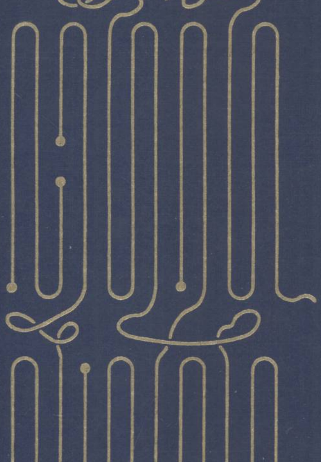
Second Edition

INTRODUCTION TO PHYSICAL POLYMER SCIENCE

L.H. SPERLING



INTRODUCTION TO PHYSICAL POLYMER SCIENCE

SECOND EDITION

L. H. Sperling

Lehigh University
Bethlehem, Pennsylvania

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INTRODUCTION TO PHYSICAL POLYMER SCIENCE

This book is dedicated to my grandsons, Ryland Everett Sweigard, born October 13, 1988, and Tresten Andrisen Sweigard, born February 18, 1991. They think that plastics are to play with.

PREFACE TO THE SECOND EDITION

When I was small, the books and songs I knew just *were*, with no particular authorship. I got my lesson on the rights and duties of authorship from my mother one day, discussing the Bible. "If we don't think that a given passage is worded in the best way for today, why don't we just rewrite it?" I asked.

My mother was horrified. "That Book was written thousands of years ago! It was handed down from generation to generation as it was set down on paper by its authors!" Books were sacred to her.

So it was that I learned that all books, songs, plays, and operas are written by particular men and women who have a strong and clear message to be expressed. Only they have the privilege of revising their works. If someone wasn't satisfied, they could write their own book!

Now, after a period of still less than a decade, I find that many new ideas have come to the fore in physical polymer science. A few important concepts somehow got left out of the first edition of this book. A handful of pages and paragraphs wandered in that should not have been there. I, the author of this work, joyfully take the privilege that is only mine to prepare this second edition. Thank you for giving me the opportunity.

Major specific changes include the following: three new chapters were added. The first one resulted from a split of the chapter titled, "The Bulk State," into two chapters, "The Amorphous State" and "The Crystalline State." The second one resulted from the vast increase in importance of the liquid crystalline state, resulting in a chapter entitled "Polymers in the Liquid Crystalline State." This chapter absorbed some of the material originally in the chapter entitled "Mechanical Behavior of Polymers." The third new chapter, at the end of the book, is entitled, "Modern Topics."

Other major changes include the addition of the macromolecular hypothesis and historical development to Chapter 1, photophysics and fluorescence to Chapter 2, movement of the sections on thermodynamics of mixing and phase separation and fractionation from Chapter 4 to Chapter 3, ahead of molecular weight determination, and additional material on thermodynamics of blending polymers and polymer–polymer phase diagrams to Chapter 4.

The following changes refer to the new chapter numbers. Additional material on self-diffusion of polymers was added to Chapter 5, and fiber spinning and structure were added to Chapter 6. As mentioned previously, Chapter 7 is an entirely new chapter on polymer liquid crystals. Greater discussion of dynamic mechanical behavior is given in Chapter 8. A discussion of gelatinous materials was added to Chapter 9. To Chapter 10, a discussion of rheology and a new demonstration were added (in the appendix). Chapter 11 was given a complete reorganization, because of the new material on stress–strain behavior and crack healing. Chapter 12 is an entirely new chapter, concerned with a variety of topics, emphasizing surface and interfacial behavior, electrical behavior of polymers, nonlinear optics, and high-temperature materials.

Again, I want to take this opportunity to thank the many students who helped in proofreading the manuscript. In proofing the first edition, a student said to me: "Dr. Sperling! You always taught us to write and rewrite manuscripts until they read like a thousand violins playing in the night! This paragraph here, however, reads like 50 violins playing in the day, and two of them are squeaking!" In preparing the second edition, a student again said to me: "Look at this equation! All three terms must always be positive, yet you have equated the sum of them to zero!" The result in each case, of course, is one fewer error that future students will have to endure.

Many thanks must also be given to the Department of Chemical Engineering and the Department of Materials Science and Engineering, as well as the Materials Research Center and the Center for Polymer Science and Engineering at Lehigh University. Dr. D. A. Thomas, long my research partner, contributed some juicy study problems. Special thanks must be given to Ms. Gail Kriebel and her staff at the E. W. Fairchild–Martindale Library, Ms. Andrea Pressler, photographer, and Ms. Virginia Newhard, my secretary.

L. H. SPERLING

Bethlehem, Pennsylvania
June 1992

PREFACE TO THE FIRST EDITION

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 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
Boltzmann's constant	K	1.380×10^{-16} erg/K
		1.380×10^{-23} J/K
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} dynes · cm/mol · K
Planck's constant	h	6.626×10^{-34} J · sec
Speed of light in vacuum	c	2.997×10^{8} m/sec

Useful Conversion Factors

1 dyne/cm^2 = 1.450×10^{-5} lb/in.^{2} = 1.02×10^{-5} kg/cm^2
1 Pa = 10 dynes/cm^2 = 7.5×10^{-3} mm Hg = 10^{-5} bar
= 1.02×10^{-5} kg/cm^2
1 Pa = 1 N/m^2
1 bar = 1 atm pressure
1 J = 2.387×10^{-1} cal = 1×10^{7} ergs
1 Pa · sec = 10 poise
1 MPa = 1×10^{7} dynes/cm^2 = 145 lb/in.^{2}
1 nm = 10 Å
1 N = 10^5 dynes = 1.02×10^{-1} kgf = 2.248×10^{-1} lbf

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

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