INTRODUCTION TO

PHYSICAL POLYMER SCIENCE

L.H. SPERLING



PHYSICAL POLYMER SCIENCE

L. H. Sperling

Lehigh University Bethlehem, Pennsylvania

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York • Chichester • Brisbane • Toronto • Singapore

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Library of Congress Cataloging in Publication Data:

Sperling, L. H. (Leslie Howard), 1932– Introduction to physical polymer science.

3.* * * *

Includes index.

1. Polymers and polymerization. I. Title.

85-16724

QD381.S635 1985 547.7 ISBN 0-471-89092-8

Printed in the United States of America

10 9 8 7 6 5 4 3

Dedicated to my father, Irving Sperling, selfeducated because of the events of war. He came to America, and rose to be a community and religious leader. He made certain his children were afforded the opportunity of a college education.

Preface

Research in polymer science continues to mushroom, producing a plethora of new elastomers, plastics, adhesives, coatings, and fibers. All of this new information is gradually being codified and unified with important new theories about the interrelationships among polymer structure, physical properties, and useful behavior. Thus, the ideas of thermodynamics, kinetics, and polymer chain structure work together to strengthen the field of polymer science.

Following suit, the teaching of polymer science in colleges and universities around the world has continued to evolve. Where once a single introductory course was taught, now several different courses may be offered. The polymer science and engineering courses at Lehigh University include physical polymer science, organic polymer science, and polymer laboratory for interested seniors and first-year graduate students, and graduate courses in emulsion polymerization, polymer blends and composites, and engineering behavior of polymers. There is also a broad-based introductory course at the senior level for students of chemical engineering and chemistry. The students may earn degrees in chemistry, chemical engineering, metallurgy and materials engineering, or polymer science and engineering, the courses being both interdisciplinary and cross-listed.

The physical polymer science course is usually the first course a polymer-interested student would take at Lehigh, and as such there are no special prerequisites except upper-class or graduate standing in the areas mentioned above. This book was written for such a course.

The present book emphasizes the role of molecular conformation and configuration in determining the physical behavior of polymers. Two relatively new ideas are integrated into the text. Small-angle neutron scattering is doing for polymers in the 1980s what NMR did in the 1970s, by providing an

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entirely new perspective of molecular structure. Polymer blend science now offers thermodynamics as well as unique morphologies.

Chapter 1 covers most of the important aspects of the rest of the text in a qualitative way. Thus, the student can see where the text will lead him or her, having a glimpse of the whole. Chapter 2 describes the configuration of polymer chains, and Chapter 3 describes their molecular weight. Chapter 4 shows the interactions between solvent molecules and polymer molecules. Chapters 5–7 cover important aspects of the bulk state, both amorphous and crystalline, the glass transition phenomenon, and rubber elasticity. These three chapters offer the greatest depth. Chapter 8 describes creep and stress relaxation, and Chapter 9 covers the mechanical behavior of polymers, emphasizing failure, fracture, and fatigue.

Several of the chapters offer classroom demonstrations, particularly Chapters 6 and 7. Each of these demonstrations can be carried out inside a 50-minute class, and are easily managed by the students themselves. In fact, all of these demonstrations have been tested by generations of Lehigh students, and they are often presented to the class with a bit of showmanship. Each chapter is also accompanied by a problem set.

The author thanks the armies of students who studied from this book in manuscript form during its preparation and repeatedly offered suggestions relative to clarity, organization, and grammar. Many researchers from around the world contributed important figures. Dr. J. A. Manson gave much helpful advice, and served as a Who's Who in highlighting people, ideas and history.

The Department of Chemical Engineering, the Materials Research Center, and the Vice-President for Research's Office at Lehigh each contributed significant assistance in the development of this book. The Lehigh University Library provided one of their carrels during much of the actual writing. In particular, the author thanks Sharon Siegler and Victoria Dow and the staff at Mart Library for patient literature searching and photocopying. The author also thanks Andrea Weiss, who carefully photographed many of the figures in this book.

Secretaries Jone Susski, Catherine Hildenberger, and Jeanne Loosbrock each contributed their skills. Lastly, the person who learned the most from the writing of this book was...

L. H. SPERLING

Bethlehem, Pennsylvania November 1985

Values of Often-Used Constants†

Avogadro's number	N_A	6.022×10^{23} molecules/mol
Gas constant, molar	R	8.314 J/mol-deg K
		82.05 cm ³ -atm/mol-deg K
		1.987 cal/mol-deg K
		8.31×10^7 dyne-cm/mol-deg K
Planck's constant	h	$6.626 \times 10^{-34} \text{ J} \cdot \text{sec}$
Speed of light in vacuum	c	$2.997 \times 10^{8} \text{ m/sec}$

[†]J. A. Dean, Ed., Lange's Handbook of Chemistry, 12th ed., McGraw-Hill, New York, 1979, pp. 2-3.

Useful Conversion Factors

1 dyne/cm² =
$$1.450 \times 10^{-5}$$
 lb/in.² = 1.02×10^{-5} kgm/cm²
1 Pa = 10 dyne/cm² = 7.5×10^{-3} mm Hg = 10^{-5} bar
1 J = 2.387×10^{-1} cal = 1×10^{7} erg
1 Pa · sec = 10 poise
1 MPa = 1×10^{7} dyne/cm² = 145 lb/in.²
1 nm = 10 Å

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