., Jr., 192, 195, 335, 336 (ref.
55), 360, 385 (ref. 25), 388
- Miller, A. R., 159, 160, 195, 221, 250
- Miller, R. F., 28, 29, 48, 52
- Misch, L., 78 (ref. 99), 92, 100 (ref. 89), 102
(ref. 89), 104 (ref. 89), 112, 143
- Mojen, H. P., 177 (ref. 52), 195
- Mondain-Monval, P., 83 (ref. 100), 92
- Montonna, R. E., 151, 195, 219 (ref. 69),
250
- Mooney, M., 206 (ref. 70), 250, 273, 298
- Mooney, R. C. L., 122, 123, 143
- Morgan, L. B., xxvii (ref. 12), xxxix
- Morgan, S. O., 4, 54
- Morris, R. E., 32, 54, 82 (ref. 101), 92,
351 (ref. 56), 360
- Morris, V. N., 414, 416, 429
- Morss, H. A., 112, 143
- Moureu, C., 366
- Mühlhausen, K., xxvii (ref. 20), xxxix
- Müller, A., 4, 11, 54, 104 (ref. 68), 120
(ref. 67), 138 (ref. 69), 143
- Müller, F. H., 21 (ref. 82), 26, 54
- Muller, R., 21
- Myers, 32, 54
- N**
- Nagai, H., 31, 54
- Namikawa, N., 6, 8 (ref. 57), 53
- Natta, G., 79 (ref. 17), 89
- Naunton, W. J. S., 141, 143, 320, 353
(ref. 58), 360, 363-366, 369, 371, 377
(ref. 12), 378, 384, 385, 388, 394, 403,
420, 429
- Naylor, R. F., 316 (ref. 7), 327 (ref. 7),
328 (ref. 7), 331 (ref. 7), 332 (ref. 7),
333 (ref. 7), 334 (ref. 7), 339 (ref. 7),
342 (ref. 7), 343 (ref. 7), 344 (ref. 7),
347 (ref. 7), 359
- Neumann, W., 60 (ref. 55), 63, 72, 75
(ref. 55), 90, 91
- Nichols, J. B., xv, xx, xxii, xxiii, 224
(ref. 55), 225 (ref. 55), 226 (ref. 55),
238 (ref. 55), 250
- Nicodemus, O., xxix (ref. 18), xxxix
- Nix, F. C., 10 (ref. 85), 54
- Nutting, R. D., 47, 351, 360
- O**
- Oakes, W. G., 2 (ref. 20), 11 (ref. 20), 52,
59 (ref. 72), 62 (ref. 72), 81 (ref. 72), 91
- Obrastzov, J., 15, 52
- Ornstein, L. S., 61 (ref. 102), 92
- Orr, W. J. C., 162, 195
- Osborne, D. W., 262 (ref. 40, 55), 298
- Osterhoff, H. J., 418, 429
- Ostromslensky, I. I., 316 (ref. 59), 317,
360, 377, 378, 388
- Ostwald, W., 166 (ref. 40), 170, 180, 195
- Ott, E., 65 (ref. 104), 74 (ref. 103), 92
- Owens, W. M., 304 (ref. 34), 360
- P**
- Pankow, G. W., 131 (ref. 63), 132 (ref.
63), 142

- Pape, N. R., 4, 52, 80 (ref. 47), 83 (ref. 46, 48), 90, 125-129, 131, 137, 142
- Park, C., 72 (ref. 105, 106), 92
- Park, C. R., 356, 360, 390, 394, 404, 408 (ref. 52), 409, 412, 414, 416, 418, 428, 429
- Parker, L. F. C., 432
- Parkinson, D., 390 (ref. 43), 391 (ref. 44), 392 (ref. 44, 58), 395 (ref. 44), 396 (ref. 44), 397 (ref. 44), 398 (ref. 44), 399 (ref. 44), 401 (ref. 44), 402 (ref. 44), 404 (ref. 44), 407 (ref. 44), 408 (ref. 44), 410 (ref. 43), 411 (ref. 43), 412 (ref. 27, 44), 414 (ref. 42, 58), 416 (ref. 44), 421, (ref. 43), 422 (ref. 44), 428, 432
- Parks, G. S., 2 (ref. 31), 10, 12 (ref. 31), 13 (ref. 86), 15, 17, 22 (ref. 88), 52-54, 74, 87, 92, 135 (ref. 74), 143
- Pasternack, D. S., 180, 195, 374 (ref. 23), 388
- Patnode, W., 2 (ref. 89), 54
- Patrick, J. C., 357, 360
- Patterson, R. F., 11, 54
- Paul, E. B., xxvi, (ref. 19), xxxix
- Pauling, L., 4, 5, 10, 22, 54, 107 (ref. 9), 141
- Pearce, W. H., 402 (ref. 34), 428
- Pedersen, K. O., xv, xxiii, 224 (ref. 55), 225 (ref. 55), 226 (ref. 55), 238 (ref. 55), 250
- Peek, R. L., 31, 33 (ref. 64), 36, 53
- Peters, C. G., 7, 55, 59 (ref. 146), 70 (ref. 146), 78 (ref. 146), 93
- Peters, H., xxvi, xxxix, 153, 177, 178, 191, 192, 195, 212, 214, 218, 226, 234, 238, 250
- Peterson, L. E., 287 (ref. 41), 292 (ref. 41), 298
- Petrov, K. D., 350 (ref. 93), 361
- Philpott, M. W., 352, 360
- Pickles, S. S., 59, 70 (ref. 108), 74 (ref. 108), 92
- Piper, S. H., 11, 54
- Pitzer, K. S., 135 (ref. 74), 143, 262 (ref. 42), 264 (ref. 32), 298
- Polanyi, M., 137 (ref. 30), 142
- Pope, W. J., 335 (ref. 31), 360
- Popova, M. K., 334
- Porritt, B. D., 320, 360, 363, 365, 371, 388
- Posnjak, G., 150, 151, 154 (ref. 41), 164, 166 (ref. 41), 195
- Powell, R. E., 87 (ref. 109), 92, 265 (ref. 43), 267 (ref. 43), 298
- Powers, P. O., 180, 194
- Prather, J. L., 2 (ref. 92), 8, 9, 54, 60 (ref. 112), 92
- Prawirodipoero, R. S., 367 (ref. 16), 388
- Prins, H. J., 324, 360
- Proske, G., 179, 195
- Puddington, I. E., 27 (ref. 41), 52
- Pummerer, R., 65 (ref. 110), 92, 153, 173, 181 (ref. 43), 195, 238, 320, 360, 363-365, 366 (ref. 15), 368 (ref. 15), 369 (ref. 15), 370, 371, 386, 388

R

- Radcliffe, M. R., 177 (ref. 44), 187 (ref. 44), 195
- Raine, H. C., 2 (ref. 20), 11 (ref. 20), 52, 60 (ref. 111), 75 (ref. 111), 81 (ref. 111), 92
- Ralston, A. W., 17 (ref. 25, 26), 52
- Rands, R. D., Jr., 2 (ref. 92), 8, 9, 54, 60 (ref. 112), 92
- Ransom, W. W., 135 (ref. 52), 142
- Rautenstrauch, C. W., xxvii (ref. 15), xxxix
- Raynolds, J. W., 177 (ref. 44), 187 (ref. 44), 195
- Record, B. R., 151 (ref. 6), 194
- Reed, M. C., 28 (ref. 92a), 54
- Rehner, J., Jr., 24, 52, 244, 245, 249, 258, 274, 280 (ref. 11), 297, 424, 429, 432
- Reid, E. E., 326, 332, 360
- Reinhardt, R. C., 81 (ref. 113), 92
- Renoll, M. W., 192, 195
- Rhiem, H. E., 351 (ref. 43), 360
- Rhodes, E., 314 (ref. 66), 360
- Rhodes, H. D., 421, 428
- Rice, W. W., 262 (ref. 6, 33), 297, 298
- Richards, R. B., 2 (ref. 20), 11 (ref. 20), 52, 60 (ref. 111), 75 (ref. 111), 81 (ref. 111, 114), 85 (ref. 114), 88, 92, 119 (ref. 71), 143
- Richards, W. T., 5, 54
- Rideal, E. K., 314 (ref. 67), 361
- Roberts, K. C., 141, 143, 314 (ref. 66), 360
- Robertson, J. M., 102 (ref. 73), 115 (ref. 29), 142, 143
- Robey, R. F., 432
- Robinson, H. A., 180, 194
- Roelig, H., 401, 429
- Roniger, F. H., 414, 429
- Rosbaud, P., 60 (ref. 62, 64), 91
- Rossem, A. van, 59, 60, 62, 72 (ref. 115), 74 (ref. 115), 92, 367, 388
- Rossini, F. D., 135 (ref. 74), 143
- Rossmann, R. P., 383, 404, 429
- Roth, F. L., 62 (ref. 147), 65, 72 (ref. 147), 75 (ref. 147), 80, 81 (ref. 147), 82, 92, 93
- Ruby, I. R., 412, 416, 428
- Ruhemann, M., 6, 27, 53, 54, 60, 92
- Russell, J. J., 28, 32, 34 (ref. 95), 44, 54
- Russell, W. F., 355 (ref. 68), 356 (ref. 68), 361, 379 (ref. 18), 388
- Rust, F. F., 331 (ref. 86), 361
- Rutherford, H., 215 (ref. 79), 250

Ryder, H., 2 (ref. 20), 11 (ref. 20), 52, 60 (ref. 111), 75 (ref. 111), 81 (ref. 111), 92
 Rynkiewicz, L. M., 2 (ref. 20), 11, 52, 59 (ref. 20), 81 (ref. 20), 89

S

- Sachs, G., 83 (ref. 58), 90
 Sachse, H., 74 (ref. 118), 92
 Sackur, O., 170, 195, 241
 Sakurela, I., 209, 249
 Sandhaas, W., xxvii (ref. 20), xxxix
 Sanigar, E. B., xx, xxiii, xxiv
 Sauter, E., 111, 143
 Saville, W. B., 138 (ref. 69, 76), 143
 Saylor, C. P., 59, 61, 66 (ref. 123, 125, 126), 72, 93, 140 (ref. 81), 143, 386, 388
 Scatchard, G., 213, 222, 250
 Schallamach, A., 13, 14 (ref. 100), 15, 54, 60, 92, 140, 141, 143
 Scheiber, W. J., 2 (ref. 89), 54
 Schippel, H. F., 424, 429
 Schmidt, H., 155, 194, 419 (ref. 33), 428
 Schönberg, A., 348, 361
 Schoon, T., 129, 143, 392, 429
 Schulz, G. V., 151 (ref. 46), 170, 175, 176, 190, 195, 209, 215, 219, 222 (ref. 72), 223, 224, 231, 235, 247, 250
 Scott, A. H., 2 (ref. 96), 8 (ref. 96), 13, 15-18, 26, 52, 54
 Scott, J. H., 338, 361
 Scott, J. R., 62, 92, 178, 179, 195
 Scott, R. B., 2 (ref. 11), 8, 51, 60 (ref. 12), 89
 Scott, W., 351 (ref. 71), 361
 Scott-Blair, G. W., 47
 Sears, G. R., xxii
 Sebrell, L. B., 76 (ref. 120), 80 (ref. 120), 81 (ref. 120), 82 (ref. 121), 92, 125 (ref. 80), 143, 214, 250, 410, 428
 Selker, M. L., 32, 33 (ref. 98), 34, 41-45, 54, 334, 344, 345 (ref. 72), 361
 Seyer, W. F., 11, 54
 Shearer, G., 138 (ref. 76), 143
 Shepard, A. F., 335 (ref. 54), 336 (ref. 55), 360
 Shepard, N. A., 390, 394, 404, 408 (ref. 52), 418, 429
 Sheppard, N., 432
 Shipley, F. W., 316 (ref. 7), 327 (ref. 7), 328 (ref. 7), 331 (ref. 7), 332 (ref. 7), 333 (ref. 7), 334 (ref. 7), 339 (ref. 7), 342 (ref. 7), 343 (ref. 7), 344 (ref. 7), 347 (ref. 7), 359
 Shockley, W., 10 (ref. 85), 54
 Shriver, G. E., 432
 Sigdwick, N. V., 323 (ref. 73), 361
 Sinner, R., 225, 244, 250
 Silver, L., 11, 55
 Silverman, A., 22 (ref. 45), 53
 Simha, R., 10 (ref. 101), 13, 54, 84, 203, 204, 243, 244, 249, 250
 Simon, F., 6, 27, 53, 54, 60, 92
 Simonsen, J. L., xxxi, xxxii, xxxiv, xxxix
 Singer, W. E., 65 (ref. 87), 78 (ref. 1, 87), 88, 91
 Slater, J. C., 49 (ref. 103), 54
 Smallwood, H. M., 40, 54, 403 (ref. 25), 410, 411 (ref. 25), 428, 433
 Smith, C. C., 341 (ref. 91), 342 (ref. 91), 361
 Smith, D. M., 310 (ref. 81), 361
 Smith, F. L., Jr., xxii
 Smith, W. H., 59 (ref. 25, 28, 122, 123, 125, 126), 61, 66 (ref. 25, 28, 123, 125, 126), 72, 74 (ref. 122), 89, 92, 93, 132 (ref. 23), 140, 141 (ref. 23), 141, 143, 386, 388
 Smith, W. R., 390, 392 (ref. 53), 393, 404, 416 (ref. 53), 420, 421, 423 (ref. 57), 428, 429
 Smyth, C. P., 4, 5 (ref. 7), 17 (ref. 27), 18 (ref. 106), 47, 51, 52, 54
 Somerville, A. A., 379 (ref. 18), 388
 Sookne, A. M., 215 (ref. 79), 250
 Sparks, W. J., 314 (ref. 74), 361
 Spear, E. B., 423, 429
 Spence, D., 318, 320, 338, 361
 Spencer, R. S., 2 (ref. 13), 3 (ref. 13), 10 (ref. 13), 13 (ref. 13), 21 (ref. 14), 22 (ref. 14a), 25 (ref. 14a), 26 (ref. 14), 28 (ref. 14), 30 (ref. 14), 52, 59 (ref. 15), 74 (ref. 15), 89, 431
 Spurlin, H. M., 215, 219, 249, 250
 Squires, L., 351, 360
 Stambaugh, R. B., 403, 428
 Stamberger, P., 147, 148, 150, 154 (ref. 50), 166 (ref. 50), 195, 409, 410, 412, 429
 Stamm, A. J., xxii
 Staudinger, H., xvi, 24, 43, 54, 97, 143, 170, 171 (ref. 51), 172 (ref. 51), 174 (ref. 51), 177 (ref. 52), 195, 198, 200, 201 (ref. 81), 207-209, 216, 218, 228, 229, 231-236, 238, 239, 248, 250, 302, 303, 313, 361
 Stevens, H. P., 320, 338 (ref. 83), 361, 363, 366 (ref. 22), 371 (ref. 22), 374 (ref. 20), 375 (ref. 21), 380 (ref. 21), 381 (ref. 21), 382 (ref. 19), 386 (ref. 22), 388, 432
 Stevens, W. H., 338 (ref. 83), 361
 Stewart, T. D., 310, 361
 Stickney, P. B., 230, 231 (ref. 27), 249
 Stiratelli, B., 188 (ref. 27), 194
 Stock, A. H., xxiv
 Stone, S. B., 205 (ref. 84), 251
 Storks, K. H., 107, 126, 143

Street, J. N., 390, 394, 404, 408 (ref. 52),
418, 429
Streeter, S. F., 2, 10 (ref. 73), 53
Stull, D. R., 11, 54
Sturgis, B. M., 318 (ref. 84), 361
Sun, Kuan-Han, 22 (ref. 45), 53
Susich, G. v., 60 (ref. 127), 65 (ref. 110), 79
(ref. 65), 87 (ref. 98), 91-93, 99 (ref.
59), 105 (ref. 44, 48, 59), 106, 111, 142,
258, 298, 305 (ref. 49), 360
Sutherland, G. B. B. M., 432
Sutton, D. A., 302 (ref. 20, 22), 318 (ref.
22), 359
Svedberg, T., XIII, XV, XVII, XVIII, XXI,
XXIII, 221, 224 (ref. 55), 225 (ref. 55),
226 (ref. 55), 238 (ref. 55), 250

T

Tammann, G., 4, 22, 54, 83, 85, 93
Taylor, H. S., XIX, XXII
Temperley, H. N. V., 49, 55
Thibodeau, W. E., 61, 93
Thies, H. R., 141, 143
Thiessen, P. A., 27 (ref. 111), 55, 61, 65,
75 (ref. 133), 93
Thompson, H. W., xxx (ref. 21), xxxv,
XL, 107 (ref. 85), 135 (ref. 86), 143
Thornhill, F. S., 390, 392 (ref. 53), 416
(ref. 58), 420, 421, 423 (ref. 57), 428, 429
Tichenor, R. L., 28 (ref. 76), 54
Tidmus, J. S., 392 (ref. 58), 414 (ref. 58),
429
Tingey, H. C., 71, 76 (ref. 54), 90, 210,
215, 216 (ref. 85), 251
Tobolsky, A. V., 23, 55, 248, 250, 265
(ref. 43), 267 (ref. 43), 298, 432
Tompkins, H. K., 212, 251
Torkington, P., xxx (ref. 21), xxxv, XL
Treloar, L. R. G., 59 (ref. 135), 61, 63, 65,
67, 71, 72, 74, 77, 86, 93, 132 (ref. 87),
136 (ref. 87), 143, 147 (ref. 21), 148-
150, 151 (ref. 21), 154, 156 (ref. 21), 165,
166 (ref. 21), 167, 170 (ref. 21), 172, 194,
258, 265 (ref. 48), 267, 273, 289, 296, 298,
433
Trumbull, H. L., xxvi (ref. 22), XL, 141,
143
Tuckett, R. F., 4, 19, 24, 27, 28, 35, 37, 39,
52, 55, 85, 90
Turner, L. B., 314 (ref. 74), 361
Twiss, D. F., 353 (ref. 85), 361, 408, 429,
432

U

Ubbelohde, A. R., 11, 13 (ref. 116), 55
Ubbelohde, L., 205, 251
Überreiter, K., 2 (ref. 117), 3, 8, 23-27, 41,
53, 55

V

Valko, E. I., 87 (ref. 98), 92, 258, 298
VanBibber, K., 11 (ref. 42), 53
Van Hook, A., 11, 55
Van Natta, F. J., XXII, 209, 218, 230, 250
Vasil'ev, A. A., XXXVI, XL
Vaughan, W. E., 331 (ref. 86), 361
Vila, G. R., 77 (ref. 138), 93
Villari, E., 288
Vincent, J. R., 318 (ref. 84), 361
Vogel, M. R., 177 (ref. 44), 187 (ref. 44),
195
Vold, M. J., 13 (ref. 121), 55
Vold, R. D., 13 (ref. 121), 55
Volmer, M., 83 (ref. 139), 93
Volquartz, K., 176 (ref. 4), 190 (ref. 4),
194

W

Wall, F. T., 258, 273, 296, 297, 298
Wallder, V. T., 34 (ref. 55), 53
Ward, A. L., 17 (ref. 65), 53
Waring, J. R. S., 394, 403, 420, 428, 429
Warren, B. E., 392, 428
Warth, H., 231, 251
Waters, W. A., 315 (ref. 35), 317 (ref. 35),
360
Watson, R. W., xxxvi (ref. 19), xxxix
Weigert, F., 383 (ref. 10), 388
Weil, L., xxiii
Weiss, J., 422-424, 429
Weissbach, K., 347 (ref. 11), 359
Werkenthin, T. A., 32, 54
Wertheim, M., 239, 250
Westhead, J., 355 (ref. 15), 359
Whitby, G. S., xxxviii (ref. 23), XL, 59
(ref. 140), 68, 70 (ref. 140), 74 (ref. 140),
78 (ref. 140), 93, 132 (ref. 3), 141, 180,
187, 188, 195, 325, 353 (ref. 88), 361,
374 (ref. 23), 385, 388
White, A. H., 392 (ref. 61), 429
White, F. L., 337 (ref. 32), 352, 360
White, L. M., 432
Wiegand, W. B., xxviii, xxxix, 390-392,
395, 399, 400, 407, 413, 417-420, 422,
429
Wiese, H. K., 432
Wildschut, A. J., 63, 73, 93
Wiley, F. E., 2 (ref. 122), 21 (ref. 122), 22,
55
Wilkins, E. S., xxii
Willer, R., xxxvi (ref. 25), XL
Williams, I., 79 (ref. 23), 89, 116 (ref. 20),
141, 188 (ref. 54), 189, 195, 341, 342
(ref. 91), 343 (ref. 89), 344, 346, 347,
361, 385, 388
Williamson, R. V., XXI
Willoughby, C. E., xxii

- Wilson, E. B., Jr., 18 (ref. 106), 54, 135
(ref. 74), 143
- Wing, H. J., 59 (ref. 126), 61 (ref. 126), 66
(ref. 126), 93, 140 (ref. 81), 143
- Winspear, G. G., 31, 32, 33 (ref. 98), 34
(ref. 98), 36, 41-45, 53, 54, 188 (ref. 27),
194
- Wittstadt, W., 61 (ref. 133, 142), 65, 75
(ref. 133), 93
- Woehlich, E., 258, 267 (ref. 53), 298
- Wolff, E., 107 (ref. 90), 143, 219, 250
- Wolthuis, E., 59 (ref. 28), 66 (ref. 28), 89
- Wood, L. A., 7, 15, 18, 55, 59 (ref. 13, 14,
146), 60 (ref. 144), 61 (ref. 143), 62, 65,
68, 69 (ref. 13), 70 (ref. 146), 71 (ref.
14), 72 (ref. 147), 74 (ref. 14), 75 (ref.
14, 147), 76 (ref. 14), 78 (ref. 146) 80,
81 (ref. 147), 82 (ref. 116), 89, 92, 93,
431
- Woodford, D. E., 403, 428
- Woods, H. J., 131 (ref. 2), 141
- Woodward, I., 115 (ref. 29), 142
- Wouda, J., 61 (ref. 102), 92
- Wright, J. M., 317, 318 (ref. 92), 361
- Wurstlin, F., 29, 30, 55
- Wyk, A. J. A. van der, 78 (ref. 99), 92,
112, 143, 149 (ref. 2), 166 (ref. 2), 194
- Y
- Yakubchik, A. I., xxxvi, xl
- Yerzley, F. L., 62, 72 (ref. 149), 79 (ref.
149), 93
- Yiengst, H. A., 59 (ref. 75), 91
- Yost, D. M., 262 (ref. 55), 298
- Young, D. W., 177 (ref. 81), 194, 212, 249
- Young, J., 338 (ref. 78), 361
- Z
- Zeïde, O. A., 350 (ref. 93), 361
- Zhabina, V. M., xxxvi, xl
- Zhurkov, S. N., 431
- Ziegler, K., xxxvi, xl
- Zimm, B. H., 227, 228, 249, 251
- Zocher, H., 61 (ref. 150), 93

SUBJECT INDEX

A

- Abrasion resistance of vulcanized rubber
 - effect of fillers, 398
- Accelerator(s), action, 346
 - dibenzothiazyl disulfide as, 349
 - dibenzothiazyl monosulfide as, 350
 - mercaptobenzothiazole as, 349
- Adhesion tension, definition, 418
- ϵ -Aminocaproic acid polymers, intrinsic viscosity *vs.* degree of polymerization, 237
 - molecular weight, 236
- Aniline points of mineral oils, relation to swelling power, 180
- α -Anomaly of rubber, 6
- Antioxidants, and gelling, 369
- Autoxidation in rubber and olefins, 310
- Azo compounds and vulcanization, 315

B

- Balata, crystallization in, 78
 - osmotic pressure curves, solutions, 172
- Base mole, 198
- Benzoyl peroxide and vulcanization, 315
- Brittle point(s), definition, 31, 35
 - effect of fillers, 40, 45
 - of molecular weight, 37, 41
 - of plasticizers, 39, 44
 - of sample thickness, 36
 - of sulfur, 43
 - of vulcanization, 39, 43
 - table of values*, 33
 - and Young's modulus, 46
- Brittle point tests, methods, 31
 - theory, 35
- Bromination of rubber, 310
- Brownian motion and viscosity, 242, 243
- Bulk rubber, kinetic model, 267
- Buna N, swelling, 186
 - volume sorption of vapors and solidification temperature, 431
- Buna S, solubility of sulfur in, 188
 - swelling, 185
- Butadiene and styrene, copolymerization, 27
 - methacrylonitrile copolymer, ozonolysis of, XXXV
 - methyl methacrylate copolymer, ozonolysis of, XXXII

- polymers, crystallization, 82, 117
 - styrene copolymer, ozonolysis of, XXXIV
- Butyl rubber, crystallization of, 80, 279
 - crystal structure, 125
 - thermal effects during stretching, 432
 - vulcanization of, 313

C

- Capillary size and viscosity, 201
- Carbon black, particle dimensions, 391
- Cellulose acetate, molecular weight, 236
 - swelling factor *vs.* concentration, 246
- Chain branching, effect on polymer properties, XXXVI
- Chain molecules, long, statistical treatment, 275
- Chloranil and vulcanization, 326
- Chlorination of rubber, 310
- Chloroprene. *See* Polychloroprene.
- Coefficient of thermal expansion, 275
 - of viscosity, definition, 200
- Cohesive energy density, definition, 163, 212
 - and heat of mixing, 213
 - of rubbers, and swelling, 182
 - table of values*, 186
 - and solvent power, 211
 - of sulfur, 189
- Compounding of natural and synthetic rubbers, XXXIX
- Compounding ingredients, properties, 389-429
- Compressibility and second-order transitions, 13
- Constitution and reactivity, 308
- Copolymerization, effect on transition temperature, 26
 - styrene and butadiene, 27
- Creep effects and crystallinity, 72
- Cresol-formaldehyde resins, swelling factor, 245
- Critical point, temperature and concentrations for rubber solutions, 174
- Cross linkage, formation, 262
 - and photogelation, 380
 - and transition temperature, 25
 - and vulcanization, 315
- Cryoscopic measurements, rubber solutions and gels, 153

- Cryptostegia**, xxvi
- Crystal(s), in high polymers, 87
 melting of, 133
 nuclei, 71
- Crystal dimensions of stretched rubber, 140
- Crystalline regions in high polymers, 87
- Crystalline rubber, hardness, 62
 mechanical properties, 62
 melting, 66, 431
 size of crystallites, 77
 Young's modulus, 62
- Crystallinity and second-order transitions, 12
- Crystallization, 138
 in balata, 78
 in butadiene polymers, 82
 of Butyl rubber, 80, 279
 and creep, 72
 degree of, 282
 and elasticity, 279
 entropy effects during, 86
 general characteristics, 63
 in gutta-percha, 78
 high-pressure studies, 431
 in isobutene polymers, 80
 kinetics, 83
 and mechanical properties, 71
 and melting range, 85
 in natural and synthetic rubbers, 57-93
 of natural rubber, 78, 279
 of neoprene, 79, 279
 nucleus of, 83
 in Oppanol B, 80
 and plastic flow, 72
 of polychloroprene, 79, 279
 in polyethylene, 81
 of polymers, 97
 of polysulfide polymers, 80
 in Polythene, 81
 of polyvinylidene chloride, 81
 quantitative determination, 73
 rate, 63
 and pressure, 65
 requirements for, 125
 and rupture, 72
 and stress, 284
 and stretching, 65, 98, 139
 and sulfur, 75
 and temperature, 282
 thermal effects of, 60
 of Thiokol, 80
 and transition temperature, 6, 8
 in Vistanex, 80
 and vulcanization, 75
 x-ray diffraction study, 60
 and Young's modulus, 71
- Crystallization temperature and melting range, 68, 87
- Crystal structure, butadiene polymers, 117
 of Butyl rubber, 125
 methods of determination, 98
 of polychloroprene, 116
 of polyesters, 128
 of polyethylene, 119
 of polyisobutene, 125
 of polyvinyl chloride, 123
 of rubber, 111, 114
 of rubber hydrochloride, 118
 of rubberlike polymers, 98
 of polyvinyl alcohol, 121
- Curing, kinetic interpretation, 268
- Cyclization, of dihydromyrcene, 304
 of polyisoprene, 404
 of rubber, 141, 302
 of squalene, 304
 and vulcanization, 304
- Cyclized rubber, 141
- ### D
- Deformations and elastic energy, 272
- Degradation of rubber, 303
- Degree of crystallization, 282
- Degree of polymerization, *vs.* intrinsic viscosity, for ϵ -aminocaproic acid polymers, 237
vs. transition temperature, 29
- Dibenzothiazyl disulfide, as accelerator, 349
- Dibenzothiazyl monosulfide, as accelerator, 350
- Dibenzoyl peroxides and vulcanization, 315
- Dielectric constant, 17
- Dielectric properties, and second-order transitions, 17
 and vulcanization, 18
- Diene polymers, structure, xxx
- Dihydromyrcene, cyclization of, 304
- Dilution, free energy of (rubber) by various liquids, 154
 heat of (rubber), 155
- Dipole rotation at transition temperature, 20
- Dispersability and molecular integrity, 340
- Dispersing agents, 413
- Dispersion and fillers, 408
 and piperidine, 342
 and zinc oxide, 343
- Dissociation energies of bonds in rubber, 260
- ### E
- Elastic energy, derivation, 272
- Elasticity, and crystallization, 279
 theory, *vs.* experiment, 285

- Flory and Rehner, 297
 James and Guth, 277
 kinetic, 253-298
 Kuhn, 294
 molecular significance of constants, 278
 Wall, 296
 and van der Waals' forces, 432
 Elastomer, definition, xxv, 384
 double bonds in, 432
 peroxides in, 432
 Electrical characteristics of vulcanized rubber, effect of fillers, 403
 Elongation, "secondary," 72
 Emollients, functions, 413
 Entropy changes during crystallization, 86
 Entropy curves for rubber solutions and gels, 161
 Entropy of mixing, statistical calculation, 156
 Equation of state for single flexible chains, 266
- F**
- Filler(s), and abrasion resistance of vulcanized rubber, 398
 and brittle point, 40, 45
 and dispersion, 408
 and dynamic hysteresis of vulcanized rubber, 401
 and electrical characteristics of vulcanized rubber, 403
 and flocculation, 408
 flocculation of, and reinforcement, 416
 and hardness of vulcanized rubber, 397
 and mixing, 404
 in natural and synthetic rubber, **xxix**
 particle shape and structure, 392
 particle size, 390
 particle size, as factor in reinforcement, 414
 vs. tensile strength of product, 395
 particle structure and reinforcement, 415
 physical characteristics, 390
 and rebound resilience of vulcanized rubber, 401
 reinforcement by, 393
 specific surface, as factor in reinforcement, 414
 state in rubber, 422
 and static hysteresis of vulcanized rubber, 400
 and stiffness of vulcanized rubber, 396
 in synthetic rubber, 404
 and tear resistance of vulcanized rubber, 397
 and tensile strength of vulcanized rubber, 394
 and vulcanized rubber, 393
- and work of extension of vulcanized rubber, 399
 and work of retraction of vulcanized rubber, 400
 Firmness vs. temperature, 46
 Flexibility, internal, of linear macromolecules, 262
 Flexible chains, equation of state, 266
 Flocculation, of filler, and reinforcement, 416
 and stiffening, 412
 Flory and Rehner, theory of elasticity, 297
 Flow and crystallization, 72
 definition, 73
 normal and pseudo, 73
 viscous, general characteristics, 199
 Fractionation of rubber, 190
 Free energy of dilution, equation, 164
 of rubber, by various liquids, 154
 Free energy of mixing, rubber solutions, 162
 Free energy of solution, equation, 164
 Free rotation, and rubber elasticity, 262
 in the solid state, 5
- G**
- Gases and rubbers, 255
 Gaussian distribution law, deviation, 275
 Gelling, and antioxidants, 369
 by light, in elastomers other than rubber, 384
 and oxygen, 364, 365
 and physical condition of rubber, 369
 and purity of rubber, 370
 Geranylamine hydrochloride, 110
 Grignard reagents and vulcanization, 336
Grundmol, 198
 Guth-James model, structure of bulk rubber, 268
 Gutta-percha, α and β , 106
 crystallization in, 78
 crystal structure, 106
 osmotic pressure curves, solutions, 172
- H**
- Halogenation of rubber, 310
 Hardness of crystalline rubber(s), 62
 and light, 432
 of vulcanized rubber, effect of fillers, 397
 and Young's modulus, 71
 Heat capacity vs. temperature, 8
 Heat of dilution of rubber, 155
 Heat of mixing, and cohesive energy density, 213
 rubber solutions, 162
Hevea. See Natural rubber.

- Hycar, stress-strain curves, 292
 Hydrocarbons, anomaly of specific heat, 11
 Hydrogenation of rubber, 302
 Hydrogen bonding and vulcanization, 323
 Hydrogutta, osmotic pressure curve for solutions, 172
 Hydrorubber, osmotic pressure curves for solutions, 172
 vulcanization, 313
 ω -Hydroxydecanoic acid polymers, ultracentrifugal studies, 225
 viscosity and molecular weight studies, 230
 ω -Hydroxyundecanoic acid polymers, viscosity and molecular weight studies, 230
 Hysteresis, and carbon black, 426
 definition, 400
 dynamic, of vulcanized rubber, effect of fillers, 401
 static, of vulcanized rubber, effect of fillers, 400
- I**
- Insolubility, development during rubber treatment, 323
 Interaction constant(s), definition, 213
 of solvents, *table of values*, 214
 Intrinsic viscosity, *vs.* degree of polymerization, for ϵ -aminocaproic acid polymers, 237
 of fractions and whole polymers, 215
 and molecular weight, 216
 and particle shape, 242
 of rubber fractions and whole polymers, *table of values*, 216
 and swelling, 213
 and swelling factor, 245
 and temperature, 214
 Isobutene polymers, crystallization in, 80
 Isomerism of rubber, 305
 Isoprene, crystal structure, 108
 photosynthesis of rubber from, 386
- K**
- Kinetic theory of rubber elasticity, 253-298
 Kraemer, E. O., *biography*, **xiii**
 Kuhn theory of rubber elasticity, 294
- L**
- Lambda point, specific heat interpretation, 10
 Lambda transitions in paraffins, 11
 Light, action on solid rubber, 373
 and rubber, 363-388, **432**
 and vulcanization, 319
 Light, wave length, for photogelation, 372
 Light scattering, of high-polymer solutions, 226
 Light transmission in rubber, 61
 Linear chain molecule, kinetic picture, 266
 statistical thermodynamics, 265
 Linear macromolecules, internal flexibility, 262
 Liquids, Newtonian and non-Newtonian, 200
 and rubbers, 254
 Long-chain molecule, configurational statistics, 263
 isolated, probable length, 265
 statistical treatment, 275
 Loss factor, and second-order transitions, 19
 and sulfur content, 19
- M**
- Mechanical properties, of crystalline rubber, 62
 and crystallization, 71
 Melting of crystalline rubber(s), 66, 431
 Melting point, effect of pressure, 68, 431
 Melting range, effect of crystallization, 85
 effect of crystallization temperature, 68, 87
 Mercaptobenzothiazole as accelerator, 349
 Methacrylonitrile-butadiene copolymer, ozonolysis of, **xxxv**
 Methyl methacrylate-butadiene copolymer, ozonolysis of, **xxxii**
 Micellar theory of rubber structure, 173
 Milkweed, **xxvi**
 Modulus of elasticity and second-order transitions, 16
 Molecular length, variation with temperature, 96
 Molecular structure, of diene polymers and copolymers, **xxx**
 and physical properties, 132
 of polybutadiene, sodium-polymerized, **xxxv**
 of rubber, 301
 and transition temperature, second-order, 3
 Molecular weight, of ϵ -aminocaproic acid polymers, 236
 average, definition, 217
 rubbers, 261
 and brittle point, 37, 41
 of cellulose acetate, 236
 determination, by end groups, 218
 by freezing point, 218
 of high polymers, 216

by light scattering in solution, 226
 by osmotic methods, 219, 432
 of polystyrene, 235, 432
 by viscosity, discussion, 239
 and intrinsic viscosity, 216
 of polyisobutene, 234
 of polystyrene, 227
 and reduced viscosity, 208
 of rubber by osmotic methods, 238
table of values, 173
 of rubber and polychloroprene, by ultra-
 centrifuge, 226
 and sedimentation velocity, 225
 and solution viscosity, 228
 and transition temperature, 23
 ultracentrifugal studies, 224
 variation with fractionation of rubber,
 192
vs. viscosity, for rubber, 237
 and viscosities of solutions, 198
 Molecular "wriggling," 88

N

Natural rubber, crystallization, 78, 279
 origin, **xxxvii**
 physical and chemical characteristics,
 260
 solution in various solvents, osmotic
 pressure curves, 171
 stress-strain curves, 290
 swelling, 185
vs. synthetic rubber, **xxviii**
 vulcanized, swelling, 187
 Neoprene, crystallization, 79, 279
 swelling, 185
 swelling power of mineral oil on, 180
 Network, Guth-James model, 269
 under stress, 270
 Newtonian and non-Newtonian liquids,
 200
 Nitro compounds and vulcanization, 317
 Noncrystallizable polymers, 82

O

Olefins, autoxidation, 311
 Oppanol B, crystallization in, 80
 Optical creep, 61
Optical double refraction, in rubber, 61
 Orientation, and activation energy, 30
 and crystal structure, 98
 plane, 99
 of stretched rubber, 140
 studies on, 138
 and transition temperature, 21
 Osmometer, description and use, 152, 219
 Osmotic balance, 221
 Osmotic pressure, *vs.* concentration, ther-
 modynamic treatment, 221

constants for polystyrene, 236
 curves, balata solutions, 172
 gutta-percha solutions, 172
 hydrogutta solutions, 172
 hydrorubber solutions, 172
 polybutadiene solutions, 171
 polyisobutene solutions, 172
 natural rubber, in various solvents, 171
 of rubber solutions, 146
 rubber solutions and gels, determina-
 tion, 151
 Overcuring, 344
 Oxygen, and gelling, 364, 365
 and hardness of polymers, 432
 and photogelling, 364, 365
 as plasticizer for rubber, 432
 and vulcanization, 334
 Ozonolysis of polymers, **xxx**

P

Paracon, **xxvii**
 Paraffins, lambda transitions, 11
 Partial molar entropy of dilution and
 solution, 158
 Particle shape and intrinsic viscosity, 242
 Particle size as factor in reinforcement by
 fillers, 414
 of fillers, 390
 Perbunan, swelling power of mineral oil
 on, 180
 Peroxides, in elastomers, 432
 and vulcanization, 367
 Phase diagram, second-order, for high
 polymers, 50
 Phase transition effects, second-order, 1-55
 definition, 2
 Phenol-formaldehyde resins, swelling fac-
 tor, 245
 Photogelation, and cross linkage, 380
 in elastomers other than rubber, 384
 light sources for, 371
 Photogelling and oxygen, 364, 365
 Photogels, 320
 dried properties of, 376
 formation in inactive solvents, 364
 properties, 372
 and rubber photovulcanizates, 363-388
 syneresis in, 372
 Photopolymerization, of isoprene, 386
 of styrene, 386
 Photosynthesis of rubber from isoprene,
 386
 Photovulcanizates and photogels of rubber,
 363-388
 Photovulcanization, mechanism, 381
 Pigments. *See* Filler(s).
 Piperidine and dispersion, 342
 Plastic flow, effect of crystallization, 72

- Plasticizer(s), effect on brittle point, 39, 44
effect on transition temperature, 27
- Polyamides, rubbery and fiber-forming, **xxxviii**
- Polybutadiene, osmotic pressure curves for solutions, 171
ozonolysis, **xxxix**
photogelation, 384
sodium polymerized, structure, **xxxv**
volume sorption of vapors and solidification temperature, 431
- Polychloroprene, crystallization, 79, 279
crystal structure, 116
photogelation, 384
swelling, 185
swelling power of mineral oil on, 180
- Polydecamethylene adipate, molecular weight by viscosity, 230
- Polyesters, **ii, iii**
crystal structure, 128
melting point and crystal structure, 137
- Polyethylene, configurational statistics, 263
crystallization, 81
crystal structure, 119
mechanical data, 431
melting point and crystal structure, 136
molecular structure, 431
thermal data, 431
- Polyisobutene, crystal structure, 125
intrinsic viscosity *vs.* molecular weight, 234
melting point and crystal structure, 136
molecular weight studies, 233
osmotic pressure curves for solutions, 172, 221
reduced viscosity of solutions, 212
volume sorption of vapors and solidification temperature, 431
- Polyisobutylene. *See* Polyisobutene.
- Polyisoprene, cyclization, 304
melting and crystal structure, 134
- Polymerization, degree of, 262
and vulcanization, 307
- Polymethyl methacrylate, molecular weight, 231
volume sorption of vapors and solidification temperature, 431
- Polyoxyethylene glycols, viscosity data, 229
- Polystyrene, axial ratio and molecule length, 243
cross-linked, deswelling, 432
molecular weight, 235
molecular weight by light scattering and osmotic data, 227
osmotic pressure of solutions, 235
photopolymerization, 386
solutions, specific viscosity *vs.* velocity gradient, 201
viscosity *vs.* concentration, 208
viscosity and osmotic constants, 236
- Polysulfide polymers, crystallization, 80
organic, 131
- Polythene. *See* Polyethylene.
- Polyvinyl alcohol, crystal structure, 121
- Polyvinyl chloride, crystal structure, 123
molecular weight, 231
- Polyvinylidene chloride, brittle point, 42
crystallization, 81
thermal expansion process, 21
- Pressure, influence on transition temperature, 26
- Proof resilience, definition, 399
- R**
- Rebound resilience of vulcanized rubber
effect of fillers, 401
- Recrystallization, 71
- Refractive index and second-order transitions, 16
- Reinforcement. *See also* Filler(s).
causes, 414
by compounding ingredients, 389-429
criteria, 406
definition, 393
by fillers, 393
and flocculation of filler, 416
mechanism, 417
and particle size of filler, 414
as physical phenomenon, 421
plastic solid film theory, 423
specific surface of filler as factor, 414
and structure of filler particles, 415
as vulcanization, 420
Wiegand theory, 419
- Resilience, rebound, of vulcanized rubber
effect of fillers, 401
- Resistivity, and heat treatment of filled rubber, 411
- Reversion, 344
- Rotation, in the solid state, 5
at transition temperature, 20
- Rubber, additive reactions, 308
autoxidation, 311
chemical structure, 259
cohesive energy densities, *table of values*, 186
and swelling, 182
crystal structure, 111, 114
cyclization, 302
degradation, 303
elasticity, and free rotation, 262
history of theory, 257
fractionation, 190
and gases, 255
gels, thermodynamic study, 145-195
Guth-James model, 268
halogenation, 310

- as high polymer, 255
 hydrogenation, 302
 insolated, stress-strain curves, 374
 irradiated, properties, 376
 and light, 363-388
 and liquids, 156, 254, 418
 mechanical characterization, 253
 from milkweed, **xxvi**
 molecular structure, 301
 molecular weight, average, 261
 by osmotic methods, 173, 238
 variation in fractionation, 192
 natural. *See* Natural rubber.
 photogels and photovulcanizates, 363-388
 photosynthesis from isoprene, 386
 soft, stress-strain curve, 288
 and solids, 254
 solubility of solids in, 188
 solubility in various liquids, 174
 solutions, heat and free energy of mixing, 162
 thermodynamic study, 145-195
 solutions and gels, cryoscopic measurements, 153
 entropy curves, 161
 osmotic pressure determination, 151
 swelling pressure, 150
 thermodynamic study, comparison of theory and experiment, 165
 statistical calculations, 156
 vapor pressures, 147
 solvent power of various liquids on, 177
 stretched, crystal dimensions, 140
 plane orientation, 140
 structural transformations in, 301
 structure, micellar theory, 173
 substitution reactions, 308
 swelling, and cohesive energy density, 182
 limited, 179
 synthetic. *See* Synthetic rubber.
 thermal decomposition, 302
 thermoelastic behavior, 255
 unstretched, Young's modulus, 46
 velocity of sound in, 15
 viscosity *vs.* molecular weight, 237
 vulcanized. *See* Vulcanized rubber.
- Rubber hydrochloride**, crystal structure, 118
 melting point and crystal structure, 136
Rubberiness, characteristics, 95, 259
Rubberlike elasticity, theory, 256
Rubberlike polymers, crystal structure, 98
Rubbery state of matter, characteristics, **xxvi**, 254
Rupture, effect of crystallization, 72
- S**
- Saran**, crystallization, 81
Secondary elongation, 72
Sedimentation velocity, 225
Shape of solute particle, and viscosity, 240
Shearing stress, and velocity gradient, 200
Silicone rubber, x-ray study, 431
Smilax, rubber from, **xxvi**
Sodium polybutadiene, structure, **xxxv**
Softeners, functions, 413
Solidification temperature of polymers and volume sorption of vapors, 431
Solids and rubbers, 254
Solubility, of polymers, theory, 175
 of rubbers in various liquids, 174
 of solids in rubber, 188
Solvation, during polymer solution, 178
Solvent power, and cohesive energy density, 211
 of various solvents for rubber(s), 177
Sound, velocity in rubber, 15
Specific heat, discontinuity, 10, 11
 vs. temperature, 9
Specific viscosity, definition, 201
Specific volume, in crystallization study, 59
Staggered bonds, principle, 118
 "Stark rubber," 70
Stearic acid, as compounding ingredient, 413
Stiffening and flocculation, 412
Stiffening point, 32
Stiffness of vulcanized rubber, effect of fillers, 396
Stress and crystallization, 284
Stress-strain curves, and elasticity theory, 286
 for Hycar, 292
 for insolated rubber, 374
 for natural rubber, 290
 resolved, and theory, 290
 for soft rubber, 288
 theory *vs.* experiment, discussion, 293
Stress-strain relation, unilateral, 270
Stress-temperature curves, isometric, 289
Stretching, and fiber diagrams, 425
 and rate of crystallization, 65
 and thermoelastic behavior, 255
Stretch, unilateral, stress-strain relation, 270
Structure. *See* Crystal structure and Molecular structure.
Styrene, photopolymerization, 386
Styrene-butadiene, copolymerization, 27
Styrene-butadiene copolymer, ozonolysis, **xxxiv**
Sulfur, and brittle point, 43
 and crystallization, 75
 cohesive energy density, 189

- solubility in rubber(s), 188
and transition temperature, 8, 24
and vulcanization, 324
- Sulfur content, and loss factor, 19
in vulcanizates, 337
- Sulfur monochloride, and vulcanization, 335
- Swelling, of Buna N, 186
of Buna S, 185
initial and "increment," 179
and intrinsic viscosity, 213
kinetic theory, 273
limited, of rubber, 179
of natural rubber compounds, 185
of neoprene, 185
of polychloroprene, 185
of rubbers, and cohesive energy density, 182
theoretical treatment, 181
of Thiokol, 186
and viscosity, 244
of vulcanized natural rubber, 187
- Swelling factor, 223
vs. concentration, cellulose acetate, 246
and intrinsic viscosity, 245
for three-dimensional polymers, 245
- Swelling power of mineral oils, and aniline points, 180
on rubbers, 180
- Swelling pressure, of natural rubber gels, curves, 150
of rubber solutions and gels, determination, 150
- Syneresis, in photogels, 372
- Synthetic elastomers, definition, 384
- Synthetic rubber, definition, **xxvi**
fillers in, 404
vs. natural rubber, **xxviii**
physical and chemical characteristics, 260

T

- Tear resistance of vulcanized rubber, effect of fillers, 397
- Temperature, and firmness, 46
vs. heat capacity, 8
vs. specific heat, 9
vs. volume, curves, 6
- Tensile strength, *vs.* particle size of filler, 395
of vulcanized rubber, effect of fillers, 394
- Tetramethylthiuram disulfide and vulcanization, 75, 347
- Thermal conductivity and second-order transitions, 13
- Thermal expansion, coefficient, 275
correction to stress-strain relation, 274

- Thermal vibration and x-ray diffraction, 104
- Thermodynamics of rubber solutions and gels, applications to specific problems, 169
theory *vs.* experiment, 165
of rubber solutions, experimental study, 147
- Thermoclastic behavior, 255
- Thermoelastic inversion, 274
- Thermoelasticity, history of theory, 257
- Thiokol, crystallization, 80
swelling, 186
- Time effects of second-order transitions, 4, 22
- Transitions, second-order, comparison of common tests, 49
second-order, and crystallinity, 12
experimental results, 6
kinetic interpretation, 4
time effects, 4
- Transition effects, second-order, 1-55
- Transition temperature, and copolymerization, 26
and cross linkage, 25
and crystallinity, 6, 8
vs. degree of polymerization, 29
dipole rotation at, 20
and molecular weight, 23
and orientation, 21
and plasticizers, 27
and pressure, 26
second-order, and molecular structure, 3
table of values, 2
and sulfur, 24
and sulfur content, 8
and vulcanization, 24
and Young's modulus, 46

U

- Ultracentrifuge, use in molecular weight determinations, 224
- Unit cell dimensions, 100
- Unsaturation and vulcanization, 338

V

- Vapor pressure, of rubber solutions and gels, 147
in various solvents, curves, 149
- Velocity gradient and shearing stress, 200
- Vinyl side groups, effect on polymer properties, **xxxvi**
- Viscometer, capillary, sources of error, 205
rotating cylinder, 206
- Viscosity, and capillary size, 201
vs. concentration for polystyrene, 208
constants for polystyrene, 236
definition, 199

- determination, methods, 204
of dilute solutions of high polymers,
 significance, 197
falling ball measurements, 207
of ω -hydroxydecanoic acid polymers,
 230
influence of degree of polymerization *vs.*
 molecular weight, 229
intrinsic, 209
 variation with solvent, 211
kinetic interpretation, 202
measurements, experimental results, 207
 of high polymer solutions, 197-251
and molecular weight, discussion, 239
vs. molecular weight, curves for rubber,
 237
of polyoxyethylene glycols, 229
"reduced," 207
 and molecular weight, 208
 of polyisobutene solutions, 212
and size and shape of solute particle, 240
and solution concentration, 198
specific, definition, 201
 and velocity gradient, for polystyrene
 solutions, 201
and swelling, 244
theoretical treatment, 239
Viscosity coefficient, definition, 200
Viscous flow, general characteristics, 199
Vistanex, crystallization, 80
Volume change and second-order transi-
 tions, 22
Volume *vs.* temperature, curves, 6
Vulcanization, 299-361. *See also* Vul-
 canized rubber.
 and azo compounds, 315
 and carbonyl compounds, 368
 and brittle point, 39, 43
 of Butyl rubber, 313
 as chain reaction, 334
 and chloranil, 326
 and cross linkage, 315
 and crystallization, 75
 cyclization during, 304
 and dibenzoyl peroxides, 315
 and dielectric properties, 18
 with ferricyanide, 318
 and Grignard reagents, 336
 and hydrogen bonding, 323
 of hydrorubber, 313
 isomeric changes during, 306
 kinetic interpretation, 268
 by light, 319
 mechanism, 381
 and nitro compounds, 317
 oxidation during, 306
 and oxygen, 334
 and peroxides, 367
 photochemical, 378
 and physical properties, 300
 and polymerization, 307
 products, constitution, 337
 and sulfur, 324
 and sulfur monochloride, 335
 and tetramethylthiuram disulfide, 347
 thermal, 378
 and transition temperature, 24
 and unsaturation, 313, 338
 and zinc oxide, 350, 355
Vulcanized rubber(s), effect of fillers on
 abrasion resistance, 398
 on dynamic hysteresis, 401
 on electrical characteristics, 403
 on hardness, 397
 on rebound resilience, 401
 on static hysteresis, 400
 on stiffness, 396
 on tear resistance, 397
 on tensile strength, 394
 on work of extension, 399
 on work of retraction, 400
- W**
- Wall theory of elasticity, 296
Wave length of light for photogelation, 372
Wiegand theory of reinforcement, 419
- X**
- X-ray diffraction, in crystallization study,
 60
 methods, 95-143
 patterns, high polymers, precision, 101
 study of silicone polymers, 431
 and thermal vibration, 104
- Y**
- Young's modulus, and brittle point, 46
 of crystalline rubber, 62
 and crystallization, 71
 and hardness, 71
 and temperature, 46
 and transition temperature, 46
- Z**
- Zinc oxide and dispersion, 343
 and vulcanization, 350, 355

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