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THE STRUCTURE AND PROPERTIES OF POLYMERIC MATERIALS.(U)
JAN 77 P J FLORY

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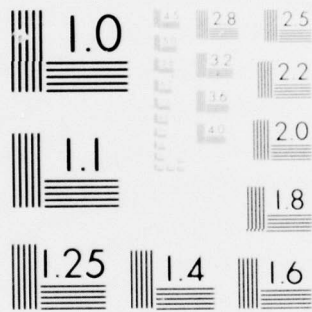
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FINAL SCIENTIFIC REPORT

The preponderance of the results of the research investigations carried out under Grant No. 73-2441 covering the period from 15 August 1972 to 31 January 1977 have been published or are in press. Reprints and manuscripts covering these results have been submitted previously to AFOSR.

A total of thirty-five publications have been generated from this research. A publication list including all publications during the period of this report is appended. Those publications representing investigations supported in whole or in part by AFOSR are indicated by an asterisk. These papers have appeared, or will appear, in thirteen primary journals.

The following co-workers have been resident at Stanford for varying period of time, and have collaborated in the researches covered by this report:

- Professor Wilma K. Olson, Rutgers University, New Brunswick, N.J.
- Dr. G. D. Patterson, Bell Laboratories, Murray Hill, N. J.
- Dr. R. T. Ingwall, Polaroid Corporation
- Dr. H. Shih, duPont, Wilmington, Del.
- Dr. C. J. Pickles, Lever Bros. Research, Liverpool, England
- Prof. J. E. Mark, U. of Cincinnati, Cincinnati, Ohio
- Dr. E. A. Czurylo, Warsaw University, Poland
- Dr. S. Bluestone, California State U., Fresno, Ca.
- Mr. L. C. DeBolt, Polytechnic Institute, New York
- Dr. M. H. Liberman, U. S. Customs Laboratory, San Francisco, Ca.
- Dr. P. R. Sundararajan, Xerox, Ontario, Canada
- Dr. D. Y. Yoon, IBM, San Jose, Ca.
- Professor Y. Tatara, Shizuoka University, Japan
- Dr. U. W. Suter, Eidgenössische Technische Hochschule, Zürich, Switzerland

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Dr. C. W. Carlson, duPont, Wilmington, Del.

Research as yet incomplete or awaiting preparation for publication is briefly summarized below:

Rubber Elasticity

It is now well established that the stress in a deformed rubber originates within the chains of the network. Inter-chain interactions contribute negligibly to the stress. The elastic properties of this broad class of materials (which includes nearly all linear polymers under suitable conditions) must therefore reflect the configurational characteristics of the polymer chains comprising the rubber network. In view of the copious interactions between neighboring chains in an amorphous polymer, this assertion may appear implausible. However, both theory and experiment provide abundant support. It is the objective of rubber elasticity theory therefore to compound the contributions of the individual chains additively, a task which is rendered difficult by the complexities of network structure and topology.

The connection between two traditional theoretical approaches to the treatment of rubber elasticity has been bridged by recent studies (see papers 46 and 49 of the publication list). One of these is the theory of "phantom" networks, developed originally by James and Guth, in which the integrity of the chains is ignored and the junctions (cross linkages) are allowed to seek their preferred positions without regard for the entanglements of chains that severely limit configurational rearrangements in real systems. The other follows the precepts of W. Kuhn elaborated by Wall,

Treloar, Flory and Rehner and others, according to which the cross linkages are firmly embedded in their surroundings and hence must undergo ("affine") displacements in proportion to the macroscopic strain. The two theoretical approaches yield a stress-strain relationship of the same form, which for simple elongation is

$$f = \xi (kT/L_i) (\langle r^2 \rangle_i / \langle r^2 \rangle_0) (\alpha - \alpha^{-2})$$

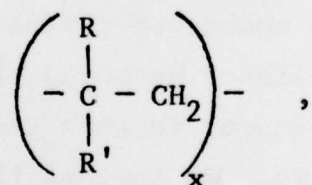
where f is the force, α is the extension ratio relative to the length L_i of the unstretched specimen at the prevailing volume, $\langle r^2 \rangle_i$ is the mean-square length of a network chain in this rest state of length L_i , and $\langle r^2 \rangle_0$ is the mean-square length for a free chain. For a phantom network ξ is the cycle rank, i.e., the number of scissions required to reduce the network to a "tree." According to the theory for a network whose junctions (cross linkages) are subject to displacements that are "affine" in the strain, ξ is the number of chains. For a tetrafunctional network (i.e., a cross-linked network) the number of chains is twice the cycle rank. Hence, in this case the respective theories differ by a factor of two. We suggest that the unswollen network at small deformations conforms approximately to the latter (affine) behavior, but that it approaches the phantom model at high elongations and/or high degrees of swelling. Hence, the numerical factor multiplying the equation above must be considered to decrease with strain and with dilution. This change may account for departures from the theoretical relationship.

Statistical Thermodynamics of Stiff Chains

The theory of order-disorder in systems of rigid extended polymer chains and of phase equilibria in such systems (Proc. Roy. Soc. London, A234, 73(1956)) has been adapted without difficulty to semiflexible chains consisting of rigid rod-like segments connected by flexible joints. The behavior predicted conforms closely to that of the system of disconnected rods of the length of the segments comprising the semi-flexible chain. Additionally, the equations have been elaborated to comprehend heterodisperse systems in which the lengths of the rods, or their axis ratios, are variable according to a specified distribution. Calculations on phase equilibria in such systems are difficult and are incomplete at this time.

Configurational Statistics of Vinyl Polymer Chains

Disubstituted vinyl polymers,



are of particular interest because of the rigidity imparted by the presence of two substituents, R and R'. These substituents introduce severe steric repulsions which occur in all conformations. We have calculated conformational energies for poly(methyl methacrylate) chains, in which $\text{R} = \text{COOCH}_3$ and $\text{R}' = \text{CH}_3$, and have deduced a relatively simple rotational isomeric state scheme for the analysis of its configurational statistics and configuration-dependent properties (see paper 24). The superficially simpler polyisobutylene chain in which $\text{R}' = \text{R} = \text{CH}_3$

presents difficulties of interpretation which thus far have resisted our efforts to bring theory into agreement with experiments. We propose to continue this investigation in order to establish a satisfactory basis for the interpretation of properties of this important polymer.

PAPERS PUBLISHED SINCE 1 JANUARY 1972

(Asterisks denote investigations supported by AFOSR)

1. * "Spatial Configurations of Polynucleotide Chains. I. Steric Interactions in Polyribonucleotides: A Virtual Bond Model," Wilma K. Olson and Paul J. Flory, Biopolymers, 11, 1-23 (1972).
2. * "Spatial Configuration of Polynucleotide Chains. II. Conformational Energies and the Average Dimensions of Polyribonucleotides," Wilma K. Olson and Paul J. Flory, Biopolymers, 11, 25-56 (1972).
3. * "Spatial Configurations of Polynucleotide Chains. III. Polydeoxyribonucleotides," Wilma K. Olson and Paul J. Flory, Biopolymers, 11, 57-66 (1972).
4. * "Theory of Optical Anisotropy of Chain Molecules," Paul J. Flory, J. Chem. Phys., 56, 862-866 (1972).
5. * "Depolarized Rayleigh Scattering and the Mean-Squared Optical Anisotropies of N-Alkanes in Solution," G. D. Patterson and P. J. Flory, J. Chem. Soc., Faraday Trans. II, 68, 1098-1110 (1972)
6. * "Optical Anisotropies of Polyoxyethylene Oligomers," G. D. Patterson and P. J. Flory, J. Chem. Soc., Faraday Trans. II, 68, 1111-1116 (1972).
7. * "Optical Anisotropy of Polypeptide Chains," R. T. Ingwall and P. J. Flory, Biopolymers, 11, 1527-1539 (1972).
8. * "Stress-Optical Behavior of Polymethylene and Poly(dimethylsiloxane)," M. H. Liberman, Y. Abe, and P. J. Flory, Macromolecules, 5, 550-558 (1972).
9. "Molecular Configuration and States of Aggregation of Biopolymers," P. J. Flory, Polymerization in Biological Systems, Ciba Foundation 7 (1972).
10. * "Equation-of-State Parameters for Poly(dimethylsiloxane)," Hsiang Shih and P. J. Flory, Macromolecules, 5, 758-761 (1972).

11. * "Thermodynamics of Solutions of Poly(dimethylsiloxane) in Benzene, Cyclohexane, and Chlorobenzene," P. J. Flory and Hsiang Shih, Macromolecules, 5, 761-766 (1972).
12. * "Stereochemical Equilibrium in 2,4,6-Trichloro-n-Heptane with Applications to Poly(Vinyl Chloride)," Paul J. Flory and Christopher J. Pickles, J. Chem. Soc., Faraday Transactions II, 69, 632-642 (1973).
13. * "The Temperature Coefficient of the Unperturbed Dimensions of Polyoxyethylene," J. E. Mark and P. J. Flory, Macromolecules, 6, 300-301 (1973).
14. * "Conformational Energies, Stereoregularity, and the Role of Non-staggered Conformations in Polymer Chains," Paul J. Flory, J. Polymer Sci.: Polymer Phys. Ed., 11, 621-634 (1973).
15. * "Moments of the End-to-End Vector of a Chain Molecule, Its Persistence and Distribution," Paul J. Flory, Proc. Nat. Acad. Sci., 70, 1819-1823 (1973).
16. * "Depolarized Light Scattering by Amides and Peptides," R. T. Ingwall and P. J. Flory, Biopolymers, 12, 1123-1135 (1973).
17. * "Kerr Constants of Amides and Peptides," R. T. Ingwall, E. A. Czurylo, and P. J. Flory, Biopolymers, 12, 1137-1148 (1973).
18. * "Molecular Configuration in Bulk Polymers," Paul J. Flory, International Symposium on Macromolecules, Helsinki, Finland, 2-7 July 1972, Pure & Appl. Chem., Macromolecular Chem., 8, 1-15 (1972). Also, Rubber Chem. and Tech., 48, No. 3, 513-525, July-Aug. 1975.
19. * "Optical Anisotropy of Polyisobutylene-Strain Birefringence," M. H. Liberman, L. C. DeBolt, and P. J. Flory, J. Polym. Sci., Polym. Phys. Ed., 12, 187-200 (1974).
20. * "The Elastic Properties of Elastin," C. A. J. Hoeve and P. J. Flory, Biopolymers, 13, 677-686 (1974).
21. * "The Interpretation of Viscosity-Temperature Coefficients for Poxoxyethylene Chains in a Thermodynamically Good Solvent," S. Bluestone, J. E. Mark, and P. J. Flory, Macromolecules, 7, 325-328 (1974).

22. * "Foundations of Rotational Isomeric State Theory and General Methods for Generating Configurational Averages," P. J. Flory, Macromolecules, 7, 381-392 (1974).
23. * "Configurational Statistics of Vinyl Polymer Chains," P. J. Flory, P. R. Sundararajan, and L. C. DeBolt, J. Amer. Chem. Soc., 96, 5015-5024 (1974).
24. * "Configurational Characteristics of Poly(methyl methacrylate)," P. R. Sundararajan and P. J. Flory, J. Amer. Chem. Soc., 96, 5025-5031 (1974).
25. * "Moments and distribution functions for polymer chains of finite length. I. Theory," P. J. Flory and D. Y. Yoon, J. Chem. Phys., 61, 5358-5365 (1974).
26. "Moments and distribution functions for polymer chains of finite length. II. Polymethylene," D. Y. Yoon and P. J. Flory, J. Chem. Phys., 61, 5366-5380 (1974).
27. * "The Elastic Free Energy and the Elastic Equation of State: Elongation and Swelling of Polydimethylsiloxane Networks," Paul J. Flory and Yoh-Ichi Tatara, J. Polymer Sci.: Polymer Phys. Ed., 13, 683-702 (1975).
28. "Spatial Configuration of Macromolecular Chains," Paul J. Flory, Science, 188, 1268-1276 (1975).
29. "Small angle neutron and X-ray scattering by poly(methyl methacrylate) chains," D. Y. Yoon and P. J. Flory, Polymer, 16, 645-648 (1975).
30. * "Conformational Energy and Configurational Statistics of Polypropylene," U. W. Suter and P. J. Flory, Macromolecules, 8, 765-775 (1975).
31. * "Conformational Characteristics of Polystyrene," D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, Macromolecules, 8, 776-783 (1975).
32. "Conformational Characteristics of Poly(methyl acrylate)," D. Y. Yoon, U. W. Suter, P. R. Sundararajan, and P. J. Flory, Macromolecules, 8, 784-789 (1975).

- 33.* "Theoretical Predictions on the Configurations of Polymer Chains in the Amorphous State," Paul J. Flory, J. Macromol. Sci., Phys. Ed., B12(1), 1-11 (1976).
34. "Moments and Distribution Functions for Poly(Dimethylsiloxane) Chains of Finite Length," Paul J. Flory and Vincent W. C. Chang, Macromolecules, 9, 33-40 (1976).
35. "Moments and Distribution Functions for Polypeptide Chains, Poly-L-Alanine," Joan C. Conrad and Paul J. Flory, Macromolecules, 9, 41-47 (1976).
36. "Small Angle X-ray and Neutron Scattering by Polymethylene, Polyoxyethylene and Polystyrene Chains," D. Y. Yoon and P. J. Flory, Macromolecules, 9, 294-299 (1976).
37. "Small Angle Neutron and X-ray Scattering by Poly(methyl methacrylate) Chains. II.," D. Y. Yoon and P. J. Flory, Macromolecules, 9, 299-303 (1976).
38. "Dipole Moments of Vinyl Polymers with Flexible Side Chains," Akihiro Abe, J. Polymer Sci.: Symp. 54, 135-144 (1976).
39. "Conformational Energies, and the Random-Coil Dimensions and Dipole Moments of the Polyoxides $\text{CH}_3\text{O}[(\text{CH}_2)_y\text{O}]_x\text{CH}_3$," Akihiro Abe and James E. Mark, J. Amer. Chem. Soc., 98, 6468 (1976).
40. "Conformational Analysis of 2-Methoxytetrahydropyran in Relation to the Anomeric Effect," Akihiro Abe, J. Amer. Chem. Soc., 98, 6477 (1976).
41. "Macrocyclization Equilibria. 1. Theory," P. J. Flory, U. W. Suter, and M. Mutter, J. Amer. Chem. Soc., 98, 5733-5739 (1976).
42. "Macrocyclization Equilibria. 2. Poly(dimethylsiloxane)," U. W. Suter, M. Mutter and P. J. Flory, J. Amer. Chem. Soc., 98, 5740-5745 (1976).
43. "Macrocyclization Equilibria. 3. Poly(6-aminocaproamide)," M. Mutter, U. W. Suter, and P. J. Flory, J. Amer. Chem. Soc., 98, 5745-5748 (1976).

44. "Persistence Vectors and Higher Moment Tensors of Polyoxyalkanes," Akihiro Abe, J. W. Kennedy, and P. J. Flory, J. Polym. Sci.: Polym. Phys. Ed., 14, 1337-1349 (1976).
45. "Persistence Vectors for Polypropylene, Polystyrene, and Poly(methyl methacrylate) Chains," D. Y. Yoon and P. J. Flory, J. Polym. Sci.: Polym. Phys. Ed., 14, 1425-1431 (1976).
- 46.* "Statistical Thermodynamics of Random Networks," P. J. Flory, Proc. R. Soc. Lond. A., 351, 351-380 (1976).

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47. "Small Angle Neutron Scattering by Semicrystalline Polyethylene," D. Y. Yoon and P. J. Flory, Polymer.
48. "The Molecular Theory of Rubber Elasticity," Paul J. Flory, J. Amer. Chem. Soc.
- 49.* "Theory of Elasticity of Polymer Networks. The Effect of Local Constraints on Junctions," P. J. Flory, J. Chem. Phys.
- 50.* "Separation of Collision-Induced from Intrinsic Molecular Depolarized Rayleigh Scattering: the Optical Anisotropy of the C-Cl Bond," C. W. Carlson and P. J. Flory, J. Chem. Soc., Faraday Trans.
- 51.* "Optical Anisotropy of Polystyrene and Its Low Molecular Analogs," U. W. Suter and P. J. Flory, J. Chem. Soc., Faraday Trans.
52. "Optical Anisotropies of Para Halogenated Polystyrenes and Related Molecules," E. Saiz, U. W. Suter and P. J. Flory, J. Chem. Soc., Faraday Trans.
- 53.* "Analysis of Nuclear Magnetic Resonance Spectra of Protons in Predominantly Isotactic Polystyrene," D. Y. Yoon and P. J. Flory, Macromolecules.
- 54.* "Dipole Moments of Poly(p-Chlorostyrene) Chains," E. Saiz, J. E. Mark, and P. J. Flory, Macromolecules.
- 55.* "Statistical Thermodynamics of Macromolecular Liquids and Solutions," P. J. Flory, Berichte Der Bunsen-Gesellschaft Für Physikalische Chemie.

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Treloar, Flory and Rehner and others, according to which the cross linkages are firmly embedded in their surroundings and hence must undergo ("affine") displacements in proportion to the macroscopic strain. This research suggests that the unswollen network at small deformations conforms approximately to the affine behavior, but that it approaches the phantom model at high elongations and/or high degrees of swelling. Decreases with strain and dilution may account for departures from the theoretical relationship. The theory of order-disorder in systems of rigid extended polymer chains and of phase equilibria in such systems (Proc. Roy. Soc. London, A234, 73 (1956) has been adapted without difficulty to semiflexible chains consisting of rigid rod-like segments connected by flexible joints.

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