JAMES E. MARK BURAK ERMAN

ELASTOMERIC POLYMER NETWORKS

PRENTICE HALL POLYMER SCIENCE AND ENGINEERING SERIES

ELASTOMERIC POLYMER NETWORKS

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Prentice Hall
Englewood Cliffs, New Jersey 07632

Library of Congress Cataloging-in-Publication Data
Elastomeric polymer networks / edited by James E. Mark and Burak Erman.
p. cm.
Includes bibliographical references and index.
ISBN 0-13-249483-3
1. Polymer networks. 2. Elastomers. I. Mark, James E., II. Erman, Burak.
QD382.P67E53 1992
678'.2—dc20 91-20412
CIP

Acquisitions editor: Michael Hays
Editorial/production supervision and
interior design: Fred Dahl, Inkwell
Cover design: Lundren Graphics
Prepress buyer: Kelly Behr
Manufacturing buyer: Susan Brunke

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

ISBN 0-13-249483-3

Prentice-Hall International (UK) Limited, *London*
Prentice-Hall of Australia Pty. Limited, *Sydney*
Prentice-Hall Canada Inc., *Toronto*
Prentice-Hall Hispanoamericana, S.A., *Mexico*
Prentice-Hall of India Private Limited, *New Delhi*
Prentice-Hall of Japan, Inc., *Tokyo*
Simon & Schuster Asia Pte. Ltd., *Singapore*
Editora Prentice-Hall do Brasil, Ltda., *Rio de Janeiro*

Eugene Guth

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Series Foreword

POLYMER SCIENCE AND ENGINEERING SERIES

One of the most exciting areas in chemistry, chemical engineering, and materials science is the preparation, characterization, and utilization of polymers. The growing importance of polymers has been truly astounding, to the point that it is difficult to imagine our lives without them. They are under development in virtually every industrialized country in the world with activities accelerating rather than abating.

Not surprisingly, the amount of information relevant to polymer science and engineering is increasing correspondingly, making it more and more difficult to enter new fields in this area or even to remain abreast of developments in one's current field. There is thus a real need for authoritatively written, easily accessible books on polymer science and engineering, both for the relatively uninitiated and for the better-informed professional.

The present series of books was inaugurated to help meet this need. It will cover the organic chemistry of polymers, the relevant physical chemistry and chemical physics, polymer processing and other engineering aspects, and the applications of polymers as materials. The level will range from highly introductory treatments that are tutorial and therefore particularly useful for self-study, to rather advanced treatments of more specialized subjects. Many off these books will be exceedingly useful as textbooks in formal courses at colleges and universities.

Considerable attention will be paid to polymers as "high-tech" materials. This is in response to the fact that the most exciting applications of polymers no longer involve huge tonnage amounts of materials. Rather, they involve situations in which polymers generally are not present in large amounts, but are absolutely critical for the functioning of the system. Examples are polymer matrices and encapsulants for the controlled release of drugs and agricultural chemicals, biopolymers and synthetic polymers for biomedical applications, conducting polymers for batteries and other electrical devices, polymers having non-linear optical properties for optoelectronic applications, high-temperature polymers for use in outer space and in other hostile environments, ultra-oriented polymers for high-strength materials, new types of polymer-based composites, photosensitive polymers for microlithography, and inorganic and organometallic polymers for use as ceramic precursors. These are all rapidly developing fields, and there is a particularly great need for authoritative, comprehensive treatments of these subject areas.

It is hoped that this series of volumes will meet these needs, and be of lasting value to the polymer community.

J. E. Mark
University of Cincinnati
Series Editor

Preface

In February of 1990, Dr. Michael A. S. Guth and the two editors conspired to produce a book celebrating the 85th birthday of Eugene Guth. The joyous nature of the project, however, turned to sadness when Eugene passed away on July 5, just short of his birthday on August 21. The present book is instead, therefore, a memorial to him by some of his many friends, colleagues, and admirers.

Eugene Guth was a remarkably versatile scientist, with interests in nuclear physics and condensed matter physics as well as in polymer science. It is unquestionably in this last area, however, that he was most prolific, particularly in the elasticity of rubberlike materials. His phantom theory of networks, developed with Hubert M. James in the 1940s and 50s, is universally admired and is a milestone in all of polymer science. It is still the starting point of many of the molecular theories being constructed today, nearly a half-century later!

Some of the details of Eugene's career are given in several of the papers in this book and elsewhere.[1] Of greater importance here, however, are

[1] H. Schweinler, A. Weinberg, J. E. Mark, and B. Erman, *Physics Today*, June 1991: 44, 10, p. 154.

the less tangible aspects of his life, in particular how he and his work provided inspiration to several generations of polymer scientists. As is demonstrated in this collection of papers dedicated to his memory, he will long continue to be a model for those of us who knew him, and for many other polymer scientists as well.

James E. Mark
Burak Erman

Recollections of My Earliest Collaborations with Eugene Guth

In the early 1920s, Dr. I. R. Katz of the Netherlands worked in Berlin/Dahlem with the group of Michael Polanyi and, specifically, with me. We published two papers on the X-ray behavior of cellulose and cellulose derivatives. A while later Dr. Katz left our institute and continued his work at the University of Copenhagen, where he made an important discovery, namely, that rubber upon stretching develops a certain degree of crystallinity that disappears again upon relaxation.

We, in Berlin/Dahlem and later at the research laboratory of I. G. Farben, investigated this "Katz Effect" more closely. A number of my associates and I published some 10 articles on this phenomenon; they are all essentially descriptive and qualitative.

Then, in 1932, I moved as a Professor to the University of Vienna. I felt that now we ought to try to obtain a more quantitative and theoretically founded explanation for the "Katz Effect" since as a university professor I was supposed to look after the fundamental side of our materials and their behavior.

However, my own mathematical training was not at all sufficient to tackle such a problem and I therefore contacted a good friend, Professor

Hans Thirring, the head of the Department of Theoretical Physics, for help. He recommended to me one of his associates, Dr. Eugene Guth, who had graduated in 1928 as a Ph.D. in theoretical physics. Although his interests were essentially focused on the theory of relativity, he was a very thoroughly trained scientist with a great deal of general mathematical knowledge.

Dr. Guth joined my group of coworkers and immediately started to educate us in the problems of molecular statistics and thermodynamics. He was an extremely able teacher and, for us, a guardian angel and a father confessor at the same time.

Eugene was always in good spirits and he never lost his patience, even if I, or some member of our group, did not immediately understand what he was explaining to us. His patience was endless. After having discussed for a year or two the general problem of the Katz Effect and certain similar phenomena, Guth and I started to publish an article on it which appeared in 1934. I was the instigator of this paper, but everything else was done by Eugene Guth. He remained at our institute until about 1937, when I had a chance to help him to get out of Nazi-threatened Austria and go to the United States. There he began his career as an assistant professor at Notre Dame University until he moved to the U.S. government laboratory at Oak Ridge, Tennessee, in 1945.

Some of Eugene Guth's many contributions to the area of rubberlike elasticity are described in this excellent book edited by Professors James E. Mark and Burak Erman.

Already, as a postgraduate student, Guth had developed an understanding of complex problems and had a marvelous capacity to explain them, and to make them more comprehensible.

We shall all miss him—sadly and with great regret.

H. Mark

H. Mark

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CHAPTER

1

Recollections of Eugene Guth*

Walter H. Stockmayer
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My first glimpse of Eugene Guth came at a Saturday morning conference at Brooklyn Poly some time in the fall of 1942, or perhaps early in '43. This was one of a series of such meetings organized by Herman Mark and his colleagues to stimulate the interest of the local scientific community in high polymers. This particular meeting was devoted to the subject of rubberlike elasticity, and several of us had come down from Columbia University on the subway to learn about a field relatively new to us. Somehow Lars Onsager was there, and in my recollection the total attendance may have been as great as 150.

As I recall it, the first talk of the day dealt with experimental results; the second, by a speaker whom I shall not name here, dealt with the large departures, at higher elongations, from the classical proportionality of the retractive force to $(L - L^{-2})$, where L is the length of the sample relative to its unstretched state. The speaker sought to attribute these departures to some kinds of intra- and interchain energetic effects, but these were (at least to me) not very clearly identified. When the call for discussion came, Onsager was recognized, and I paraphrase his remarks: "It seems to me," he said, "that the large upturn in the stress-strain curve at high elongations must be due to the finite contour length of the network chains. In that case, if we consider the chains to consist of freely-jointed links, there should be a

* The writer's memory is not to be regarded as infallible.

complete analogy between the orientation of such links by the tensile force and the orientation of electric or magnetic dipoles by external electric or magnetic fields. Consequently, I suggest that the elongation should be proportional to the Langevin function of the (properly normalized) tensile force."

A moment later there arose the man later identified to me as Eugene Guth. He said. "Professor Onsager is exactly right! Professor James and I have in fact recently treated this model, and the result is precisely the one he just predicted." That really caught my attention: a living demonstration of Onsager's stature, and a direct connection of rubber elasticity to the dipole problem that I already knew well. Moreover, I soon learned that "Professor James" was none other than the Hubert M. James who, with Albert Sprague Coolidge at Harvard in 1933, had performed heroic desk-top variational calculations proving that quantum mechanics could give the correct binding energy of the H_2 molecule to within experimental error. If people of this stature could work on polymers, I thought, polymers might be worth more than passing attention.

It was pointed out to me after the morning session, probably by Charlie Beckmann, that Eugene Guth was the man who with Herman Mark had written the very first paper on the statistical theory of rubber elasticity, treating the behavior of a single chain in tension and emphasizing that the restoring force, being proportional to absolute temperature, was entropic in origin.

Guth and Mark did this truly pioneering work in Vienna, not long after Mark had assumed a chair of physical chemistry there following his years at I. G. Farben/BASF in Ludwigshafen. During the same period, Guth, Gold, and Simha published brief reports disclosing the numerical value of the quadratic term in the equation for the viscosity of a suspension of spheres:

$$\frac{\eta}{\eta_o} = 1 + \frac{5}{2}\phi + 14.1\phi^2 + \cdots \tag{1}$$

where ϕ is the volume fraction of spheres and η, η_o are the viscosities of suspension and pure solvent, respectively. Full details of the derivation of this extension of Einstein's result seem not to have been published in a standard journal, possibly because of the political disruptions and personal dangers attending the imminent invasion by Hitler's troops. In later happier years in the United States, the story was current that the authors had done the calculations on a tablecloth during a long evening in a Vienna cafe and had forgotten to take them home. They allegedly returned on a soberer morrow only to learn that the laundry had already obliterated everything. (As a matter of fact, the details were given in Gold's 1937 doctoral thesis in Vienna.)