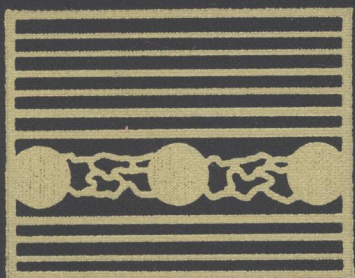# Elastomers and Rubber Elasticity

Elastomers and Rubber Elasticity

James E. Mark, EDITOR
The University of Cincinnati

Joginder Lal, EDITOR
The Goodyear Tire & Rubber Company

Elastomers and Rubber Elasticity

ACS Symposium Series

M. Joan Comstock, *Series Editor*

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

THE LAST FEW YEARS HAVE BROUGHT remarkable progress in research on elastomers and rubberlike elasticity. For example, regarding the synthesis and structural characterization of new elastomers, there are multi-phase block copolymers, the organophosphazenes, and polymers of carefully controlled microstructure and capacity for strain-induced crystallization. In the area of new cross-linking techniques, there are very specific chemical reactions used to form model or ideal networks of known structure; for example, end-linking of chains having reactive groups placed at both ends. Important advances in the molecular theories of rubberlike elasticity, with particular regard to the forms of the elastic equation of state, the importance of junction fluctuations, and the nature or degree of non-affineness of the elastic deformation have been reported. Also, improvements in experimental techniques, including the use of model networks to test newly developed theoretical concepts, and neutron scattering measurements to characterize the structure of elastomeric networks and the nature of the deformation process have developed.

A wide variety of such topics are covered in this book. Most of the chapters are from papers presented at a symposium held in August 1981. This symposium was preceded by a half-day tutorial session, with corresponding introductory review articles on synthesis of elastomers by G. Odian and rubber elasticity by J. E. Mark (published in the November 1981 issue of the *Journal of Chemical Education*). To aid the reader, a brief review of thermoplastic elastomers is included in this book.

Hoechst Corporation, Ashland Chemical Company, Cabot Corporation, Dow Chemical U.S.A., Dunlop Research Centre, E. I. du Pont de Nemours & Company, The Firestone Tire & Rubber Company, The General Tire & Rubber Company, The BF Goodrich Company, The Goodyear Tire & Rubber Company, Monsanto Company, Polysar Limited, Shell Development Company, 3M Chemicals Division, and Uniroyal Chemical Division.

JAMES E. MARK
The University of Cincinnati
Cincinnati, OH 45221

JOGINDER LAL
The Goodyear Tire & Rubber Company
Akron, OH 44316

FOREWORD

BY PAUL J. FLORY

Rubber elasticity is a property that is unique to polymers consisting of long, flexible chains. No substance otherwise constituted will sustain, without rupture, the high deformation that is typical of rubberlike materials, while simultaneously retaining the capacity to recover its original dimensions. Moreover, rubber elasticity is a nearly universal property of long chain polymers under suitable conditions, i.e., in the amorphous state above the glass transition. It is not peculiar to a restricted class of such materials; nearly all conventional polymers are rubberlike when neither crystalline nor glassy, provided however that the long chains are so interconnected as to yield a network whose permanency extends beyond the "use life" of the material in a practical application or the duration of an experiment in the laboratory. In addition to common organic polymers, rubber elasticity is manifested also in certain inorganic polymers, notably elastic sulfur and the polyphosphazenes (Singler and Hagnauer). Biopolymers such as the prominent structure proteins, elastin, denatured collagen, and myosin, display rubber elasticity, a characteristic that is requisite to their functions in living organisms.

Covalent cross-linkages usually serve to bind the long chains into a network. The necessary interconnections may, however, be provided by other means, e.g., by small crystalline regions (Morton) or by chelate linkages (Eichinger).

It was recognized a half century ago by K. H. Meyer, by E. Guth and H. Mark, and by W. Kuhn that rubber elasticity originates in the capacity for randomly coiled long-chain molecules to adopt diverse configurations, and that recovery from deformation is a manifestation of the tendency of such chains to assume the most probable distribution of configurations. Early theories of rubber elasticity were developed on the basis of these well-conceived insights. Subsequent experimental investigations, especially the analysis of stress-temperature coefficients and observations on effects of swelling, confirmed that the retractive force originates primarily within the chains of the network, and not to an appreciable degree from forces of attraction between chains and their neighbors in the space they share. The elastic free energy of an elastomeric network is therefore appropriately treated as the sum of contributions of its individual chains, the resultant being sensibly independent of their mutual interactions.

The chains of typical networks are of sufficient length and flexibility to justify representation of the distribution of their end-to-end lengths by the most tractable of all distribution functions, the Gaussian. This facet of the problem being so summarily dealt with, the burden of rubber elasticity theory centers on the connections between the end-to-end lengths of the chains comprising the network and the macroscopic strain.

Early theories of Guth, Kuhn, Wall and others proceeded on the assumption that the "microscopic" distribution of end-to-end vectors of the chains should reflect the macroscopic dimensions of the specimen, i.e., that the chain vectors should be affine in the strain. The pivotal theory of James and Guth (1947), put forward subsequently, addressed a network of Gaussian chains free of all interactions with one another, the integrity of the chains which precludes one from the space occupied by another being deliberately left out of account. Hypothetical networks of this kind came to be known later as phantom networks (Flory, 1964, 1976). James and Guth showed rigorously that the *mean* chain vectors in a Gaussian phantom network are affine in the strain. They showed also that the fluctuations about the mean vectors in such a network would be independent of the strain. Hence, the instantaneous distribution of chain vectors, being the convolution of the distribution of mean vectors and their fluctuations, is not affine in the strain. Nearly twenty years elapsed before his fact and its significance came to be recognized (Flory, 1976, 1977).

In deformed real networks attainment of the molecular state predicted by phantom network theory is generally precluded by non-specific, diffuse entanglements of the chains, which restrict fluctuations of the junctions of the network about their mean positions. The stress consequently is enhanced to a degree that depends on the strain. With proper account of this restriction, the relationship of stress to strain in typical rubbers is well reproduced by recent theory (Flory, 1977) over the full range of uniaxial and biaxial deformations accessible to experiment (Erman and Flory, 1980, 1982). At large strains, including dilation, the effects of restrictions on fluctuations vanish and the relationship of stress to strain converges to that for a phantom network. The primary connectivity of the network may thus be ascertained. Experimental results (J. E. Mark 1977–1981; Rehage and Oppermann; Erman and Flory) show the measured stress in this limit to be in close agreement with that calculated from chemical degrees of cross-linking. Topological entanglements (alias "trapped entanglements") that allegedly intertwine chains with one another, and hence should act like cross-linkages, do not contribute appreciably to the stress.

This deduction from analysis of experiments according to recent theory contradicts entrenched views on the role of chain entanglements.

Two conditions must be met if this conclusion is to be revealed by the analysis. First, appropriate experimental procedures must be adopted to assure establishment of elastic equilibrium. Second, the contribution to the stress from restrictions on fluctuations in real networks must be properly taken into account, with due regard for the variation of this contribution with deformation and with degree of cross-linking. Otherwise, the analysis of experimental data may yield results that are quite misleading.

PAUL J. FLORY
Stanford University
Stanford, CA 94305

# CONTENTS

Basic Concepts in Elastomer Synthesis

GEORGE ODIAN

College of Staten Island, City University of New York, Staten Island, NY 10301

The synthesis of elastomers by step, chain, and ring-opening polymerizations is reviewed. These reactions are characterized as to the process variables which must be controlled to achieve the synthesis and crosslinking of an elastomer of the required structure. Both radical and ionic chain polymerizations are discussed as well as the structural variations possible through copolymerization and stereoregularity.

Requirements of an Elastomer

An elastomer or rubber is a material which undergoes very large (up to 400% or more), reversible deformations at relatively low stresses. These characteristics are met by flexible, cross-linked polymer molecules ($\underline{1}$). Only polymer molecules have the ability to undergo very large deformations. A long-chain molecule can respond to stress, without distortions of bond angles or bond lengths, by conversion from a random coil to a more extended chain through rotations of the bonds in the polymer chain. The polymer must be essentially completely amorphous (non-crystalline) with a low glass transition temperature and low secondary forces so as to obtain high flexibility of the polymer chains. Precluded from use as elastomers are polymers such as nylon-6 (I), polyethylene (II), and polystyrene (III). Highly polar polymers (e.g., nylon-6) or those with highly regular

$$\{(CH_2)_5CONH\}_n \qquad \{CH_2CH_2\}_n \qquad \{CH_2CH\phi\}_n$$
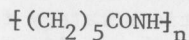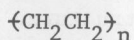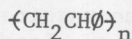
$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$

structures (e.g., polyethylene) are quite crystalline and, thus,

do not have the necessary chain flexibility. Polymers with large
bulky substituents (e.g., polystyrene), although non-crystalline,
are also too rigid to be elastomers. (These polymers do, however,
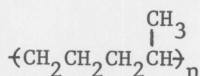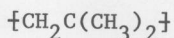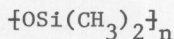find large-scale use -- polyethylene and polystyrene as plastics
and nylon-6 as both a plastic and fiber.) Polymers which find
uses as elastomers are those which have irregular or unsymmetrical
structures [e.g., ethylene-propylene copolymer (IV)], or non-
polar structures, [e.g., polyisobutylene (V)] or flexible units
in the polymer chain [e.g., polysiloxane (VI), polysulfide (VII),
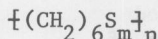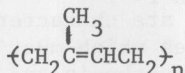1,4-polyisoprene (VIII)].

$$\left(CH_2CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH}\right)_n \qquad \left(CH_2C(CH_3)_2\right) \qquad \left(OSi(CH_3)_2\right)_n$$

$$\text{IV} \qquad\qquad\qquad\qquad \text{V} \qquad\qquad\qquad\qquad \text{VI}$$

$$\left((CH_2)_6S_m\right)_n \qquad\qquad \left(CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_2\right)_n$$
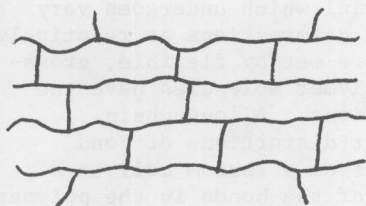
$$\text{VII} \qquad\qquad\qquad\qquad \text{VIII}$$

The reversible recovery of a deformed elastomer to its
original (undeformed) state is due to an entropic driving force.
The entropy of polymer chains is minimum in the extended con-
formation and maximum in the random coil conformation. Cross-
linking of an elastomer to form a network structure (IX) is

IX

necessary for the recovery from deformation to be rapid and
complete. The presence of a network structure prevents polymer
chains from irreversibly slipping past one another upon deforma-
tion. Either chemical or physical crosslinking can be used to
obtain the required network structure. The synthetic strategy for
producing an elastomer differs depending on whether chemical or
physical crosslinking is involved. The synthesis of a chemically-
crosslinked elastomer requires the polymerization of an
appropriate low molecular weight reactant or mixture of reactants
(referred to as monomers) such that the polymer molecules

produced contain functional groups capable of subsequent reaction to form crosslinks between polymer chains. An example is 1,4-polyisoprene which is found in nature and also produced by polymerization of isoprene. 1,4-Polyisoprene is crosslinked by heating with sulfur. Sulfur crosslinks are formed between polymer chains through reaction of the double bonds present in 1,4-polyisoprene. Thus, the overall process involves two separate synthetic reactions. First, a polymer is synthesized from a monomer or mixture of monomers. Second, the polymer is fabricated (e.g., by compression molding) into the desired shape (e.g., an automobile tire) and chemically-crosslinked while in that shape. The crosslinking and polymer synthesis reactions are carried out separately.

Certain block copolymers comprise a category of elastomer in which crosslinking occurs by a physical process. The two main types of block copolymers which have been commercialized are the ABA and $\{AB\}_n$ block copolymers (X and XI) where A and B represent
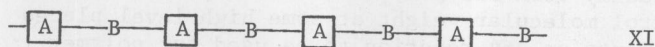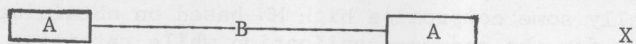
alternating blocks of two different chemical structures, e.g., polystyrene and 1,4-polyisoprene blocks. The ABA and $\{AB\}_n$ block copolymers, referred to as triblock and multiblock copolymers, respectively, are synthesized such that the A blocks are hard (e.g., polystyrene) and short while the B blocks are flexible (e.g., 1,4-polyisoprene) and long. These block copolymers, referred to as thermoplastic elastomers (TPE), behave as elastomers at ambient temperatures but are thermoplastic at elevated temperatures where they can be processed by molding, extrusion, or other fabrication techniques. The behavior of thermoplastic elastomers is a consequence of their micro-heterogenous, two-phase structure. The hard A blocks from different polymer chains aggregate to form rigid domains at ambient temperatures. The rigidity of the A blocks is a consequence of either their T_m or T_g being above ambient temperatures. The rigid domains constitute a minor, non-continuous phase dispersed (on a microscopic scale) within the major, continuous phase composed of the rubbery B blocks from different polymer chains. The rigid domains act as physical crosslinks to hold the soft, rubbery B blocks in a network structure. However, the physical crosslinking is reversible since heating above the crystalline melting or glass transition temperature of the A blocks softens the rigid domains and the polymer flows. Cooling reestablishes the rigid domains and the material again behaves as a crosslinked elastomer. Thermoplastic elastomers have the advantage over conventional elastomers that no additional chemical