

MACROMOLECULES
*An Introduction
to Polymer Science*

Edited by

F. A. BOVEY

and

F. H. WINSLOW

MACROMOLECULES

An Introduction to Polymer Science

Edited by

F. A. BOVEY

and

F. H. WINSLOW

BELL LABORATORIES

MURRAY HILL, NEW JERSEY

ACADEMIC PRESS New York San Francisco London 1979

A Subsidiary of Harcourt Brace Jovanovich, Publishers

**COPYRIGHT © 1979 BELL TELEPHONE LABORATORIES, INCORPORATED
ALL RIGHTS RESERVED.**

**NO PART OF THIS PUBLICATION MAY BE REPRODUCED OR
TRANSMITTED IN ANY FORM OR BY ANY MEANS, ELECTRONIC
OR MECHANICAL, INCLUDING PHOTOCOPY, RECORDING, OR ANY
INFORMATION STORAGE AND RETRIEVAL SYSTEM, WITHOUT
PERMISSION IN WRITING FROM THE PUBLISHER.**

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Main entry under title:

Macromolecules.

Includes bibliographies.

1. Macromolecules. I. Bovey, Frank Alden, Date
 - II. Winslow, Field Howard, Date
- QD381.M352 547'.7 78-20041
ISBN 0-12-119755-7

PRINTED IN THE UNITED STATES OF AMERICA

79 80 81 82 9 8 7 6 5 4 3 2 1

0 631
B 783

MACROMOLECULES

An Introduction to Polymer Science

M. J. Bowden
T. W. Kwei
L. D. Iann
S. Malsin
F. H. Winslow

180 0
897 H

CONTRIBUTORS

F. A. Bovey
M. J. Bowden
T. W. Kwei
L. D. Loan
S. Matsuoka
F. H. Winslow

LIST OF CONTRIBUTORS

Numbers in parentheses indicate the pages on which authors' contributions begin.

F. A. BOVEY (1, 207, 317, 445), Bell Laboratories, Murray Hill, New Jersey 07974

M. J. BOWDEN (23), Bell Laboratories, Murray Hill, New Jersey 07974

T. K. KWEI (207, 273, 339), Bell Laboratories, Murray Hill, New Jersey 07974

L. D. LOAN (409), Bell Laboratories, Murray Hill, New Jersey 07974

S. MATSUOKA (339), Bell Laboratories, Murray Hill, New Jersey 07974

F. H. WINSLOW (1, 409), Bell Laboratories, Murray Hill, New Jersey 07974

FOREWORD

Polymer science and technology have been among the most important areas of discovery during the twentieth century. Much of the vitality of macromolecular research and development has come from the diversity of interests, skills, and viewpoints with which they have been pursued in science and engineering.

Chemists, physicists, engineers, designers, market developers, and production workers have all made important contributions to the creation, provision, and use of the range of plastics, rubbers, adhesives, fibers, and finishes that play so large a part in modern civilization.

We now know that the polymer molecule is the common factor in all of this. But bringing diverse themes together and combining the interests in polymers has been a historic role of teachers and researchers in universities and other basic science laboratories. Thus, the dominant part played by macromolecules in all living things—plants, animals, and single cells—has extended the community of interests into a realm reaching from agriculture through biomedicine to zoology.

Books about polymers go beyond the usual expectations for scientific and technical monographs. In an age characterized by a flood of information, writers are therefore challenged to communicate with a vast potential readership with diverse viewpoints and experience and to find a common language with which to express their ideas. The present work draws upon the editors' and authors' special knowledge of the uses of polymeric matter and upon their participation in an institution where much of the century's materials science and engineering began, and where modern principles of solids and their mechanical, electromagnetic, and thermodynamic properties were established. The editors have, themselves, been associated with a major coordinated application of polymers in communication and information processing. These projects range from the replacement of lead as a sheath in electrical cable to meeting the most exacting requirements for dielectrics for transoceanic communication; from the design of films for circuit stabilization to the preparation of adjuncts to light guides and optical circuitry. In one way or another these polymers—plastics, rubbers, and adhesives—are crucial to our enter-

prise, which over the past three decades has provided five to ten percent of the yearly national investment in capital facilities.

Thus, these editors and their collaborators can write for a principal component of the macromolecular constituency—the users and adapters and those who must live with the results of polymer synthesis and fabrication. Such a position stimulates discovery and development of polymers in ways that complement the more conventional view of the producer. For instance, this will involve especially the effects of processing on properties. Our particular applications include extensive high-speed fabrication of polymers in virtually all forms except fibers. Accordingly, from the community in which these authors have worked have come original findings of significance concerning the effect of thermal history on the mechanical, electrical, and chemical properties of thermoplastics. Similarly, strong interest in polymer stability under a variety of atmospheric and other exposures has been stimulated by the work of these authors and their associates.

The user aspect of polymer science and engineering, typical of the communications and information processing industries, has led to the establishment of significant principles. Among those noted in this volume are: establishment of the qualities of three-dimensional nets of molecular dimensions, which stimulated the modern light scattering concepts of Debye and which are now used to modify natural and synthetic rubbers; early determinations of entropy consequences in the melting of polar polymers, such as polyesters and polyamides; and novel electrical and mechanical properties of densely netted hydrocarbons showing a continuous transition between highly insulating and highly semiconducting states. These are a few examples of how user interests in special functions can interact with basic understanding.

Thus, although the range of books on polymers is now very extensive, the present volume provides a different and useful vision of both the known and the expected.

W. O. BAKER

PREFACE

This book arose from the need for a text to accompany an introductory course in polymer science at Bell Laboratories. The authors are all staff members in this organization. The book provides a fairly complete treatment of all phases of macromolecular chemistry and physics at the undergraduate or first year graduate level. It is primarily fundamental rather than technological in orientation.

Because there are now a number of textbooks in this field, one may well ask what special virtues can be claimed for this one. We feel that it covers several areas more completely and perhaps also more authoritatively than most other general introductory treatments. Polymerization kinetics is treated in Chapter 2 with unusual completeness. Chapter 3 includes a discussion of the rotational isomeric state method of calculation of polymer chain dimensions, which will provide the reader with at least a survey of this important discipline, not normally described in introductory texts. An entire chapter (Chapter 7) is devoted to chemical reactions and degradation of macromolecules, usually treated very cursorily if at all. Finally, biological molecules are discussed with exceptional thoroughness in Chapter 8.

It appears customary to introduce a general book on macromolecular science by pointing out the great importance of this field and by, at the same time, deploring the inadequate training which most chemists receive in it. We heartily agree with both these sentiments and can only hope that this volume may contribute toward finding a remedy for any educational shortcomings.

We thank Dr. A. E. Tonelli for material assistance with Chapter 3, Dr. H. D. Keith and Mr. F. J. Padden for helpful discussions and many of the illustrations in Chapter 5, and Dr. W. H. Starnes, Jr. for several helpful comments on Chapter 7. We are also grateful to many authors for permission to use numerous illustrations and figures appearing throughout the text.

MACROMOLECULES

An Introduction to Polymer Science

CONTENTS

List of Contributors	ix
Foreword	xi
Preface	xiii

CHAPTER 1. The Nature of Macromolecules

F. A. BOVEY AND F. H. WINSLOW

1.1. Introduction	1
1.2. Formation of Macromolecules	2
1.3. Structure of Macromolecules	4
1.4. Morphology and Mechanical Properties	6
1.5. Biological Macromolecules and Biopolymers	13
1.6. Historical Perspective	14
References	21

CHAPTER 2. Formation of Macromolecules

M. J. BOWDEN

2.1. Introduction	23
2.2. Vinyl and Diene Polymerization	24
2.3. Ring Opening Polymerization	156
2.4. Step-Reaction Polymerization	174
References	202

CHAPTER 3. Microstructure and Chain Conformation of Macromolecules

F. A. BOVEY AND T. K. KWEI

3.1. Introduction	208
3.2. Vibrational Spectroscopy	208
3.3. Nuclear Magnetic Resonance Spectroscopy	217

3.4.	Stereochemical Configuration	222
3.5.	Geometrical Isomerism	229
3.6.	Copolymer Sequences	231
3.7.	Ring-Opening Polymers	235
3.8.	Branches and Defect Structures	237
3.9.	Chain Conformation	241
	References	268
	General References	270

CHAPTER 4. Macromolecules in Solution

T. K. KWEI

4.1.	Introduction	273
4.2.	Thermodynamics of Macromolecules in Solution	274
4.3.	Phase Equilibrium	287
4.4.	Measurement of Molecular Weight and Size	296
4.5.	Polyelectrolytes	312
	References	314
	General References	316

CHAPTER 5. Macromolecules in the Solid State: Morphology

F. A. BOVEY

5.1.	Introduction	317
5.2.	Polymer Crystallinity	318
5.3.	Crystallization from Solution	320
5.4.	Crystallization from the Melt	328
	References	336
	General References	337

CHAPTER 6. Physical Behavior of Macromolecules

S. MATSUOKA AND T. K. KWEI

6.1.	Introduction	339
6.2.	Viscoelastic Properties of Macromolecules in the Rubbery State	342
6.3.	Glassy and Crystalline Polymers	363
6.4.	Transport	398
	References	406

CHAPTER 7. Reactions of Macromolecules

L. D. LOAN AND F. H. WINSLOW

7.1.	Introduction	405
7.2.	Mechanochemical Reactions	41

7.3. Cross-Linking Reactions	413
7.4. Oxidative Degradation	419
7.5. Hydrolytic Degradation and Biodegradation	431
7.6. Thermal Degradation	431
7.7. Flammability	441
References	442

CHAPTER 8. Biological Macromolecules

F. A. BOVEY

8.1. Introduction	445
8.2. Polypeptides	446
8.3. Proteins	474
8.4. Nucleic Acids	498
8.5. Polysaccharides	517
References	524

Chapter 1

THE NATURE OF MACROMOLECULES

F. A. BOVEY AND F. H. WINSLOW

1.1. Introduction	1
1.2. Formation of Macromolecules	2
1.3. Structure of Macromolecules	4
1.4. Morphology and Mechanical Properties	6
1.4.1. Melting and Glass Temperatures	6
1.4.2. Interchain Forces	7
1.4.3. Mechanical Strength	12
1.5. Biological Macromolecules and Biopolymers	13
1.6. Historical Perspective	14
1.6.1. Early Studies of Rubber	15
1.6.2. Polyethylene and Other Vinyl Polymers	17
1.6.3. Nylons and Silicones	19
References	21

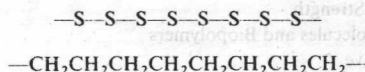
1.1. Introduction

In the early part of this century organic chemists were still confining their attention to compounds that could be readily distilled or crystallized. When substances were encountered that could not be purified by conventional procedures, they were promptly thrown away. Many of the discarded materials were *polymers*, which in those days were assumed to be impure aggregates of small molecules held together by colloidal forces. Although it may seem odd now, this concept was well entrenched when Staudinger (1920) proposed that rubber and other polymers were actually composed of giant molecules that he called *macromolecules* (Staudinger and Fritsch, 1922). At first virtually no one agreed with him. In fact, his hypothesis met with stubborn criticism all through the next decade. Meanwhile, bits of evidence corroborating the macromolecular theory began to accumulate from x-ray studies, molecular weight measurements, and similar sources. After 1930 even the most persistent doubts faded away rapidly with the introduction of numerous new polymers that gradually revolutionized the plastics, textile, rubber, and related industries.

With the exception of the Staudinger studies, nearly all pioneering work on synthetic macromolecules was done in industrial laboratories. But as academic interest grew, research turned toward the natural polymers that form so much of our food, clothing, and shelter as well as the basic structures and functions of all living things.

1.2. Formation of Macromolecules

The term polymer is derived from Greek words meaning "many parts." They are prepared by a process known as polymerization, which involves the chemical combination of many small chemical units known as *monomers* ("single parts"). The repeating units in a polymer molecule may be either single atoms as in sulfur molecules or groups of atoms such as the methylene units, $-\text{CH}_2-$, in polyethylene[†]:



The total number of repeating units in a polymer is called the *degree of polymerization* or DP.

As shown schematically in Fig. 1.1a, some polymers have a *linear* or threadlike structure. Others are *branched* or *cross-linked* in three-dimensional networks. Still others have less common shapes resembling combs, stars, or ladders. Polymers having flexible linear or branched structures are *thermoplastic*; that is, they can be molded or extruded at elevated temperatures and pressures. In contrast, the cross-linked *thermosetting* resins are permanently rigid materials.

Homopolymers consist of only one type of repeating unit, whereas *copolymers* (Fig. 1.1b) are composed of two or more different monomer units arranged in either random or alternating sequences. A few copolymers possess *block* or *graft* structures with relatively long sequences of one repeating unit bonded to similar sequences of another.

Polymer formation involves either *chain* or *step* reactions. Earlier, the terms *addition* and *condensation*, respectively, were used for describing these processes. One of the main differences between these mechanisms is outlined in Fig. 1.2. Once a chain reaction is *initiated*, monomer molecules add in rapid succession to the reactive end group of the growing polymer chain until it *terminates* and becomes unreactive. In the growth or *propagation*

[†] The commercial polymer is derived from ethylene, $\text{CH}_2=\text{CH}_2$. It has the same repeat unit as polymethylene made from diazomethane, CH_2N_2 .

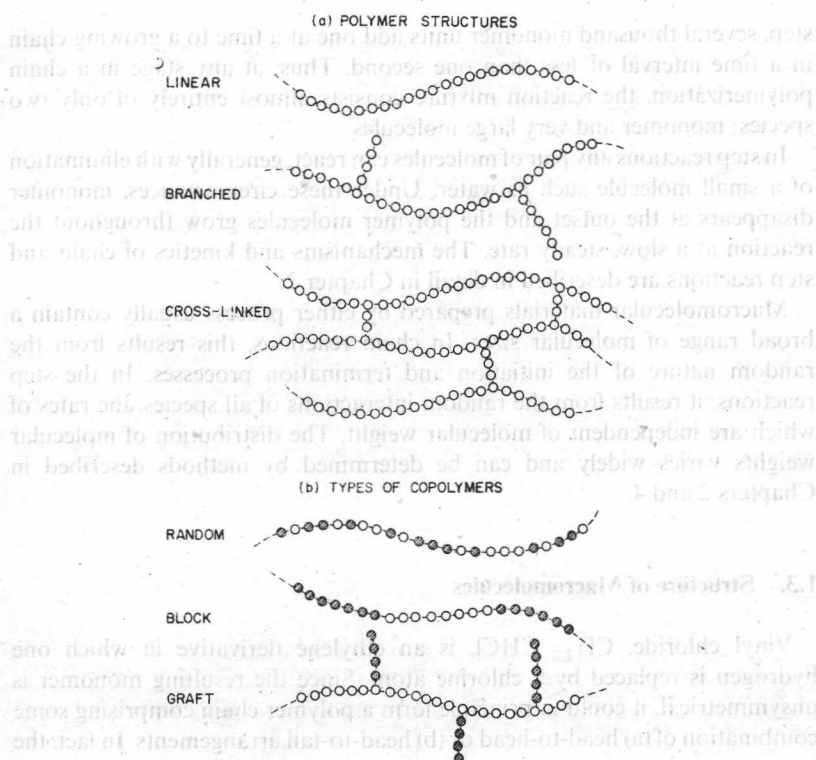


FIG. 1.1. (a) Homopolymer and (b) copolymer structures.

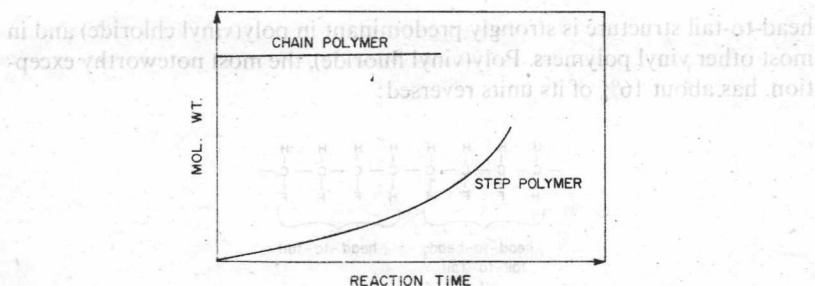


FIG. 1.2. Dependence of molecular weight on reaction time for chain and step polymerization processes.

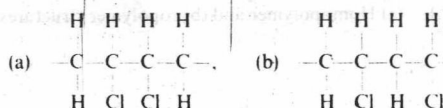
step, several thousand monomer units add one at a time to a growing chain in a time interval of less than one second. Thus, at any stage in a chain polymerization, the reaction mixture consists almost entirely of only two species: monomer and very large molecules.

In step reactions any pair of molecules can react, generally with elimination of a small molecule such as water. Under these circumstances, monomer disappears at the outset and the polymer molecules grow throughout the reaction at a slow, steady rate. The mechanisms and kinetics of chain and step reactions are described in detail in Chapter 2.

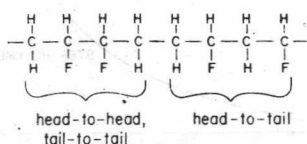
Macromolecular materials prepared by either process usually contain a broad range of molecular sizes. In chain reactions, this results from the random nature of the initiation and termination processes. In the step reactions, it results from the random interactions of all species, the rates of which are independent of molecular weight. The distribution of molecular weights varies widely and can be determined by methods described in Chapters 2 and 4.

1.3. Structure of Macromolecules

Vinyl chloride, $\text{CH}_2=\text{CHCl}$, is an ethylene derivative in which one hydrogen is replaced by a chlorine atom. Since the resulting monomer is unsymmetrical, it could in principle form a polymer chain comprising some combination of (a) head-to-head or (b) head-to-tail arrangements. In fact, the



head-to-tail structure is strongly predominant in poly(vinyl chloride) and in most other vinyl polymers. Poly(vinyl fluoride), the most noteworthy exception, has about 16% of its units reversed:



Vinyl monomers of this type may also exhibit large differences in *stereochemical configuration*, i.e., the relative handedness of successive monomer