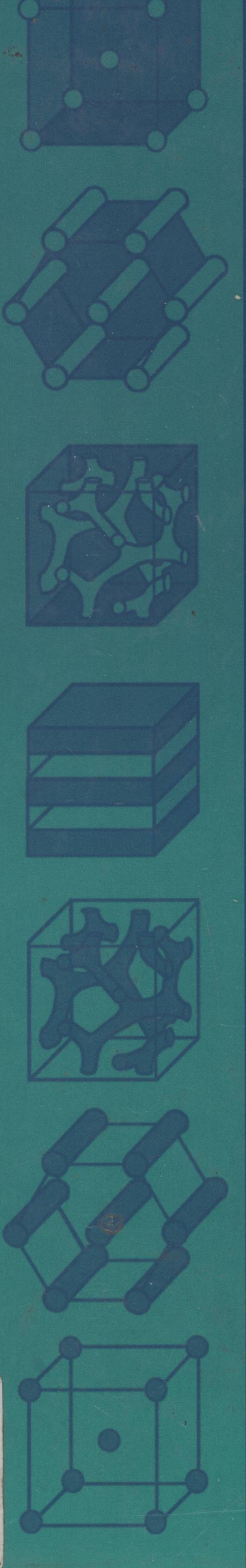

Polymer Chemistry

Second Edition

Paul C. Hiemenz
Timothy P. Lodge

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Polymer Chemistry

Second Edition

Preface to the Second Edition

Polymer science is today a vibrant field. Its technological relevance is vast, yet fundamental scientific questions also abound. Polymeric materials exhibit a wealth of fascinating properties, many of which are observable just by manipulating a piece in your hands. Yet, these phenomena are all directly traceable to molecular behavior, and especially to the long chain nature of polymer molecules. The central goal of this book is to develop a molecular level understanding of the properties of polymers, beginning with the underlying chemical structures, and assuming no prior knowledge beyond undergraduate organic and physical chemistry. Although such an understanding should be firmly based in chemistry, polymer science is a highly interdisciplinary endeavor; concepts from physics, biology, materials science, chemical engineering, and statistics are all essential, and are introduced as needed.

The philosophy underlying the approach in this book is the same as that in the first edition, as laid out in the previous preface. Namely, we endeavor to develop the fundamental principles, rather than an encyclopedic knowledge of particular polymers and their applications; we seek to build a molecular understanding of polymer synthesis, characterization, and properties; we emphasize those phenomena (from the vast array of possibilities) that we judge to be the most interesting. The text has been extensively reorganized and expanded, largely to reflect the substantial advances that have occurred over the intervening years. For example, there is now an entire chapter (Chapter 4) dedicated to the topic of controlled polymerization, an area that has recently undergone a revolution. Another chapter (Chapter 11) delves into the viscoelastic properties of polymers, a topic where theoretical advances have brought deeper understanding. The book also serves as a bridge into the research literature. After working through the appropriate chapters, the student should be able to make sense of a large fraction of the articles published today in polymer science journals.

There is more than enough material in this book for a full-year graduate level course, but as with the first edition, the level is (almost) always accessible to senior level undergraduates. After an introductory chapter of broad scope, the bulk of the text may be grouped into three blocks of four chapters each. Chapter 2 through Chapter 5 describe the many ways in which polymers can be synthesized and how the synthetic route influences the resulting molecular structure. This material could serve as the basis for a single quarter or semester chemistry course that focuses on polymer synthesis. Chapter 6 through Chapter 9 emphasize the solution properties of polymers, including their conformations, thermodynamics, hydrodynamics, and light scattering properties. Much of this material is often found in a quarter or semester course introducing the physical chemistry of polymers. Chapter 10 through Chapter 13 address the solid state and bulk properties of polymers: rubber elasticity, viscoelasticity, the glass transition, and crystallization. These topics, while presented here from a physical chemical point of view, could equally well serve as the cornerstone of an introductory course in materials science or chemical engineering.

The style of the presentation, as with the previous edition, is chosen with the student in mind. To this end, we may point out the following features:

- There are over 60 worked example problems sprinkled throughout the book.
- There are 15 or more problems at the end of every chapter, to reinforce and develop further understanding; many of these are based on data from the literature.

- There are almost 200 figures, to illustrate concepts or to present experimental results from the literature.
- Studies chosen for the examples, problems, and figures range in vintage from very recent to over 50 years old; this feature serves to give the reader some sense of the historical progression of the field.
- Concise reviews of many topics (such as thermodynamics, kinetics, probability, and various experimental techniques) are given when the subject is first raised.
- A conscious effort has been made to cross-reference extensively between chapters and sections within chapters, in order to help tie the various topics together.
- Important equations and mathematical relations are almost always developed step by step. We have avoided, wherever possible, the temptation to pull equations out of a hat. Occasionally this leads to rather long stretches of algebra, which the reader is welcome to skip. However, at some point the curious student will want to know where the result comes from, and then this book should be a particularly valuable resource. Surprisingly, perhaps, the level of mathematical sophistication is only about the same as needed in undergraduate chemical thermodynamics. As a further help in this regard, an Appendix reviews many of the important mathematical tools and tricks.

An undertaking such as writing a textbook can never be completed without important contributions from many individuals. Large sections of manuscript were carefully typed by Becky Matsch and Lynne Johnsrud; Lynne also helped greatly with issues of copyright permissions and figure preparation. My colleagues past and present in the Polymer Group at Minnesota have been consistently encouraging and have provided both useful feedback and insightful examples: Frank Bates, Shura Grosberg, Marc Hillmyer, Chris Macosko, Wilmer Miller, David Morse, Steve Prager, and Matt Tirrell. In large measure the style adopted in this second edition has been inspired by the example set by my graduate instructors and mentors at the University of Wisconsin: R. Byron Bird, John Ferry, Arthur Lodge, John Schrag, and Hyuk Yu. In particular, it was in his graduate course Chemistry 664 that Hyuk Yu so ably demonstrated that no important equation need come out of thin air.

I would like extend a special thank you to all of the students enrolled in Chemistry/Chemical Engineering/Materials Science 8211 over the period 2002–2005, who worked through various drafts of Chapter 6 through Chapter 13, and provided many helpful suggestions: Sayeed Abbas, David Ackerman, Sachin Agarwal, Saurabh Agarwal, Julie Alkatout, Pedro Arrechea, Carlos Lopez-Barron, Soumendra Basu, Jeff Becker, Joel Bell, A.S. Bhalla, Michael Bluemle, Paul Boswell, Bryan Boudouris, Adam Buckalew, Xiuyu Cai, Neha Chandra, Joon Chatterjee, Liang Chen, Ying Chen, Juhee Cho, Seongho Choi, Jin-Hwa Chung, Kevin Davis, Michail Dolgovskij, Jingshan Dong, Will Edmonds, Sandra Fritz, Carolyn Gamble, Piotr Grzywacz, Jeong-Myeong Ha, Benjamin Hamilton, Amanda Haws, Nazish Hoda, Hao Hou, Deanna Huehn, Shengxiang Ji, Karan Jindal, Young Kang, Aaron Khieu, Byeong-Su Kim, BongSoo Kim, Hyunwoo Kim, Jin-Hong Kim, Seung Ha Kim, Chunze Lai, Castro Laicer, Qiang Lan, Sangwoo Lee, Zhibo Li, Elizabeth Lugert, Nate Lynd, Sudeep Maheshwari, Huiming Mao, Adam Meuler, Yoichiro Mori, Randy Mrozek, Siddharthya Mujumdar, Jaewook Nam, Dan O'Neal, Sahban Ozair, Matt Panzer, Alhad Phatak, William Philip, Jian Qin, Benjamin Richter, Scott Roberts, Josh Scheffel, Jessica Schommer, Kathleen Schreck, Peter Simone, Zach Thompson, Kristianto Tjiptowidjojo, Mehul Vora, Jaye Warner, Tomy Widya, Maybelle Wu, Jianyan Xu, Dan Yu, Ilan Zeroni, Jianbin Zhang, Ling Zhang, Yu Zhang, Ning Zhou, Zhengxi Zhu, and John Zupancich. Last but not least the love, support, and tolerance of my family, Susanna, Hannah, and Sam, has been a constant source of strength.

Tim Lodge

Preface to the First Edition

Physical chemistry has been defined as that branch of science that is fundamental, molecular, and interesting. I have tried to write a polymer textbook that could be described this way also. To the extent that one subscribes to the former definition and that I have succeeded in the latter objective, then the approach of this book is physical chemical. As a textbook, it is intended for students who have completed courses in physical and organic chemistry. These are the prerequisites that define the level of the book; no special background in physics or mathematics beyond what is required for physical chemistry is assumed. Since chemistry majors generally study physical chemistry in the third year of the undergraduate curriculum, this book can serve as the text for a senior-level undergraduate or a beginning graduate-level course. Although I use chemistry courses and chemistry curricula to describe the level of this book, students majoring in engineering, materials science, physics, and various specialties in the biological sciences will also find numerous topics of interest contained herein.

Terms like "fundamental," "molecular," and "interesting" have different meanings for different people. Let me explain how they apply to the presentation of polymer chemistry in this text.

The words "basic concepts" in the title define what I mean by "fundamental." This is the primary emphasis in this presentation. Practical applications of polymers are cited frequently–after all, it is these applications that make polymers such an important class of chemicals–but in overall content, the stress is on fundamental principles. "Foundational" might be another way to describe this. I have not attempted to cover all aspects of polymer science, but the topics that have been discussed lay the foundation–built on the bedrock of organic and physical chemistry–from which virtually all aspects of the subject are developed. There is an enormous literature in polymer science; this book is intended to bridge the gap between the typical undergraduate background in polymers–which frequently amounts to little more than occasional "relevant" examples in other courses–and the professional literature on the subject. Accordingly, the book assumes essentially no prior knowledge of polymers, and extends far enough to provide a usable level of understanding.

"Molecular" describes the perspective of the chemist, and it is this aspect of polymeric materials that I try to keep in view throughout the book. An engineering text might emphasize processing behavior; a physics text, continuum mechanics; a biochemistry text, physiological function. All of these are perfectly valid points of view, but they are not the approach of this book. It is polymer molecules–their structure, energetics, dynamics, and reactions–that are the primary emphasis throughout most of the book. Statistics is the type of mathematics that is natural to a discussion of molecules. Students are familiar with the statistical nature of, say, the kinetic molecular theory of gases. Similar methods are applied to other assemblies of molecules, or in the case of polymers, to the assembly of repeat units that comprise a single polymer molecule. Although we frequently use statistical arguments, these are developed quite thoroughly and do not assume any more background in this subject than is ordinarily found among students in a physical chemistry course.

The most subjective of the words which (I hope) describe this book is "interesting." The fascinating behavior of polymers themselves, the clever experiments of laboratory researchers, and the elegant work of the theoreticians add up to an interesting total. I have tried to tell about these topics with clarity and enthusiasm, and in such a way as to make them intelligible to students. I can only hope that the reader agrees with my assessment of what is interesting.

This book was written with the student in mind. Even though "student" encompasses persons with a wide range of backgrounds, interests, and objectives; these are different than the corresponding experiences and needs of researchers. The following features have been included to assist the student:

1. Over 50 solved example problems are sprinkled throughout the book.
2. Exercises are included at the end of each chapter which are based on data from the original literature.
3. Concise reviews of pertinent aspects of thermodynamics, kinetics, spectrophotometry, etc. are presented prior to developing applications of these topics to polymers.
4. Theoretical models and mathematical derivations are developed in enough detail to be comprehensible to the student reader. Only rarely do I "pull results out of a hat," and I scrupulously avoid saying "it is obvious that ..."
5. Generous cross-referencing and a judicious amount of repetition have been included to help unify a book which spans quite a wide range of topics.
6. SI units have been used fairly consistently throughout, and attention is paid to the matter of units whenever these become more than routine in complexity.

The book is divided into three parts of three chapters each, after an introductory chapter which contains information that is used throughout the book.

In principle, the three parts can be taken up in any order without too much interruption in continuity. Within each of the parts there is more carryover from chapter to chapter, so rearranging the sequence of topics within a given part is less convenient. The book contains more material than can be covered in an ordinary course. Chapter 1 plus two of the three parts contain about the right amount of material for one term. In classroom testing the material, I allowed the class to decide–while we worked on Chapter 1–which two of the other parts they wished to cover; this worked very well.

Material from Chapter 1 is cited throughout the book, particularly the discussion of statistics. In this connection, it might be noted that statistical arguments are developed in less detail further along in the book as written. This is one of the drawbacks of rearranging the order in which the topics are covered. Chapters 2 through 4 are concerned with the mechanical properties of bulk polymers, properties which are primarily responsible for the great practical importance of polymers. Engineering students are likely to have both a larger interest and a greater familiarity with these topics. Chapers 5 through 7 are concerned with the preparation and properties of several broad classes of polymers. These topics are closer to the interests of chemistry majors. Chapters 8 through 10 deal with the solution properties of polymers. Since many of the techniques described have been applied to biopolymers, these chapters will have more appeal to students of biochemistry and molecular biology.

Let me conclude by acknowledging the contributions of those who helped me with the preparation of this book. I wish to thank Marilyn Steinle for expertly typing the manuscript. My appreciation also goes to Carol Truett who skillfully transformed my (very) rough sketches into effective illustrations. Lastly, my thanks to Ron Manwill for preparing the index and helping me with the proofreading. Finally, let me acknowledge that some errors and/or obscurities will surely elude my efforts to eliminate them. I would appreciate reports about these from readers so that these mistakes can eventually be eliminated.

Paul C. Hiemenz

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