WILLIAMS

POLYMER SCIENCE AND ENGINEERING

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Polymer Science and Engineering

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Preface

Polymers are ubiquitous and essential. Biological polymers are of unparelleled importance as constituents of our bodies and of the food we eat. Wood was certainly one of the first engineering materials, and its use is still widespread. Synthetic polymers—the subject of this book—enter virtually every aspect of our lives; most of the objects that surround us are, if not entirely, at least partially polymeric in constitution.

In spite of our longstanding dependence on polymers, their intensive study as a class of materials distinct from their low molecular weight counterparts is a recent phenomenon. One can fix the birth of modern polymer science in the 1920's with the pioneering work of Hermann Staudinger. In dilute solution, polymers exhibit properties analogous to suspended colloids. For this reason it was first thought that they were colloid-like aggregates of low molecular weight materials bound together by physical forces. Staudinger showed that polymers were actually giant molecules comprised of low molecular weight materials bound together by chemical bonds rather than physical forces. For the championship of this viewpoint, as well as other elements of his work, he was awarded the Nobel Prize in 1953.

Polymer science and engineering is a rapidly advancing discipline. The development of nylon in the 1930's and of synthetic rubber during World War II marked the beginning of polymers as important commodities. The polymer industry has grown at nearly four times the annual growth rate of the national economy. Today, thousands of polymer products are manufactured, and over 50% of all chemists and chemical engineers are associated with the polymer industry. Finally, when the American Institute of Chemical Engineers posed the question to a panel of chemical engineering authorities: "What are chemical engineers' ten biggest all-time feats?"; three of the choices were: establishment of the plastics, synthetic fiber, and synthetic rubber industries.*

Polymers are complex materials that exhibit correspondingly complex behavioral patterns. These complexities are reflected in the aura of excitement

* Chemical Engineering – December 4, 1967, page 81.

surrounding their study. Many aspects of polymer behavior are centers of considerable debate, and numerous fundamental problems remain to be solved. Nevertheless, there is an underlying body of knowledge that is on a firm basis and that forms the cornerstone of current thought and research. Although many fine texts discuss specific areas of technology or research, or summarize the state-of-the-art, none serve, in any satisfactory way, to bridge the gap between the fundamentals of nonmacromolecular disciplines and the underlying concepts of polymer science and engineering. My primary objective has been to bridge this gap. A firm grasp of the principles herein developed will enable the student to read this advanced literature and to establish his own position in this exciting discipline.

Emphasis is placed on discussing general classes of polymers and their general patterns of behavior. Specific polymers are referred to in citing examples, but the stress is always on the underlying concepts. In selecting and organizing the subject matter, I have been careful to balance scope and depth so as to foster interest and maintain readability. In order to add perspective and a unifying theme, I have taken the viewpoint of the polymer engineer; that is, I have stressed the relation of composition and structure to a polymer's physical and mechanical properties as well as the relevance of the synthesis process to the design of a desired polymer product.

The text centers on a discussion of synthetic organic polymers. It is most suitable for physical chemists, chemical engineers, and materials engineers at the senior or first or second year graduate school level. It is hoped that the subject matter will prove valuable and stimulating to the practicing scientist and engineer as well.

The book has been developed over a six year period through the use of class notes, with presentation to both undergraduate and graduate chemical engineers. There is ample material for a two-semester program. Problem and discussion sets have been included. References are cited in an appended bibliography. The book is divided into four parts: I Introduction, II Polymer Synthesis, III Physics of the Solid State, and IV Polymer Rheology. The nature of the subject matter contained within the four parts is discussed in an introduction preceding each part. Part I is must reading, but the others may be read independently as individual needs and interests dictate. Cross references are supplied where appropriate.

In an undertaking of this sort it is impossible to acknowledge all of one's debts. Nonetheless, special thanks are due to Professor Alois X. Schmidt for his guidance and inspiration during my early years at The City College; to the DuPont Company for their financial support during the summers of 1965 and 1966; to Michael Grancio and David Blum who made contributions to the material for the manuscript; and to Mrs. Norma Cohen who typed the bulk of the manuscript.

David J. Williams

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RETARDATION AND RELAXATION SPECTRA

THE VISCOUS CHARACTER OF POLYMER MELT FLOW

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Introductory Definitions and Concepts

High polymers are large molecules, with molecular weights on the order of 10^4 to 10^6. They may be synthetic or natural in origin. Polymeric materials are among the most common of all materials. They include such useful and essential materials as the films that package the foods we eat, the fibers that make up the clothes we wear, the rubber that goes into all our truck and auto tires, and the plastic that makes so many of the articles we use in our daily living. Polymeric materials also find their way into more exotic applications, such as in medicine and space. Indeed, our own bodies and the food we eat are largely composed of high polymers.

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These high-polymer molecules are built up by the repetitive chemical linking of small, simple units into long, chainlike structures much as a chain is constructed of links. Thus polyethylene, one of the simplest high-polymer molecules, is composed of many $—CH_2—CH_2—$ units linked together by covalent bonding. The word *polymer* is derived from the Greek and means "many parts." The starting materials from which polymers are derived are known as *monomers*. For example, polyethylene is derived from ethylene.

The units that are repeated throughout the polymer chain and that characterize the chemical composition of the polymer are known as *repeat units*. The repeat unit is generally composed of one or two monomer units and is well defined for simple polymer systems. A few examples of such systems are given in Table 1–1. Rules of polymer nomenclature are discussed in Appendix A. In polystyrene, the repeat unit is composed of one monomer unit and the chemical compositions are nearly identical. On the other hand, the repeat unit in poly(hexamethylene adipamide) is composed of two monomer units and the compositions differ by two molecules of water.

TABLE 1–1

EXAMPLES OF SOME SIMPLE POLYMER MATERIALS

Polymer	*Repeat Unit*	*Monomer Unit(s)*
Polyethylene	$—CH_2—CH_2—$	$CH_2{=}CH_2$
Polystyrene	$—CH_2—CH—$ (with pendant ring) 	$CH_2{=}CH$ (with pendant ring) 
Polyisoprene	$—CH_2—C(CH_3){=}CH—CH_2—$	$CH_2{=}C(CH_3)—CH{=}CH_2$
Poly(hexamethylene adipamide)	$—NH(CH_2)_6—NH—C({=}O)—(CH_2)_4—C({=}O)—$	$NH_2—(CH_3)_6—NH_2$ and $HOOC—(CH_2)_4—COOH$
Polycaprolactam	$—NH—(CH_2)_5—C({=}O)—$	$CH_2—(CH_2)_4—C{=}O$ (ring closed by —NH—)
Poly(dimethyl siloxane)	$—Si(CH_3)_2—O—$	$(CH_3)_2—Si—Cl_2$ and H_2O

Let us depict a single repeat unit in a polymer molecule as a bead and the entire molecule as a strand of these beads. If the repeat units are arranged in a single-stranded structure as shown in Figure 1–1(a), the molecule is said to be linear, no matter how the strand may be snaked or flexed, and we speak of a *linear polymer*. If the units are joined in a three-dimensional array as depicted in Figure 1–1(c) (in two dimensions), the polymer is said to be *crosslinked*. Such a polymer may be visualized as an array of linear molecules joined by chemical crosslinks into a network of macroscopic proportions. If an otherwise linear chain has side-chain appendages, as in Figure 1–1(b), where each molecule is still separate and discrete from its neighbors, the molecule is said to be nonlinear, and it is now referred to as a *branched polymer*. As will be explained later, fundamental differences exist between these three types, and they should not be confused. We will see that structural variations on the linear chain also occur.

In addition to the molecular shape fixed by chemical bonding, as in the linear, branched, and crosslinked varieties of molecules, variations in the overall shape and size of molecules arise through rotation of the chain atoms about primary valence bonds. Just as a chain of beads exhibits some degree of flexibility, so does a polymer molecule. For example, some molecules like polyethylene exist in the crystalline state in a planar zigzag form (bond length = 1.54Å, bond angle = 109° 28′), as illustrated in Figure 1–2(a).

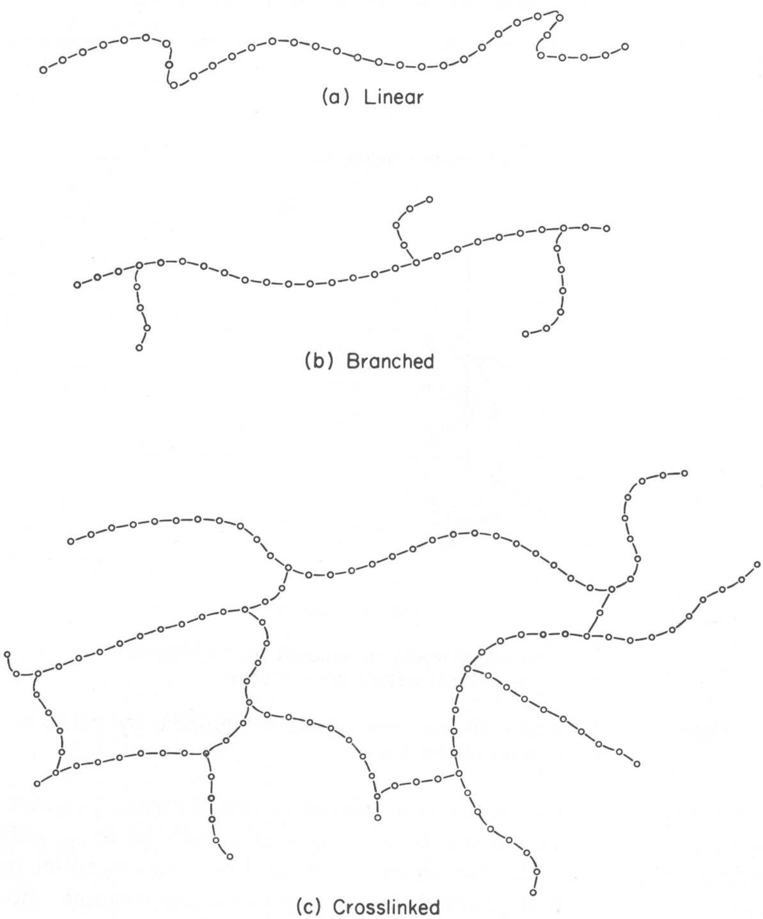

Figure 1–1. Representation of linear, branched, and crosslinked polymer systems.