

Chapter Two

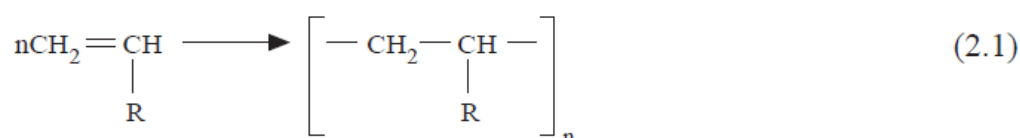
Polymerization Mechanisms

2.1 INTRODUCTION

Polymers are classified as addition or condensation polymers depending on the type of polymerization reaction involved in their synthesis. This classification scheme, however, does not permit a complete differentiation between the two classes of polymers. A more complete but still oversimplified scheme that is still based on the different polymerization processes places polymers into three classes: condensation, addition, and ring-opening polymers. This scheme reflects the structures of the starting monomers. Probably the most general classification scheme is based on the polymerization mechanism involved in polymer synthesis. Under this scheme, polymerization processes are classified as step-reaction (condensation) or chain-reaction (addition) polymerization. In this chapter, we will discuss the different types of polymers based on the different polymerization mechanisms.

2.2 CHAIN-REACTION POLYMERIZATION

Chain-reaction polymerization, an important industrial method of polymer preparation, involves the addition of unsaturated molecules to a rapidly growing chain. The most common unsaturated compounds that undergo chain-reaction polymerization are olefins, as exemplified by the following reaction of a generalized vinyl monomer.



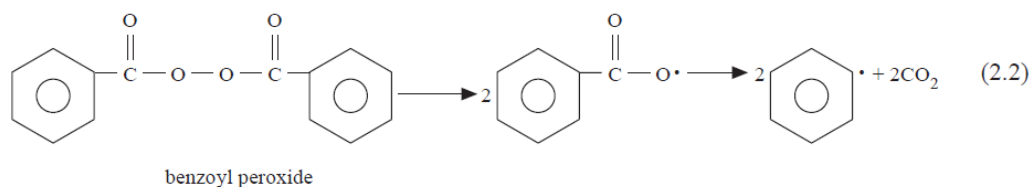
The growing polymer in chain-reaction polymerization is a free radical, and polymerization proceeds via chain mechanism. Chain-reaction polymerization is induced by the addition of free-radical-forming reagents or by ionic initiators. Like

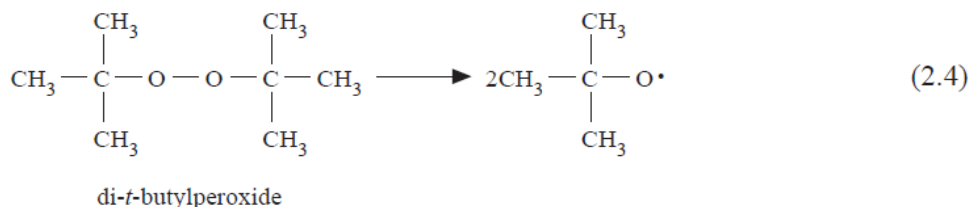
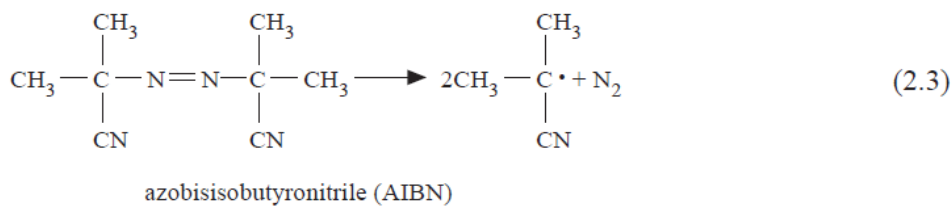
all chain reactions, it involves three fundamental steps: initiation, propagation, and termination. In addition, a fourth step called chain transfer may be involved.

A. INITIATION

Initiation involves the acquisition of an active site by the monomer. This may occur spontaneously by the absorption of heat, light (ultraviolet), or high-energy irradiation. But most frequently, initiation of free radical polymerization is brought about by the addition of small quantities of compounds called initiators.

Typical initiators include peroxides, azo compounds, Lewis acids, and organometallic reagents. However, while initiators trigger initiation of the chain and exert an accelerating influence on polymerization rate, they are not exactly catalysts since they are changed chemically in the course of polymerization. An initiator is usually a weak organic compound that can be decomposed thermally or by irradiation to produce free radicals, which molecules are containing atoms with unpaired electrons. A variety of compounds decompose when heated to form free radicals. Dialkyl peroxides (ROOR), diacylperoxides (RCO-O-O-CO-R), hydroperoxides (ROOH), and azo compounds (RN=NR) are typical organic compounds that can be decomposed thermally to produce free radicals. Benzoyl peroxide, azobisisobutyronitrile, and di-*t*-butylperoxide are commonly used free-radical initiators, as illustrated in Equations 2.2–2.4.





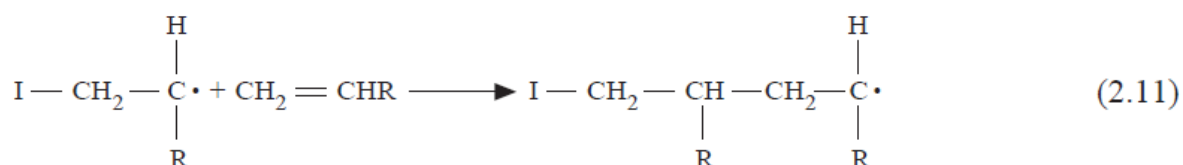
When choosing an initiator for free-radical polymerization, the important parameters that must be considered are the temperature range to be used for the polymerization and the reactivity of the radicals formed. The presence of certain promoters and accelerators and the nature of the monomer often affect the rate of decomposition of initiators. For example, the decomposition of benzoyl peroxide may be accelerated at room temperature by employing ternary or quaternary amines. Free-radical initiation processes do not require stringent exclusion of atmospheric moisture, but can be inhibited by substances such as oxygen. Free radicals are inactivated by reaction with oxygen to form peroxides or hydroperoxides. For monomers such as styrene and methylmethacrylate that are susceptible to such inhibition, initiation reactions are carried out in an oxygen-free atmosphere such as nitrogen. It must be emphasized also that organic peroxides, when subjected to shock or high temperature, can detonate. Therefore these compounds must be handled with caution.

The initiation of polymerization occurs in two successive steps. The first step involves the formation of radicals according to the processes discussed above.

The second step is the addition of the initiator radical to a vinyl monomer molecule.

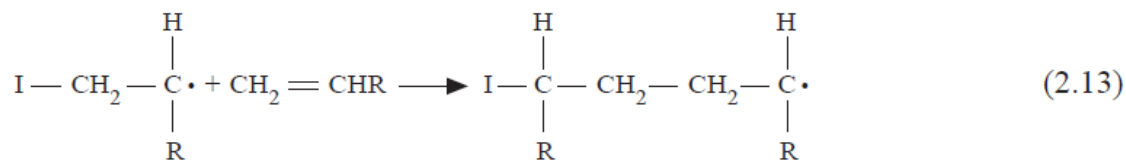
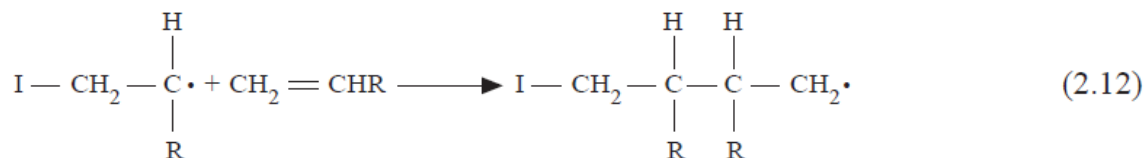
B. PROPAGATION

During propagation, the initiated monomer described above adds other monomers — usually thousands of monomer molecules. This involves the addition of a free radical to the double bond of a monomer, with regeneration of another radical. The active center is thus continuously relocated at the end of the growing polymer chain (Equation 2.11).



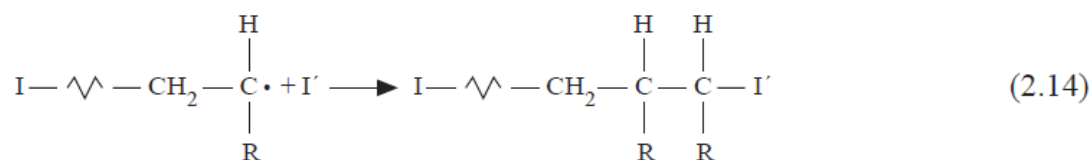
Propagation continues until the growing chain radical is deactivated by chain termination or transfer as discussed below.

The substituted carbon atom is regarded as the head and the unsubstituted carbon atom the tail of the vinyl monomer. There are, therefore, three possible ways for the propagation step to occur: head to-tail (Equation 2.11), head-to-head (Equation 2.12), and tail-to-tail (Equation 2.13). A random distribution of these species along the molecular chain might be expected. It is found, however, that head-to tail linkages in which the substituents occur on alternate carbon atoms predominate; only occasional interruptions of this arrangement by head-to-head and tail-to-tail linkages occur. In addition, exclusive head-to-head or tail-to-tail arrangements of monomers in the chain are now known.

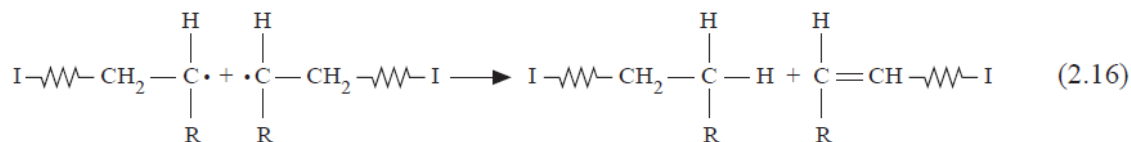
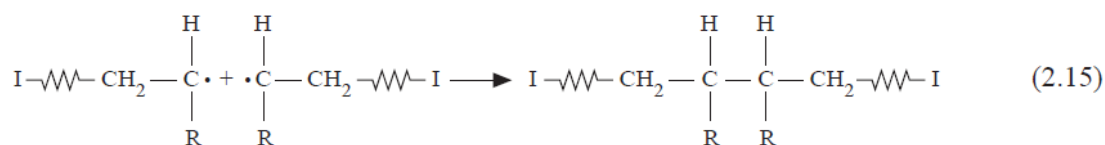


C. TERMINATION

In termination, the growth activity of a polymer chain radical is destroyed by reaction with another free radical in the system to produce polymer molecule(s). Termination can occur by the reaction of the polymer radical with initiator radicals (Equation 2.14). This type of termination process is unproductive and can be controlled by maintaining a low rate for initiation.



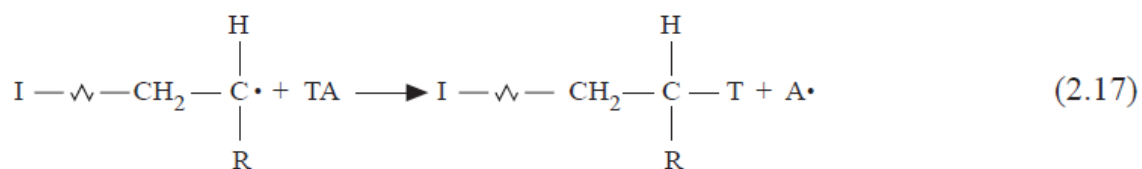
The termination reactions that are more important in polymer production are combination (or coupling) and disproportionation. In termination by combination, two growing polymer chains react with the mutual destruction of growth activity (Equation 2.15), while in disproportionation a labile atom (usually hydrogen) is transferred from one polymer radical to another (Equation 2.16).



Coupling reactions produce a single polymer, while disproportionation results in two polymers from the two reacting polymer chain radicals. The predominant termination reaction depends on the nature of the reacting monomer and the temperature. Since disproportionation requires energy for breaking of chemical bonds, it should become more pronounced at high reaction temperatures; combination of growing polymer radicals predominates at low temperatures.

D. CHAIN TRANSFER

Ideally, free-radical polymerization involves three basic steps: initiation, propagation, and termination, as discussed above. However, a fourth step, called chain transfer, is usually involved. In chain-transfer reactions, a growing polymer chain is deactivated or terminated by transferring its growth activity to a previously inactive species, as illustrated in Equation 2.17.



The species, TA, could be a monomer, polymer, solvent molecule, or other molecules deliberately or inadvertently introduced into the reaction mixture. Depending on its reactivity, the new radical, A^\bullet , may or may not initiate the growth of another polymer chain. If the reactivity of A^\bullet is comparable to that of the propagating chain radical, then a new chain may be initiated. If its reactivity toward a monomer is less than that of the propagating radical, then the overall reaction rate is retarded. If A^\bullet is unreactive toward the monomer, the entire reaction could be inhibited. Transfer reactions do not result in the creation or destruction of radicals; at any instant, the overall number of growing radicals remains unchanged. However, the occurrence of transfer reactions results in the reduction of the average polymer chain length, and in the case of transfer to a polymer it may result in branching.

2.3 IONIC AND COORDINATION POLYMERIZATIONS

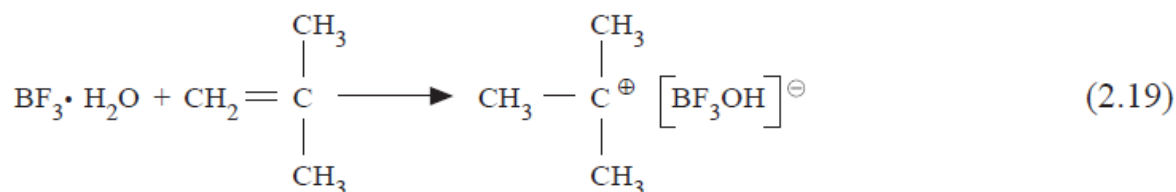
As noted earlier, chain-reaction polymerization may be classified as free-radical, cationic, anionic, or coordination polymerization depending on the nature of the reactive center. The growing polymer molecule is associated with counterions in ionic (cationic and anionic) polymerization or with a coordination complex in coordination polymerization. Ionic polymerizations involve chain carriers or reactive centers that are organic ions or charged organic groups. In anionic polymerization, the growing chain end carries a negative charge or carbanions, while cationic polymerization involves a growing chain end with a positive charge or carbonium (carbenium) ion. Coordination polymerization is thought to involve the formation of a coordination compound between the catalyst, monomer, and growing chain.

The mechanisms of ionic and coordination polymerizations are more complex and are not as clearly understood as those of free radical polymerization. Initiation of ionic polymerization usually involves the transfer of an ion or an electron to or

from the monomer. Many monomers can polymerize by more than one mechanism, but the most appropriate polymerization mechanism for each monomer is related to the polarity of the monomers and the Lewis acid–base strength of the ion formed.

A. CATIONIC POLYMERIZATION

Monomers with electron-donating groups like isobutylene form stable positive charges and are readily converted to polymers by cationic catalysts. Any strong Lewis acid like boron trifluoride (BF₃) or Friedel–Crafts catalysts such as AlCl₃ can readily initiate cationic polymerization in the presence of a cocatalyst like water, which serves as a Lewis base or source of protons. During initiation, a proton adds to the monomer to form a carbonium ion, which forms an association with the counterion. This is illustrated for isobutylene and boron trifluoride in Equation 2.19:



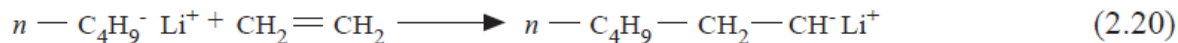
Propagation involves the consecutive additions of monomer molecules to the carbonium ion at the growing chain end. Termination in cationic polymerization usually involves rearrangement to produce a polymer with an unsaturated terminal unit and the original complex or chain transfer to a monomer and possibly to the polymer or solvent molecule. Unlike free-radical polymerization, termination by combination of two cationic polymer growing chains does not occur.

Cationic polymerizations are usually conducted in solutions and frequently at temperatures as low as –80 to –100°C. Polymerization rates at these low temperature conditions are usually fast. The cation and the counterion in cationic polymerization remain in close proximity. If the intimate association between the

ion pair is too strong, however, monomer insertion during propagation will be prevented. Therefore the choice of solvent in cationic polymerization has to be made carefully; a linear increase in polymer chain length and an exponential increase in the reaction rate usually occur as the dielectric strength of the solvent increases.

B. ANIONIC POLYMERIZATION

Monomers that are suitable for anionic polymerization generally contain electron-withdrawing substituent groups. Typical monomers include styrene, acrylonitrile, butadiene, methacrylates, acrylates, ethylene oxide, and lactones. The initiator in anionic polymerization may be any compound providing a strong nucleophile, including Grignard reagents and other organometallic compounds. Initiation involves the addition of the initiator to the double bond of the monomer, as illustrated for styrene and butyllithium in Equation 2.20.

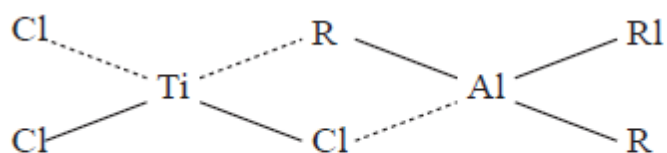


The reaction produces a carbanion at the head end to which is associated the positively charged lithium counterion. Propagation occurs by the successive insertion of monomer molecules by anionic attack of the carbanion. No chain transfer or branching occurs in anionic polymerization, particularly if reactions are carried out at low temperatures. Termination of the growth activity of the polymer chain takes place either by the deliberate or accidental introduction into the system of oxygen, carbon dioxide, methanol, water, or other molecules that are capable of reacting with the active chain ends. We note that in anionic polymerization as well as free-radical polymerization, the initiator or part of it becomes part of the resulting polymer molecule, attached to the nongrowing chain end. This contrasts

with cationic polymerization where the catalyst is necessary for initiation and propagation, but is regenerated at the termination step.

C. COORDINATION POLYMERIZATION

Monomers with side groups asymmetrically disposed with respect to the double bond are capable of producing polymers in which the side groups have a specific stereochemical or spatial arrangement (isotactic or syndiotactic). In both cationic and anionic polymerizations, the association of initiating ion and counterion permits a preferential placement of asymmetric substituted monomers, the extent of which depends on the polymerization conditions. Unbranched and stereospecific polymers are also produced by the use of Ziegler–Natta catalysts. These are complex catalyst systems derived from a transition metal compound from groups IVB to VIIB of the periodic table and an organometallic compound usually from a group IA or IIIA metal. A typical catalyst complex is that formed by trialkyl aluminum and titanium trichloride as shown below:

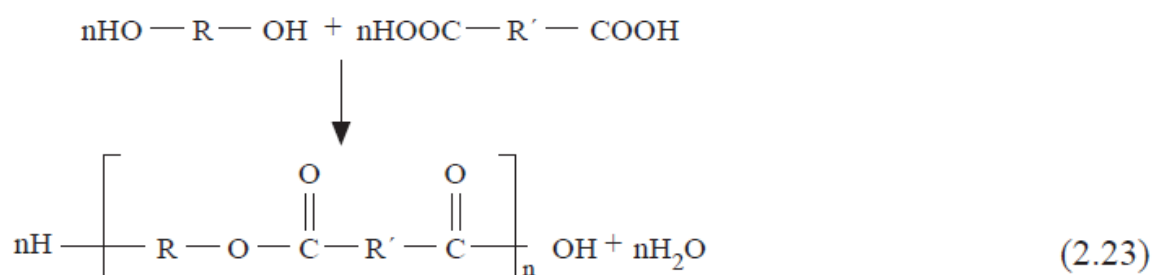


Monoolefins such as propylene and dienes such as butadiene and isoprene can be polymerized using Ziegler–Natta coordination catalysts. The catalysts function by forming transient π -complexes between the monomers and the transition metal species. The initiating species is a metal–alkyl complex and propagation involves the consecutive insertion of monomer molecules into a polarized titanium–carbon bond. Coordination polymerizations may be terminated by introducing poisons

such as water, hydrogen, aromatic alcohols, or metals like zinc into the reacting system.

2.4 STEP-GROWTH POLYMERIZATION

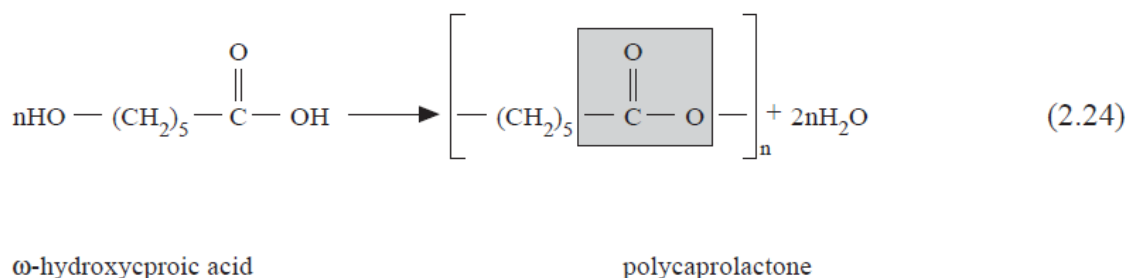
Step-growth polymerization involves a series of reactions in which any two species (monomers, dimers, trimers, etc.) can react at any time, leading to a larger molecule. Most step-growth polymerizations, as we shall see presently, involve a classical condensation reaction such as esterification, ester interchange, or amidization. In step-growth polymerization, the stepwise reaction occurs between pairs of chemically reactive or functional groups on the reacting molecules. In most cases, step-growth polymerization is accompanied by the elimination of a small molecule such as water as a by-product. A typical step-growth polymerization of the condensation type is the formation of polyester through the reaction of a glycol and a dicarboxylic acid, as shown in Equation 2.23



Where R and R' are the unreactive part of the molecules.

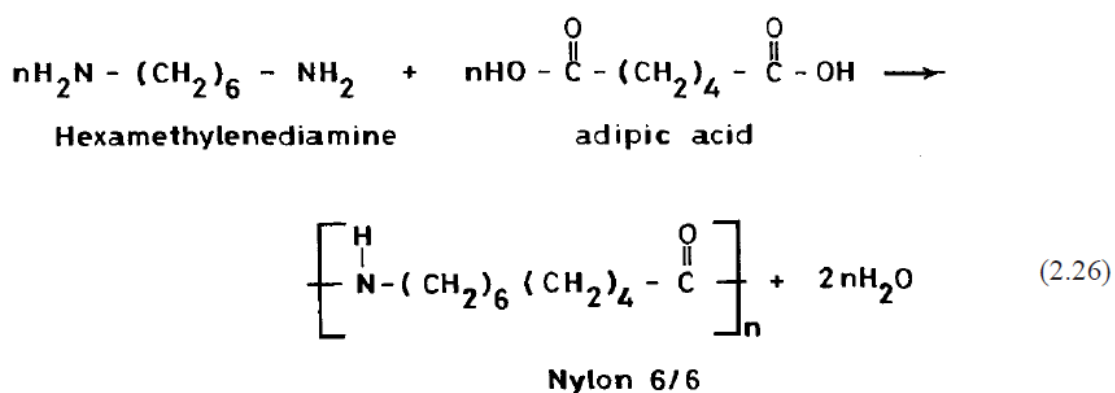
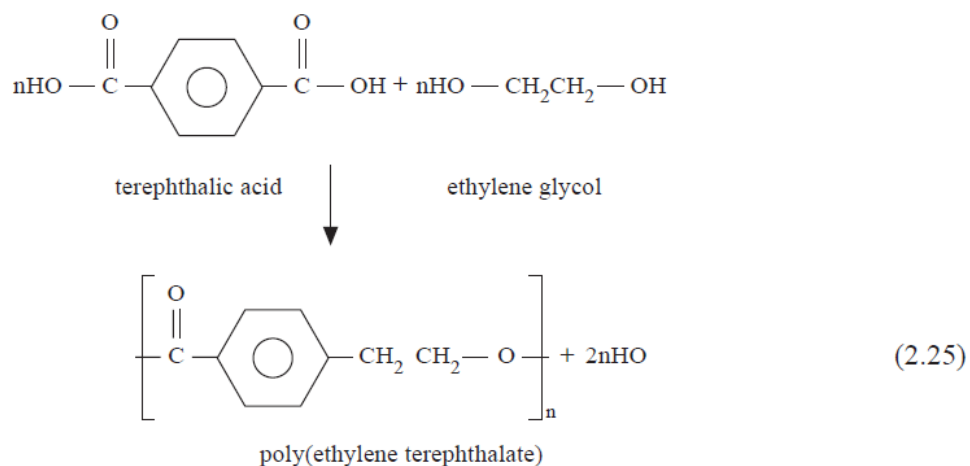
Step-growth polymerizations generally involve either one or more types of monomers. In either case, each monomer has at least two reactive (functional) groups. In cases where only one type of monomer is involved, which is known as A-B step-growth polymerization, the functional groups on the monomer are different and capable of intramolecular reactions. An example is the formation of

aliphatic polyester by the self-condensation of ω -hydroxycaproic acid (Equation 2.24).



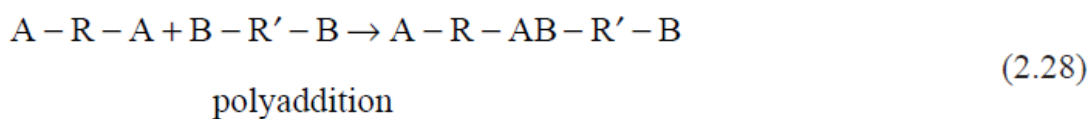
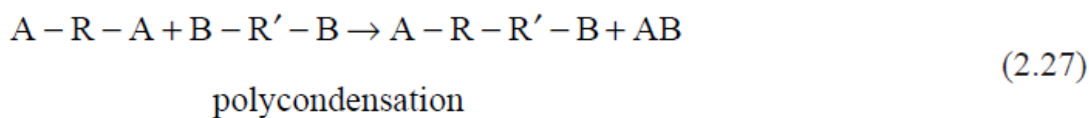
Here, each molecule contains two different functional groups: a hydroxyl group ($-\text{OH}$) and a carboxylic acid group ($-\text{COOH}$). These react to form a series of ester linkages ($-\text{O} \parallel \text{C} - \text{O}-$) shown in the shaded box.

In those cases where more than one type of molecule is involved, the functional groups on each type of monomer are the same, but capable of intermolecular reaction with the other type of monomer. This is known as the A–A/B–B step-growth polymerization and is exemplified by the preparation of poly (ethylene terephthalate) and nylon 6, 6 (Equations 2.25 and 2.26).

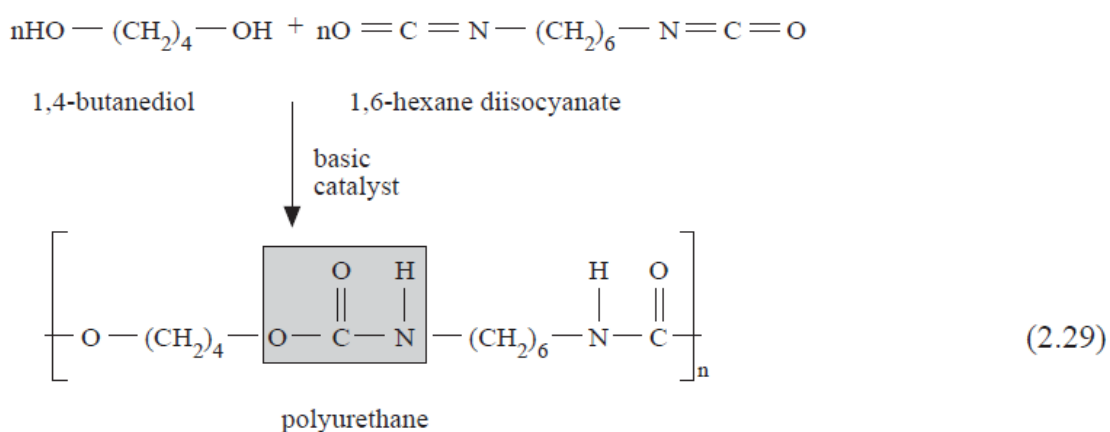


In Equation 2.25, for example, poly (ethylene terephthalate) is formed from the condensation of a dicarboxylic acid and a diol.

Step-growth polymerizations can be divided into two main categories: polycondensation, in which a small molecule is eliminated at each step, as discussed above; and polyaddition, in which, as the name suggests, monomers react without the elimination of a small molecule. These are shown in Equations 2.27 and 2.28, respectively, where R and R' are the nonreactive portions of the molecules.



An example of polyaddition-type step-growth polymerization is the preparation of polyurethane by the ionic addition of diol (1, 4 butanediol) to a diisocyanate (1, 6 hexane diisocyanate) (Equation 2.29).



Another example of polyaddition-type step-growth polymerization is the preparation of polyurea from the reaction of diisocyanate and diamine, as shown in Equation 2.30.

