2 Step-Growth Polymerization

The classical subdivision of polymers into two main groups was made around 1929 by W.H. Carothers, who proposed that a distinction be made between polymers prepared by the stepwise reaction of monomers and those formed by chain reactions. These he called:

1. *Condensation polymers*, characteristically formed by reactions involving the elimination of a small molecule such as water at each step.
2. *Addition polymers*, in which no such loss occurred.

Although these definitions were perfectly adequate at the time, it soon became obvious that notable exceptions existed and that a fundamentally sounder classification should be based on a description of the chain-growth mechanism. It is preferable to replace the term *condensation* with *step-growth* or *step-reaction*. Reclassification as step-growth polymerization now logically includes polymers such as polyurethanes, which grow by a step-reaction mechanism without elimination of a small molecule.

In this chapter, we shall examine the main features of step-growth polymerization, beginning with the simpler reactions that produce linear chains exclusively. This type of polymerization is used to produce some of the industrially important fibers such as nylon and terylene. A brief discussion of the more complex branching reactions follows to illustrate how the thermosetting plastics are formed.
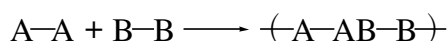
2.1 GENERAL REACTIONS

In any reaction resulting in the formation of a chain or network of high molar mass, the functionality (see Section 1.2) of the monomer is of prime importance. In step-growth polymerization, a linear chain of monomer residues is obtained by the stepwise intermolecular condensation or addition of the reactive groups in bifunctional monomers. These reactions are analogous to simple reactions involving monofunctional units as typified by a polyesterification reaction involving a diol and a diacid.

$$HO-R-OH + HOOC-R'-COOH \rightleftharpoons HO-R-OCO-R'-COOH + H_2O$$
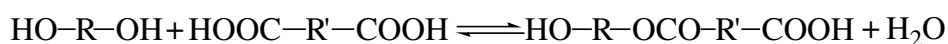
If the water is removed as it is formed, no equilibrium is established and the first stage in the reaction is the formation of a dimer, which is also bifunctional. As the reaction proceeds, longer chains, trimers, tetramers, and so on will form through

other esterification reactions, all essentially identical in rate and mechanism until, ultimately, the reaction contains a mixture of polymer chains of large molar masses M. However, the formation of samples with significantly large values of M is subject to a number of rather stringent conditions, which will be examined in greater detail later in this chapter.

Two major groups, both distinguished by the type of monomer involved, can be identified in step-growth polymerization. In the first group, two polyfunctional monomers take part in the reaction, and each possesses only one distinct type of functional group as in the previous esterification reaction, or more generally:
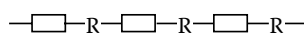
$$A\text{–}A + B\text{–}B \longrightarrow (\text{A–AB–B})$$

The second group is encountered when the monomer contains more than one type of functional group such as a hydroxyacid (HO—R—COOH), represented generally as A–B, where the reaction is

$$n\text{A–B} \longrightarrow (\text{AB})_n$$

or
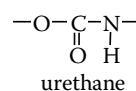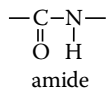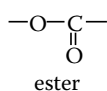
$$n(\text{HO–R–COOH}) \longrightarrow \text{H}(\text{ORCO})_n\text{OH}$$
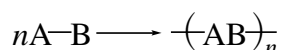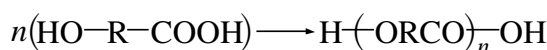
A large number of step-growth polymers have the basic structure

$$-\square-\text{R}-\square-\text{R}-\square-\text{R}-$$

where R can be $(\text{CH}_2)_x$ or ⬡— and the —$\square$— link is one of three important groups:

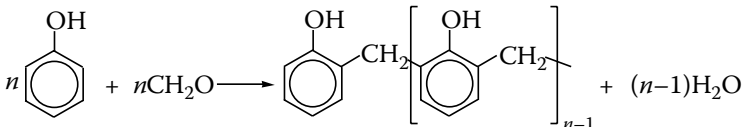|		
$-\text{O}-\underset{\text{O}}{\overset{\|}{\text{C}}}-$	$-\underset{\text{O}\ \ \text{H}}{\overset{\| \ \ \|}{\text{C}-\text{N}}}-$	$-\text{O}-\underset{\text{O}\ \ \text{H}}{\overset{\| \ \ \|}{\text{C}-\text{N}}}-$
ester	amide	urethane

Other links and groups are involved in these reactions, and some typical step-reaction polymers are shown in Table 2.1.

2.2 REACTIVITY OF FUNCTIONAL GROUPS

One basic simplifying assumption proposed by Flory, when analyzing the kinetics of step-growth systems, was that all functional groups can be considered as being equally reactive. This implies that a monomer will react with both monomer or polymer species with equal ease.

The progress of the reaction can be illustrated in Figure 2.1 where, after 25% reaction, the number-average chain length x_n is still less than two because monomers,

TABLE 2.1
Typical Step-Growth Polymerization Reactions

Polymer	Reaction

Polyester

$n\text{HO}(\text{CH}_2)_x\text{COOH} \longrightarrow \text{HO}\!\!-\!\!\big[(\text{CH}_2)_x\!\!-\!\!\underset{\overset{\|}{\text{O}}}{\text{C}}\!\!-\!\!\text{O}\big]_n\!\!-\!\!\text{H} + (n-1)\text{H}_2\text{O}$

Polyamide

$n\text{NH}_2\!\!-\!\!\text{R}\!\!-\!\!\text{COOH} \longrightarrow \text{H}\!\!-\!\!\big[\text{NH}\!\!-\!\!\text{R}\!\!-\!\!\text{CO}\big]_n\!\!-\!\!\text{OH} + (n-1)\text{H}_2\text{O}$

$n\text{NH}_2\!\!-\!\!\text{R}\!\!-\!\!\text{NH}_2 + n\text{HOOC}\!\!-\!\!\text{R'}\!\!-\!\!\text{COOH} \longrightarrow \text{H}\!\!-\!\!\big[\text{NH}\!\!-\!\!\text{R}\!\!-\!\!\text{NHCO}\!\!-\!\!\text{R'}\!\!-\!\!\text{CO}\big]\!\!-\!\!\text{OH} + (2n-1)\text{H}_2\text{O}$

Polyurethanes

$n\text{HO}\!\!-\!\!\text{R}\!\!-\!\!\text{OH} + \text{NCO}\!\!-\!\!\text{R'}\!\!-\!\!\text{NCO} \longrightarrow \big[\text{OROCONH-R'}\!\!-\!\!\text{NHCO}\big]_n$

Polyanhydride

$n\text{HOOC}\!\!-\!\!\text{R}\!\!-\!\!\text{COOH} \longrightarrow \text{HO}\!\!-\!\!\big[\text{OC}\!\!-\!\!\text{R}\!\!-\!\!\text{CO·O}\big]_n\!\!-\!\!\text{H} + (n-1)\text{H}_2\text{O}$

Polysiloxane

$n\text{HO}\!\!-\!\!\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{Si}}}\!\!-\!\!\text{OH} \longrightarrow \text{HO}\!\!-\!\!\Big[\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{Si}}}\!\!-\!\!\text{O}\Big]_n\!\!-\!\!\text{H} + (n-1)\text{H}_2\text{O}$

Phenol-formaldehyde

$$n + n\text{CH}_2\text{O} \longrightarrow \quad + \ (n-1)\text{H}_2\text{O}$$

$x_n = 1.3$ $x_n = 2$ $x_n = 4$
25 percent reaction   50 percent reaction   75 percent reaction
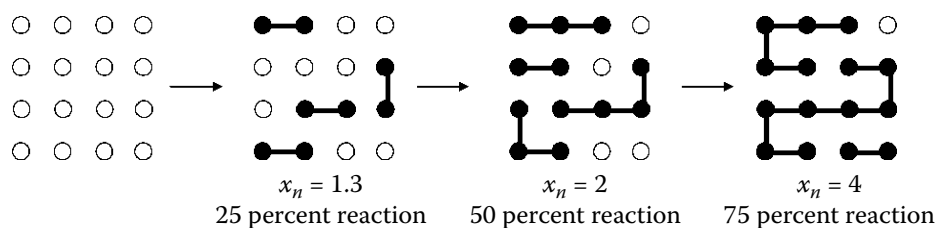
FIGURE 2.1 Diagrammatic representation of a step-growth polymerization.

being the most predominant species, will tend to react most often, and the reaction is mainly the formation of dimers and trimers. Even after 87.5% of the reaction, x_n will only be about 8, and it becomes increasingly obvious that if long chains are required, the reaction must be pushed toward completion.