

# **Textbook of POLYMER SCIENCE**

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# Preface

Like its predecessor, *Textbook of Polymer Chemistry* (1957), this book is written as a textbook in the chemistry and physics of high polymers. It includes no original work, but is an attempt to collect in one location and to classify some of the more interesting and important information about polymeric substances. It is based entirely on previously published information.

In view of the rapidly increasing size of the polymer literature,\* it is not surprising that an early and extensive revision of the previous volume became necessary. Its accomplishment at this time was made possible by the generosity of the Du Pont Company and of the Massachusetts Institute of Technology, which extended to the author the privilege of writing the revised edition while preparing and teaching courses in the chemistry and physics of polymers in the Department of Chemical Engineering at the Institute, during the academic year 1960-61.

It is hoped that this textbook will be useful for first courses in polymer chemistry at the senior or graduate level. It requires of the student some familiarity with organic and physical chemistry, elementary physics, and mathematics through elementary calculus. No prior knowledge of high polymers is assumed. [It is intended that the book be expanded in lectures and supplemented by reading assignments taken from the works listed under General References at the end of each section.] These details are left to the discretion of the instructor. Like its predecessor, *Textbook of Polymer Chemistry*, the book may, hopefully, also prove useful to the chemists and engineers working in the polymer field.

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Wilmington, Delaware  
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Finally, I am deeply grateful to my wife Annette, whose presence has made this undertaking, like all those we share, a joy and pleasure.

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# **I**

## **Introduction**



# 1

## The Science of Large Molecules

### *A. Basic Concepts of Polymer Science*

Almost half a century ago, Wolfgang Ostwald (2)\* coined the phrase "the land of neglected dimensions" to describe the range of sizes between molecular and macroscopic within which occur most colloidal particles. The term "neglected dimensions" might have been applied equally well to the world of polymer molecules, the high-molecular-weight compounds so important to man and his modern technology. It was not until the third decade of this century that the science of high polymers began to emerge, and the major growth of the technology of these materials came even later. Yet today polymer dimensions are neglected no more, for industries associated with polymeric materials employ more than a third of all American chemists and chemical engineers.

The science of macromolecules is divided between biological and non-biological materials. Each is of great importance. Biological polymers form the very foundation of life and intelligence, and provide much of the food on which man exists. This book, however, is concerned with the chemistry, physics, and technology of nonbiological polymers. These are primarily the synthetic materials used for plastics, fibers, and elastomers, but a few naturally occurring polymers, such as rubber, wool, and cellulose, are included. Today, these substances are truly indispensable to mankind, being essential to his clothing, shelter, transportation, and communication, as well as to the conveniences of modern living.

A *polymer* is a large molecule built up by the repetition of small, simple chemical units. In some cases the repetition is linear, much as a chain is


\* Parenthetical numbers refer to items in the bibliography following the immediate section.

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built up from its links. In other cases the chains are *branched* or interconnected to form *three-dimensional networks*. The *repeat unit* of the polymer is usually equivalent or nearly equivalent to the *monomer*, or starting material from which the polymer is formed. Thus (Table 1-1) the repeat unit of poly(vinyl chloride) is  $-\text{CH}_2\text{CHCl}-$ ; its monomer is vinyl chloride,  $\text{CH}_2=\text{CHCl}$ .

**TABLE 1-1. Some linear high polymers, their monomers, and their repeat units**

Polymer	Monomer	Repeat Unit
Polyethylene	$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2\text{CH}_2-$
Poly(vinyl chloride)	$\text{CH}_2=\text{CHCl}$	$-\text{CH}_2\text{CHCl}-$
Polyisobutylene	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2=\text{C} \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{C}- \\   \\ \text{CH}_3 \end{array}$
Polystyrene*	$\begin{array}{c} \text{CH}_2=\text{CH} \\   \\ \text{C}_6\text{H}_5 \end{array}$	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\   \\ \text{C}_6\text{H}_5 \end{array}$
Polycaprolactam (6 nylon)	$\begin{array}{c} \text{H}-\text{N}(\text{CH}_2)_5\text{C}-\text{OH} \\   \quad \quad \quad    \\ \text{H} \quad \quad \quad \text{O} \end{array}$	$\begin{array}{c} -\text{N}(\text{CH}_2)_5\text{C}- \\   \quad \quad \quad    \\ \text{H} \quad \quad \quad \text{O} \end{array}$
Polyisoprene (natural rubber)	$\begin{array}{c} \text{CH}_2=\text{CH}-\text{C}=\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c} -\text{CH}_2\text{CH}=\text{C}-\text{CH}_2- \\   \\ \text{CH}_3 \end{array}$

\* By convention, the symbol  is used throughout to represent the benzene ring, double bonds being omitted.

The length of the polymer chain is specified by the number of repeat units in the chain. This is called the *degree of polymerization* (DP). The molecular weight of the polymer is the product of the molecular weight of the repeat unit and the degree of polymerization. Using poly(vinyl chloride) as an example, a polymer of degree of polymerization 1000 has a molecular weight of  $63 \times 1000 = 63,000$ . Most high polymers useful for plastics, rubbers, or fibers have molecular weights between 10,000 and 1,000,000.

Unlike many products whose structure and reactions were well known before their industrial application, some polymers were produced on an

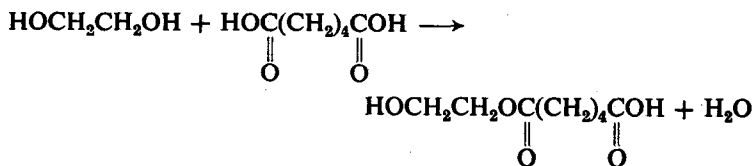
industrial scale long before their chemistry or physics was studied. Empiricism in recipes, processes, and control tests was usual.

Gradually the study of polymer properties began. Almost all were first called anomalous because they were so different from the properties of low-molecular-weight compounds. It was soon realized, however, that polymer molecules are many times larger than those of ordinary substances. The presumably anomalous properties of polymers were shown to be normal for such materials, as the consequences of their size were included in the theoretical treatments of their properties.

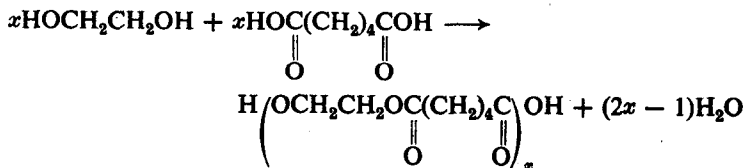
Primary chemical bonds along polymer chains are entirely satisfied. The only forces between molecules are secondary bond forces of attraction, which are weak relative to primary bond forces. The high molecular weight of polymers allows these forces to build up enough to impart excellent strength, dimensional stability, and other mechanical properties to the substances.

**Polymerization processes** The processes of polymerization were divided by Carothers and Flory (Flory, and Mark and Whitby, gen. refs.) into two groups known as *condensation* and *addition* polymerization or, in more precise terminology (Chapter 8A), *step-reaction* and *chain-reaction* polymerization.

*Condensation* or *step-reaction polymerization* is entirely analogous to condensation in low-molecular-weight compounds. In polymer formation the condensation takes place between two polyfunctional molecules to produce one larger polyfunctional molecule, with the possible elimination of a small molecule such as water. For example, a first step in the formation of the polyester poly(ethylene adipate) is the reaction:



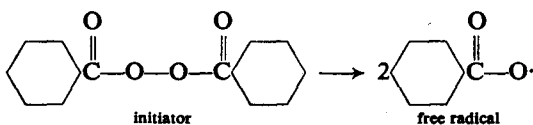
The reaction continues until all of one of the reagents is used up:



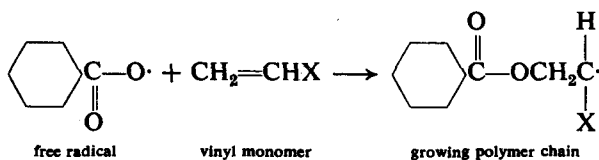
The equilibrium of this reaction can be shifted at will at high temperatures by controlling the amounts of the reactants and products.

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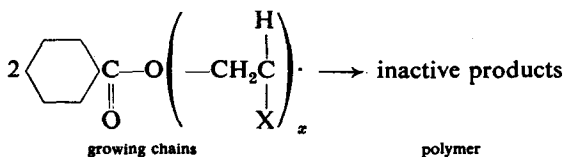
*Addition or chain-reaction polymerization* involves chain reactions in which the chain carrier may be an ion or a reactive substance with one unpaired electron called a *free radical*. A free radical is usually formed by the decomposition of a relatively unstable material called an *initiator*:



The free radical is capable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired:



In a very short time (usually a few seconds or less) many more monomers add successively to the growing chain. Finally two free radicals react to annihilate each other's growth activity and form one or more polymer molecules:



With some exceptions, polymers made in chain reactions often contain only carbon atoms in the main chain (*homochain polymers*), whereas polymers made in step reactions may have other atoms, originating in the monomer functional groups, as part of the chain (*heterochain polymers*).

**Molecular weight and its distribution** In both chain and stepwise polymerization, the length of a chain is determined by purely random events. In step reactions, the chain length is determined by the local availability of reactive groups at the ends of the growing chains. In radical polymerization, chain length is determined by the time during which the chain grows before it diffuses into the vicinity of a second free radical and the two react.

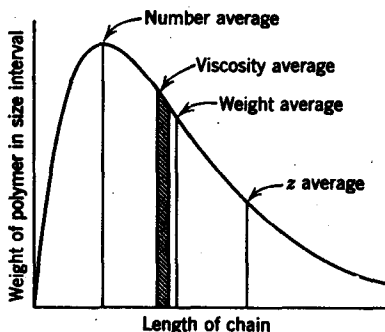


Fig. 1-1. Distribution of molecular weights in a typical polymer (1).

In either case, the polymeric product contains molecules having many different chain lengths. For some types of polymerization the resulting *distribution of molecular weights* can be calculated statistically. It can be illustrated by plotting the weight of polymer of a given size against the chain length or molecular weight (Fig. 1-1).

Since a distribution of molecular weights exists in any finite sample of polymer, the experimental measurement of molecular weight can give only an average value. Several different averages are important. For example, some methods of molecular weight measurement in effect count the number of molecules in a known mass of material. Through knowledge of Avogadro's number this information leads to the *number-average molecular weight*  $\bar{M}_n$  of the sample. For typical polymers the number average lies near the peak of the weight-distribution curve or the most probable molecular weight.

In other experiments, such as sedimentation in an ultracentrifuge, the contribution of a molecule to the observed effect is a function of its mass. Heavy molecules are favored in the averaging process; a *weight-average molecular weight*  $\bar{M}_w$  results.  $\bar{M}_w$  is equal to or greater than  $\bar{M}_n$ . The ratio  $\bar{M}_w/\bar{M}_n$  is sometimes used as a measure of the breadth of the molecular weight distribution. Values of  $\bar{M}_w/\bar{M}_n$  for typical polymers range from 1.5–2.0 to 20–50.

The molecular weight averages shown in Fig. 1-1 are defined mathematically in Chapter 3.

**Branched and network polymers** In contrast to the linear-chain molecules discussed so far, some polymers have branched chains, often as a result of side reactions during polymerization (Fig. 1-2a). The term *branching* implies that the individual molecules are still discrete. Regularly repeating side groups which are a part of the monomer structure are not



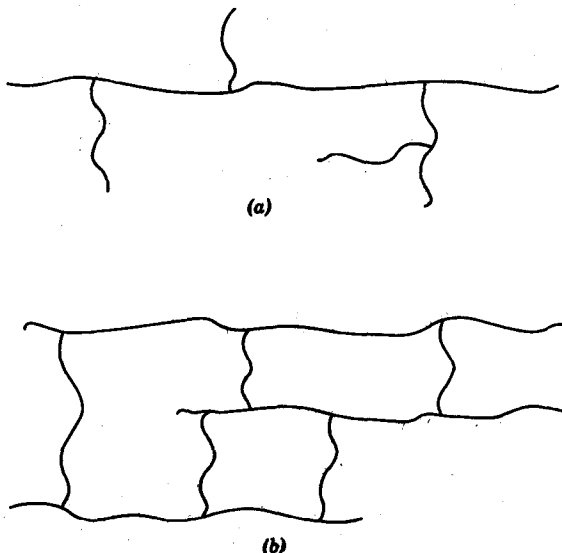
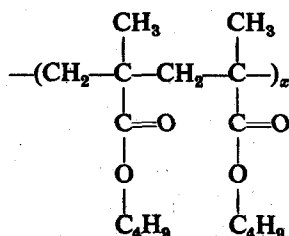


Fig. 1-2. Schematic representation of (a) branched and (b) network polymers.

considered branches. Thus, poly(butyl methacrylate) is classed as a linear polymer:



In still other cases *crosslinked* or *network structures* are formed (Fig. 1-2b), as in the use of monomers containing more than two reactive groups in stepwise polymerization. If, e.g., glycerol is substituted for ethylene glycol in the reaction with a dibasic acid, a three-dimensional network polymer results.

In commercial practice such reactions may take place during the fabrication of articles made with *thermosetting* resins. The crosslinked network extending throughout the final article is stable to heat and cannot be made to flow or melt. In contrast, most linear polymers can be made to soften and take on new shapes by the application of heat and pressure. They are said to be *thermoplastic*.