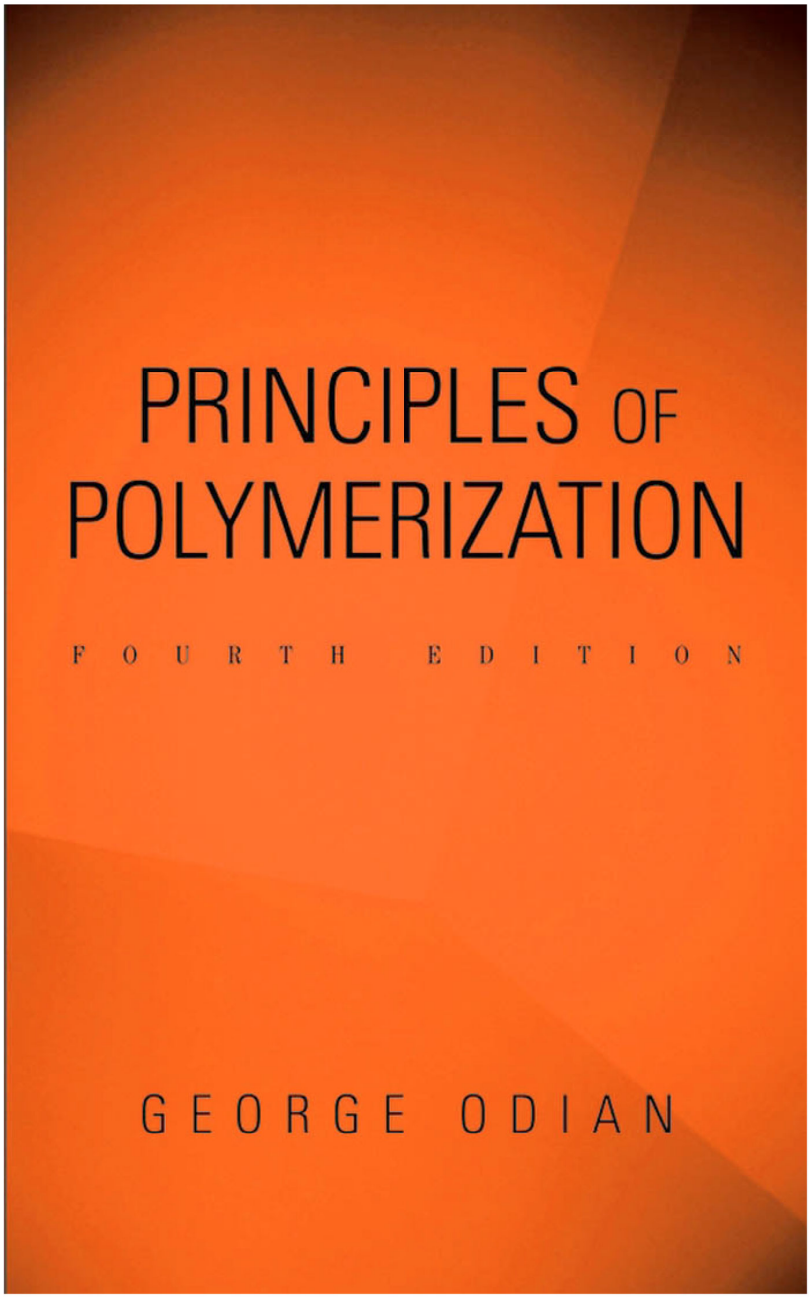

PRINCIPLES OF
POLYMERIZATION
FOURTH EDITION
GEORGE ODIAN

PRINCIPLES OF POLYMERIZATION

Fourth Edition

GEORGE ODIAN
College of Staten Island
City University of New York
Staten Island, New York

WILEY-INTERSCIENCE
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CHAPTER 1

INTRODUCTION

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed *monomers*, and the reactions by which they combine are termed *polymerizations*. There may be hundreds, thousands, tens of thousands, or more monomer molecules linked together in a polymer molecule. When one speaks of polymers, one is concerned with materials whose molecular wights may reach into the hundreds of thousands or millions.

1-1 TYPES OF POLYMERS AND POLYMERIZATIONS

There has been and still is considerable confusion concerning the classification of polymers. This is especially the case for the beginning student who must appreciate that there is no single generally accepted classification that is unambiguous. During the development of polymer science, two types of classifications have come into use. One classification is based on polymer structure and divides polymers into *condensation* and *addition* polymers. The other classification is based on polymerization mechanism and divides polymerizations into *step* and *chain* polymerizations. Confusion arises because the two classifications are often used interchangeably without careful thought. The terms *condensation* and *step* are often used synonymously, as are the terms *addition* and *chain*. Although these terms may often be used synonymously because most condensation polymers are produced by step polymerizations and most addition polymers are produced by chain polymerizations, this is not always the case. The condensation–addition classification is based on the composition or structure of polymers. The step–chain classification is based on the mechanisms of the polymerization processes.

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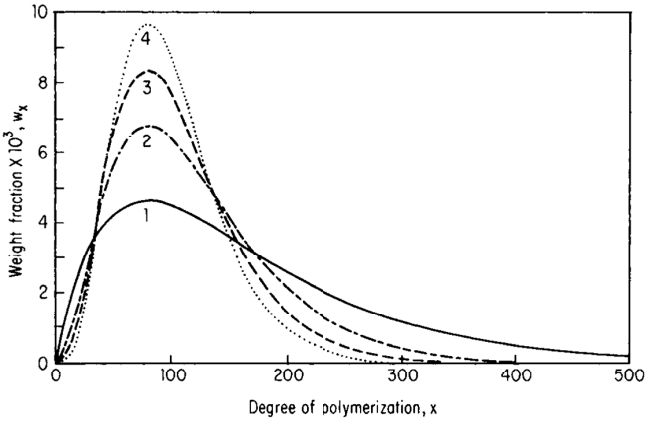


Fig. 2-14 Weight fraction distribution plot for multichain polymerization. Plot 1, $f = 1$; plot 2, $f = 2$; plot 3 $f = 3$; plot 4, $f = 4$. After Howard [1961] (by permission of Iliffe Books and Elsevier, London).

which becomes

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{1}{f} \tag{2-133}$$

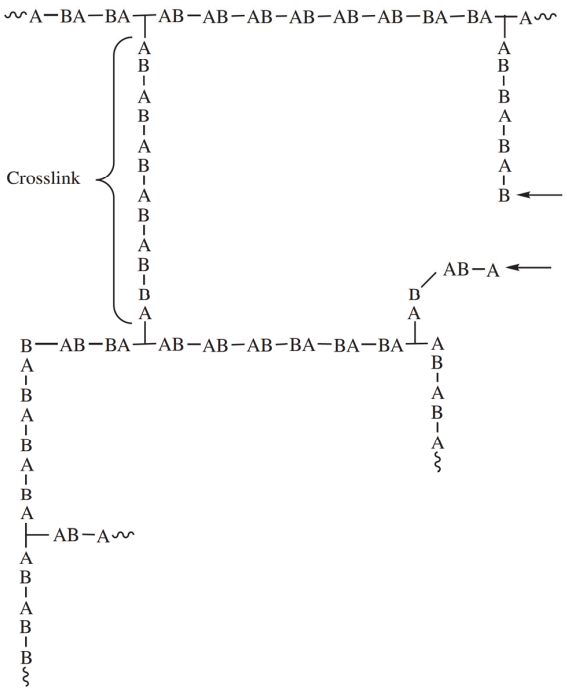
in the limit of $p = r = 1$.

The weight distribution (Eq. 2-131) is shown in Fig. 2-14 for several values of f. The extents of reaction have been adjusted to maintain a constant number-average degree of polymerization of 80 in all four cases. The size distribution becomes progressively narrower with increasing functionality of A_f. This is also evident from Eq. 2-133, where $\overline{X}_w/\overline{X}_n$ decreases from 2 for $f = 1$ to 1.25 for $f = 4$ (at $p = 1$). Linear polymers are formed for f values of 1 or 2, while branched polymers are formed when f is greater than 2. The case of $f = 1$ corresponds to the type 3 polymerization discussed in Sec. 2-6. The distribution is the exact same as the most probable distribution for linear polymerization (Sec. 2-7). Linear polymerization with $f = 2$ is of interest in that the distribution is narrower than that for the usual linear polymerization. The linking of two statistically independent A—B type polymer chains into one polymer molecule via an A—A molecule leads to a significantly narrower distribution that in the usual polymerizations of the A—B or A—A plus B—B types.

2-10 CROSSLINKING

Polymerization of the A—B plus A_f system (with $f > 2$) in the presence of B—B will lead not only to branching but also to a *crosslinked* polymer structure. Branches from one polymer molecule will be capable of reacting with those of another polymer molecule because of the presence of the B—B reactant. Crosslinking can be pictured as leading to structure **XVII**, in

which two polymer chains have been joined together (crosslinked) by a branch. The branch joining the two chains is referred to as a *crosslink*. A crosslink can be formed whenever there



XVII

are two branches (e.g., those indicated in **XVII** by the arrows) that have different functional groups at their ends, that is, one has an A group and the other a B group. Crosslinking will also occur in other polymerizations involving reactants with functionalities greater than two. These include the polymerizations

$$A\text{–}A + B_f \longrightarrow$$
$$A\text{–}A + B\text{–}B + B_f \longrightarrow$$
$$A_f + B_f \longrightarrow$$

Crosslinking is distinguished by the occurrence of *gelation* at some point in the polymerization. At this point, termed the *gel point*, one first observes the visible formation of a *gel* or *insoluble polymer fraction*. (The gel point is alternately taken as the point at which the system loses fluidity as measured by the failure of an air bubble to rise in it.) The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponds to the formation of an infinite network in which polymer molecules have been crosslinked to each other to form a macroscopic molecules. The gel is, in

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fact, considered as one molecule. The nongel portion of the polymer remains soluble in solvents and is referred to as *sol*. As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more polymer chains in the sol are crosslinked to the gel. There is a dramatic physical change that occurs during the process of gelation. The reaction mixture is transformed into a polymer of infinite viscosity.

The crosslinking reaction is an extremely important one from the commercial standpoint. Crosslinked plastics are increasingly used as engineering materials because of their excellent stability toward elevated temperatures and physical stress. They are dimensionally stable under a wide variety of conditions due to their rigid network structure. Such polymers will not flow when heated and are termed *thermosetting* polymers or simply *thermosets*. More than 10 billion pounds of thermosets are produced annually in the United States. Plastics that soften and flow when heated, that is, uncrosslinked plastics, are called *thermoplastics*. Most of the polymers produced by chain polymerization are thermoplastics. Elastomers are a category of polymers produced by chain polymerization that are crosslinked (Sec. 1-3), but the crosslinking reactions are different from those described here (Sec. 9-2).

In order to control the crosslinking reaction so that it can be used properly, it is important to understand the relationship between gelation and the extent of reaction. Two general approaches have been used to relate the extent of reaction at the gel point to the composition of the polymerization system—based on calculating when $\overline{X}_n$ and $\overline{X}_w$, respectively, reach the limit of infinite size.

2-10a Carothers Equation: $\overline{X}_n \to \infty$

2-10a-1 Stoichiometric Amounts of Reactants

Carothers derived a relationship between the extent of reaction at the gel point and the *average functionality* f_{avg} of the polymerization system for the case where the two functional groups A and B are present in equivalent amounts [Carothers, 1936]. The derivation follows in a manner similar to that for Eq. 2-78. The average functionality of a mixture of monomers is the average number of functional groups per monomer molecule for all types of monomer molecules. It is defined by

$$f_{\text{avg}} = \frac{\Sigma N_i f_i}{\Sigma N_i} \tag{2-134}$$

where N_i is the number of molecules of monomer i with functionality f_i, and the summations are over all the monomers present in the system. Thus for a system consisting of 2 mol of glycerol (a triol) and 3 mol of phthalic acid (a diacid) there is a total of 12 functional groups per five monomer molecules, and f_{avg} is $\frac{12}{5}$ or 2.4. For a system consisting of a equimolar amounts of glycerol, phthalic anhydride, and a monobasic acid, there is a total of six functional groups per three molecules and f_{avg} is $\frac{6}{3}$ or 2.

In a system containing equivalent numbers of A and B groups, the number of monomer molecules present initially is N_0 and the corresponding total number of functional groups is $N_0 f_{\text{avg}}$. If N is the number of molecules after reaction has occurred, then $2(N_0 - N)$ is the number of functional groups that have reacted. The extent of reaction p is the fraction of functional groups lost:

$$p = \frac{2(N_0 - N)}{N_0 f_{\text{avg}}} \tag{2-135}$$

high-molecular-weight polymers. Further, most step polymerizations are equilibrium reactions and the initially formed copolymer composition is rapidly changed by equilibration. This chapter is concerned entirely with chain copolymerization. The main features of step copolymerization have been covered in Sec. 2-13.

6-1 GENERAL CONSIDERATIONS

6-1a Importance of Chain Copolymerization

Chain copolymerization is important from several considerations. Much of our knowledge of the reactivities of monomers, free radicals, carbocations, and carbanions in chain polymerization comes from copolymerization studies. The behavior of monomers in copolymerization reactions is especially useful for studying the effect of chemical structure on reactivity. Copolymerization is also very important from the technological viewpoint. It greatly increases the ability of the polymer scientist to tailor-make a polymer product with specifically desired properties. Polymerization of a single monomer is relatively limited as to the number of different products that are possible. The term *homopolymerization* is often used to distinguish the polymerization of a single monomer from the copolymerization process.

Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two monomer units in the copolymer product. A prime example of the versatility of the copolymerization process is the case of polystyrene. More than 11 billion pounds per year of polystyrene products are produced annually in the United States. Only about one-third of the total is styrene homopolymer. Polystyrene is a brittle plastic with low impact strength and low solvent resistance (Sec. 3-14b). Copolymerization as well as blending greatly increase the usefulness of polystyrene. Styrene copolymers and blends of copolymers are useful not only as plastics but also as elastomers. Thus copolymerization of styrene with acrylonitrile leads to increased impact and solvent resistance, while copolymerization with 1,3-butadiene leads to elastomeric properties. Combinations of styrene, acrylonitrile, and 1,3-butadiene improve all three properties simultaneously. This and other technological applications of copolymerization are discussed further in Sec. 6-8.

6-1b Types of Copolymers

The copolymer described by Eq. 6-1, referred to as a *statistical copolymer*, has a distribution of the two monomer units along the copolymer chain that follows some statistical law, for example, Bernoullian (zero-order Markov) or first- or second-order Markov. Copolymers formed via Bernoullian processes have the two monomer units distributed randomly and are referred to as *random copolymers*. The reader is cautioned that the distinction between the terms statistical and random, recommended by IUPAC [IUPAC, 1991, in press], has often not been followed in the literature. Most references use the term *random copolymer* independent of the type of statistical process involved in synthesizing the copolymer. There are three other types of copolymer structures—alternating, block, and graft. The *alternating* copolymer contains the two monomer units in equimolar amounts in a regular alternating distribution:

$$\sim\!\!\sim M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1\sim\!\!\sim$$

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