Principles of Polymer Chemistry 2nd ed

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2nd Edition

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Preface

This book, like the first edition, is written for graduate and advanced undergraduate students in polymer chemistry. It is also intended to be used as a reference by practicing chemists and can be used for self-education, because the topics are written without assumption of prior knowledge. The reader should possess, however, thorough knowledge of organic and physical chemistry, at the undergraduate level.

The revisions for the second edition had two goals in mind. The first one was to bring the material in the first edition up to date, because many important and exciting things happened in polymer chemistry since the first edition was written. The second one is to make changes in line with comments of some reviewers. With that in mind, a section was added on the controlled/"living" free radical polymerization. While this subject was still evolving five years ago, today it is an important part of polymer chemistry. Also, such subjects as metathesis type polymerization, matallocene catalysts, and preparation of syndiotactic polystyrene received considerable attention in polymer literature and now require more detailed discussions. To meet the second goal, Chapter 1 was changed to consist of two sections. Section one remains an introduction, while section two addresses the physical properties of polymers. Discussions on the subjects of the thermodynamics of elasticity, rheology and viscoelasticity, and thermodynamics of solutions of polymers are added. In addition, a chapter on the degradation of polymers was included. It was tempting to place all the controlled polymerizations, free radical, cationic and group transfer into one separate chapter, because of similarity in the mechanisms. This was not done, however, for fear of confusing the students.

There are nine chapters in this book. Chapter 1 consists of an introduction and a discussion of physical properties of polymers. The mechanisms of chain-growth polymerizations, free radical and ionic, are discussed in Chapters 2 and 3. Chapter 3 also includes coordinated anionic polymerizations. In addition, there is a section on group-transfer polymerization. Ring-opening polymerizations are presented in Chapter 4. Chapter 5 covers commercially important chain-growth polymers, their industrial preparations, properties, and performance. Step-growth polymerizations are discussed in Chapter 6 together with industrially important step-growth polymers, preparations, and properties. Naturally occurring polymers are described in Chapter 7. While cellulose and starch are presented fully, proteins and nucleic acids are described only briefly, because detailed treatment belongs in biochemistry. Chemical modifications and reactions of polymeric materials, including polymeric reagents and functional polymers, are discussed in Chapter 8. Chapter 9 is devoted to degradation of polymeric materials. This includes causes and mechanism of degradation from thermal, hydrolytic, oxidative, photo, photo-oxidative, and radiation sources.

Greater emphasis is placed on commercially important materials. Most students find employment in industry. Familiarity with materials and commercial

practices are an essential and practical part of their training. Some trade names are included for the same reason.

In the first edition, two of the chapters contained appendixes with computer programs. They were offered to readers for practice. One program was there to help gain greater understanding of the meaning of molecular weights in polymers and to learn how they are calculated from gel permeation chromatogram (GPC) data. The other one was to understand statistical interpretations of the propagation mechanisms from nuclear magnetic resonance (NMR) data and to gain greater insight into stereochemistry of polymers. These two programs were removed from the back of the chapters and placed instead on the diskette at the end of the book, together with the material that is ready to run, so that individuals who wish to modify them to suit their particular needs can do so without having to type in the program. A new program on the kinetics of chain-growth homopolymerization was added.

There are review questions at the ends of the chapters. After reading each chapter, the students are advised to try to answer the questions first and then to compare their answers with the discussions in the book.

This book, like the first edition, is dedicated to all scientists whose names appear in the references.

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7. Naturally Occurring Polymers

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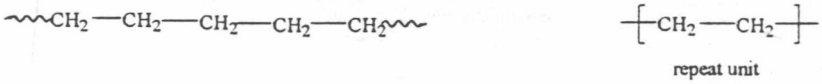
Introduction

1.1. Definitions

The word polymer is commonly understood to mean a large molecule composed of repeating units, or mers (from the Greek word *meros*-part), connected by covalent bonds. Such units may be connected in a variety of ways. The simplest is a linear polymer, or a polymer in which the units are connected to each other in a linear sequence, like beads on a string. Many examples of such linear polymers are possible, as, for instance, linear polyethylene:



The terminal units in such molecules must be different from the internal ones to satisfy valence requirements. Polyethylene, like all other polymers, can be written to show the number of repeat units, $-[-CH_2-CH_2-]_n-$, by using a number or a letter, like in this case n. It represents the quantity of mers present in the polymer and is called the *degree of polymerization*, or DP.

An alternative to a linear polymer is a branched one. The branches can be long or short. Low density polyethylene, for instance, can have both short and long branches. Linear and branched molecules are illustrated in Fig. 1.1a and b. Branched polymers can also be star of comb shaped (Fig. 1.1c and d). In addition to the above, polymer molecules can also be double stranded. Such polymers are called ladder polymers (Fig. 1.1e). It is also possible for polymers to have semi-ladder structures (Fig. 1.1 f).

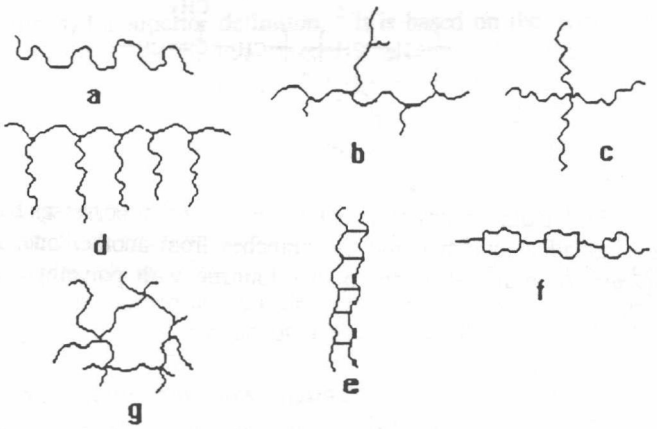


Figure 1.1 Shapes of polymer molecules. (a) linear polymer, (b) branched polymer, (c) star-shaped polymer, (d) comb shaped polymer, (e) ladder polymer, (f) semiladder polymer, and (g) network structure.