9

Chain-Growth Polymerization: General Theory and Polymer Structure

Chain-growth polymerization is based on the application of a free-radical or ionic reaction to a polymerization scheme in such a manner that the primary growth of a single polymer chain or macromolecule results from the propagation of one kinetic chain reaction. A kinetic chain reaction is a series of closely related reactions caused by one, and only one, initiator (not catalyst) molecule. That is, a kinetic chain reaction generally consists of at least three types of reactions: (*1*) an initiation step, which may involve more than one reaction; (*2*) a propagation step, which involves a long sequence of identical reactions repeated many times; and (*3*) a termination step, which kills the kinetic chain reaction.

It often happens that a single kinetic chain reaction may cause the formation of more than one polymer chain molecule through a reaction in which the active site is transferred without loss of activity from the end of a growing polymer chain molecule to another molecule from which a new polymer chain molecule can grow. This type of reaction is termed a chain-transfer reaction. The net effect of this reaction is to terminate the growth of one polymer chain molecule and to initiate the growth of another, but the continuity of that kinetic chain reaction endures. These reactions are illustrated schematically in Equations (9-1)–(9-4), in which an asterisk is

$$\textit{Initiation} \quad \begin{aligned} &A \longrightarrow A^* \\ &A^* + B \longrightarrow AB^* \end{aligned} \tag{9-1}$$

$$\textit{Propagation} \quad \begin{aligned} &AB^* + B \longrightarrow AB_2^* \xrightarrow{B} AB_3^* \\ &AB_3^* + nB \;\substack{\longrightarrow \\ \longrightarrow \\ \longrightarrow}\; AB_{n+3}^* \end{aligned} \tag{9-2}$$

$$\textit{Transfer} \quad AB_n^* + C \longrightarrow AB_n + C^* \tag{9-3}$$

$$\textit{Termination} \quad AB_n^* \longrightarrow AB_n \tag{9-4}$$

used to denote the location of an active species, either a radical or an ion, and symbols A, B, and C refer to an initiator, a monomer, and a molecule with a chain transfer site, respectively.

Each of the basic steps of a kinetic chain reaction, i.e., initiation, propagation, and termination, may involve more than one type of reactant or reaction. For example, the bromination of toluene initiated by a peroxide is a free-radical chain reaction in which the initiation step (9-5) is comprised of two types of reactions: (*1*) decomposition of the peroxide (9-5*a*) to peroxy radicals (or radicals derived therefrom), and (*2*) reaction of a peroxy radical (9-5*b*) with either molecular bromine or toluene (mostly the latter) to form either a bromine atom or a benzyl radical, respectively. Each peroxide dissociation reaction creates two radicals and starts two kinetic chains.

$$\begin{aligned}
&(a)\ \mathrm{ROOR} \longrightarrow 2\mathrm{RO}\cdot \\
&(b)\ \mathrm{RO}\cdot + \mathrm{Br_2} \longrightarrow \mathrm{ROBr} + \mathrm{Br}\cdot \\
&\qquad \mathrm{RO}\cdot + \mathrm{PhCH_3} \longrightarrow \mathrm{ROH} + \mathrm{Ph\dot{C}H_2}
\end{aligned} \qquad (9\text{-}5)$$

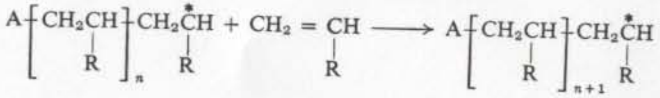
The propagation step (9-6) in this particular kinetic chain reaction also consists of two distinct reactions which are repeated in a sequential pair many times over. These reactions are: (*1*) reaction of a bromine atom (9-6*a*) with toluene to form a benzyl radical and hydrogen bromide, and (*2*) reaction of a benzyl radical (9-6*b*) with molecular bromine to form benzyl bromide, which is the desired product of the overall chain reaction, and a new bromine atom to supply reaction (9-6*a*). The propagation step, therefore, has two fundamental characteristics, which are: (*1*) that the number of active species (in this case, radicals) remains constant, and (*2*) that the same reactions are repeated in the same order throughout the lifetime of the kinetic chain reaction. That is, each pair of reactions in the propagation step (9-6) results in the formation of one molecule of product and the reformation of an active bromine atom, so that the propagation step in this case is a closed-loop series of chain-transfer reactions.

$$\begin{aligned}
&(a)\ \mathrm{Br}\cdot + \mathrm{PhCH_3} \longrightarrow \mathrm{HBr} + \mathrm{Ph\dot{C}H_2} \\
&(b)\ \mathrm{Ph\dot{C}H_2} + \mathrm{Br_2} \longrightarrow \mathrm{PhCH_2Br} + \mathrm{Br}\cdot
\end{aligned} \qquad (9\text{-}6)$$

The termination step (9-7) can be any one of three reactions, each of which involves the combination of two free radicals and, therefore, the destruction of two kinetic chains. The three possibilities are: (*1*) reaction of two bromine atoms (9-7*a*) to reform molecular bromine, or (*2*) reaction of two benzyl radicals (9-7*b*) to form bibenzyl, or (*3*) reaction of a bromine atom and a benzyl radical (9-7*c*) to form benzyl bromide. In summary, the net effect of this overall kinetic chain reaction is that one molecule of a peroxide can cause the formation of hundreds or thousands of molecules of benzyl bromide.

$$\begin{aligned}
&(a)\ 2\mathrm{Br}\cdot \longrightarrow \mathrm{Br_2} \\
&(b)\ 2\mathrm{Ph\dot{C}H_2} \longrightarrow \mathrm{PhCH_2CH_2Ph} \\
&(c)\ \mathrm{Br}\cdot + \mathrm{Ph\dot{C}H_2} \longrightarrow \mathrm{PhCH_2Br}
\end{aligned} \qquad (9\text{-}7)$$

A chain-growth polymerization reaction is a simple variation of this scheme in which each kinetic chain reaction, instead of forming thousands of small and separate molecules, forms a macromolecule containing thousands of covalently bonded reactant molecules. In the homopolymerization of a vinyl monomer, for example, the propagation step consists of only one type of reaction, that is, a one-step sequence (9-8).



$$\mathrm{A}\left[\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\right]_n\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\overset{*}{\mathrm{C}}\mathrm{H}}} + \mathrm{CH_2}=\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{A}\left[\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}\right]_{n+1}\mathrm{CH_2}\underset{\mathrm{R}}{\underset{|}{\overset{*}{\mathrm{C}}\mathrm{H}}} \qquad (9\text{-}8)$$

9.1. CHARACTERISTICS OF CHAIN REACTIONS

The rates of chain and nonchain reactions under identical conditions generally show fundamentally different patterns. In nonchain or step reactions, the rate of disappearance of reactants generally decreases with time, as shown schematically in Figure 9-1. The highest rate is observed at the beginning of the reaction simply because the reactants are present in the highest concentration. Furthermore, because separate initiation, propagation, and termination steps generally do not occur in nonchain reactions and only one type of reaction predominates, the overall rate decreases in a uniform manner.

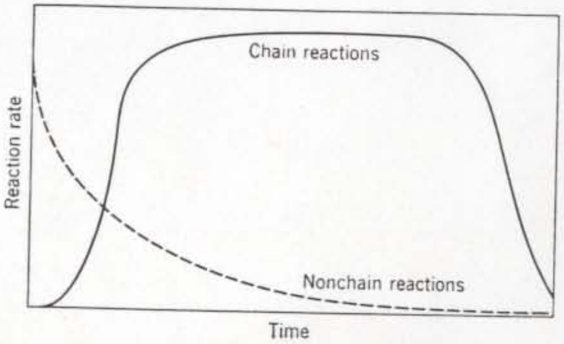


Figure 9-1. Rate versus time behavior for chain and nonchain reactions.

Chain reactions, on the other hand, generally begin at zero rate, because the active initiating species must first be generated from the more stable initiator molecule (9-1). In most cases, the rate quickly rises to a maximum and remains more or less constant at that level throughout the lifetime of the reaction before falling off when the initiator is consumed, as shown schematically in Figure 9-1. This extended constant-rate period, which occurs in many chain reactions, is the basis for the steady-state assumption used as the basis for the derivation of kinetic equations of chain reactions.

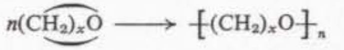
The time interval required before a significant rate of reaction is detected in a chain reaction is termed the induction period, and this type of behavior is observed in both free-radical and ionic chain-growth polymerization reactions. The need for an induction period in an ionic polymerization reaction is not as obvious as it is for a free-radical polymerization reaction because a highly reactive ionic reagent can be added directly to the reaction mixture in the former, and it is generally not possible to add reactive free radicals directly in the form of a reagent. Nevertheless, an induction period is observed if the ionic initiator is less reactive than the ion formed from the monomer or if the ionic initiator molecules are associated in the form of aggregates, and dissociation of the aggregates must precede the initiation reaction. As a result, most anionic and cationic polymerization reactions, for one reason or another, show induction periods.

A characteristic of chain reactions not observed in nonchain reactions is that many of the former are extremely susceptible to rate retardation by traces of other substances. Substances which slow down chain reactions are termed retarders or inhibitors according, respectively, to whether they merely reduce the rate or essentially stop the reaction altogether for a period of time. The true difference between retarders and inhibitors, however, is generally one of degree rather than kind.

9.2. POLYMER-FORMING CHAIN REACTIONS

Polymer-forming chain reactions of all types are referred to in the present classification scheme as chain-growth polymerization reactions, which are distinguished from step-growth polymerization reactions on the basis of the characteristics of the growth of the polymer chains. The principal feature distinguishing the two, as discussed in Section 1.1.5, is the relationship between the amount of monomer consumed in the polymerization reaction and the average degree of polymerization of the polymer produced. In an ideal, linear, chain-growth polymerization reaction, polymer molecules with a high degree of polymerization are formed from the very start, and the high percentage of monomer conversion so necessary in a step-growth polymerization reaction is unnecessary to achieve high molecular weight polymers.

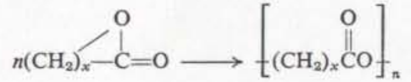
Most examples of chain-growth polymerization reactions are either multiple-bond addition reactions or ring-opening reactions. At present, the single most important organic polymerization reaction is the addition reaction of a radical or an ion to a carbon–carbon double bond. The next general type in importance is the ring-opening reactions of a number of different types of heterocyclic monomers including principally cyclic ethers, Reaction (9-9), lactams, Reaction (9-10), and lactones, Reaction (9-11).



$$n(\mathrm{CH_2})_x\mathrm{O} \longrightarrow \left[\!\!-(\mathrm{CH_2})_x\mathrm{O}-\!\!\right]_n \qquad (9\text{-}9)$$

$$n(\mathrm{CH_2})_x\!-\!\overset{\mathrm{NH}}{\overset{|}{\mathrm{C}}}\!=\!\mathrm{O} \longrightarrow \left[-(\mathrm{CH_2})_x\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH}-\right]_n \qquad (9\text{-}10)$$

Other than addition reactions to a carbon–carbon double bond, the only multiple-bond addition reaction presently receiving very much attention is the addition polymerization of the carbon–oxygen double bond in aldehydes, Reaction (9-12).



$$n(\mathrm{CH_2})_x\!-\!\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}\!=\!\mathrm{O} \longrightarrow \left[-(\mathrm{CH_2})_x\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}-\right]_n \qquad (9\text{-}11)$$

$$n\mathrm{RCHO} \longrightarrow \left[\!\!-\mathrm{CHRO}-\!\!\right]_n \qquad (9\text{-}12)$$

Of the two types of chain-growth polymerization reactions, ionic or free radical, the former seems to be applicable to a wider variety of monomers. That is, in general, a free-radical growth mechanism cannot be applied to a ring-opening polymerization reaction, and free-radical reactions are limited almost entirely to the addition polymerization of monomers containing carbon–carbon double bonds. On the other hand, both anionic and cationic chain-growth reactions can be applied to a wide variety of multiple-bond addition reactions, to ring-opening reactions, and to sundry other less common polymerization schemes covered in Chapters 13 and 14.

9.3. COMPARISON OF FREE-RADICAL AND IONIC OLEFIN POLYMERIZATION REACTIONS

There are important fundamental differences in the mechanisms of free-radical compared to ionic chain-growth polymerization reactions when each type is applied to the same olefin monomer. Indeed, in some of the mechanistic details there are even greater differences between cationic and anionic polymerization mechanisms under certain conditions than between either one of these and the free-radical mechanism for the same monomer. These differences involve not only the rate and manner of polymer chain-growth for each type of initiation, but also the selection of monomers suitable for each type of growth. Table 9-1 attempts to summarize the behavior of many of the important olefin monomers according to their experimentally proven ability to be polymerized by either radical or ionic mechanisms, or both, to high molecular weight polymers.[1] The initiation mechanisms considered in this tabulation include both homogeneous and heterogeneous polymerization reactions, and while it appears likely that the latter can include both ionic and free-radical propagation mechanisms,[2] no attempt is made in Table 9-1 to differentiate among these for heterogeneous initiation.

Table 9-1

Applicability of Various Types of Initiation Mechanisms to the Polymerization of Olefin Monomers[a]

		Homogeneous initiation			
Olefin monomer	Monomer structure	Free radical	Anionic	Cationic	Heterogeneous initiation
Ethylene	$CH_2{=}CH_2$	+	−	+	+
Propene	$CH_2{=}CHMe$	−	−	−	+
Butene-1	$CH_2{=}CHEt$	−	−	−	+
Isobutene	$CH_2{=}CMe_2$	−	−	+	−
Butadiene-1,3	$CH_2{=}CH{-}CH{=}CH_2$	+	+	−	+
Isoprene	$CH_2{=}C(Me){-}CH{=}CH_2$	+	+	−	+
Styrene	$CH_2{=}CHPh$	+	+	+	+
Vinyl chloride	$CH_2{=}CHCl$	+	−	−	+
Vinylidene chloride	$CH_2{=}CCl_2$	+	+	−	−
Vinyl fluoride	$CH_2{=}CHF$	+	−	−	−
Tetrafluoroethylene	$CF_2{=}CF_2$	+	−	−	+
Vinyl ethers	$CH_2{=}CHOR$	−	−	+	+
Vinyl esters	$CH_2{=}CHOCOR$	+	−	−	−
Acrylic esters	$CH_2{=}CHCOOR$	+	+	−	+
Methacrylic esters	$CH_2{=}C(Me)COOR$	+	+	−	+
Acrylonitrile	$CH_2{=}CHCN$	+	+	−	+

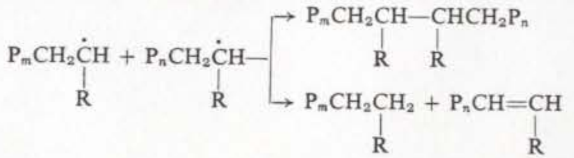
[a] Symbols: +, monomer can be polymerized to high molecular weight polymer by this form of initiation; − no polymerization reaction occurs or only low molecular weight polymers or oligomers are obtained with this type of initiator.

Of the many intimate details of mechanism and behavior by which homogeneous free-radical, anionic, and cationic polymerization reactions differ for olefin monomers, the most important are probably the following[3]:

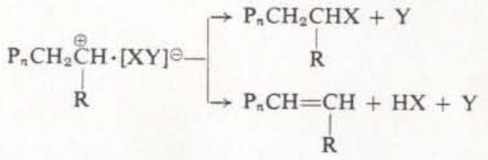
(*1*) Free-radical endgroups on growing polymer chains are truly free

species, but anionic and cationic endgroups always have counterions, more or less associated, except possibly for some very rare cases, such as in solid-state polymerization reactions. How tightly associated the counterion is to the ionic site in the endgroup depends upon such factors as the stability of the ionic endgroup, the type of counterion, the polarity of the reaction medium, the temperature, the presence of extraneous salts, and other factors. Tight ion-pair formation between the polymer chain endgroup and the counterion or ion solvation to have a considerable effect on the course of the polymerization reaction, particularly on such factors as the rate of polymerization, the rate of termination, the stereospecificity of monomer incorporation into the polymer chain, and the reactivity ratios in copolymerization reactions. In free-radical propagation, it is generally felt that solvent polarity exerts no influence on either rate or stereospecificity of homopolymerization or on reactivity ratios in copolymerization.

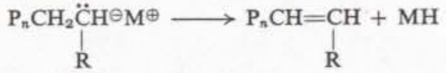
(*2*) Radical, anionic, and cationic polymerization reactions show distinctly different termination mechanisms, but the behaviors of radical and cationic polymerization reactions in this respect are, in general, more closely related than are the behaviors of cationic and anionic polymerization reactions. Radical and most cationic polymerization reactions have two types of facile kinetic chain termination reactions: namely, combination and disproportionation. In a radical polymerization reaction, both combination (9-13) and disproportionation (9-14) reactions involve two


$$\mathrm{P}_m\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \mathrm{P}_n\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}} \to \mathrm{P}_m\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}}-\underset{\mathrm{R}}{\underset{|}{\mathrm{C}\mathrm{H}}}\mathrm{CH}_2\mathrm{P}_n \qquad (9\text{-}13)$$
$$\mathrm{P}_m\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}} + \mathrm{P}_n\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\dot{\mathrm{C}}\mathrm{H}}} \to \mathrm{P}_m\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}_2}} + \mathrm{P}_n\mathrm{CH}{=}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}} \qquad (9\text{-}14)$$

growing polymer chains. In a cationic polymerization reaction, on the other hand, a type of combination (9-15) and disproportionation (9-16) reactions occur between the endgroup and the counterion of a single active polymer chain; anion capture and proton release are more appropriate terms.


$$\mathrm{P}_n\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\overset{\oplus}{\mathrm{C}}\mathrm{H}}}\cdot[\mathrm{XY}]^{\ominus} \to \mathrm{P}_n\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\mathrm{C}\mathrm{HX}}} + \mathrm{Y} \qquad (9\text{-}15)$$
$$\mathrm{P}_n\mathrm{CH}_2\underset{\mathrm{R}}{\underset{|}{\overset{\oplus}{\mathrm{C}}\mathrm{H}}}\cdot[\mathrm{XY}]^{\ominus} \to \mathrm{P}_n\mathrm{CH}{=}\underset{\mathrm{R}}{\underset{|}{\mathrm{CH}}} + \mathrm{HX} + \mathrm{Y} \qquad (9\text{-}16)$$

In contrast, most anionic and some cationic polymerization reactions are considered to have no facile or inherent termination step, excluding of course, secondary reactions between a carbanion or carbonium ion endgroup and an active solvent or an impurity, which can also occur in all types of polymerization reactions. For this reason, the active polymeric products of an anionic polymerization reaction or of selected cationic polymerization reactions before quenching have been termed living polymers. This generalization does not apply to all anionic systems because, in some of these, an intramolecular disproportionation type of termination reaction (9-17) is possible, and this type of termination reaction also occurs



$$\mathrm{P_nCH_2}\underset{\substack{|\\ \mathrm{R}}}{\ddot{\mathrm{C}}}\mathrm{H}^{\ominus}\mathrm{M}^{\oplus} \longrightarrow \mathrm{P_nCH{=}}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{H} + \mathrm{MH} \tag{9-17}$$

in heterogeneous polymerization reactions. Free-radical and cationic polymerization reactions are also alike in the extent to which chain-transfer reactions occur (that is, polymer termination without kinetic termination), while chain transfer in anionic polymerization is of negligible importance.

(*3*) Because the termination reactions in a free-radical polymerization reaction are bimolecular and of such high rates as compared to the unimolecular termination reactions in ionic polymerization reactions, it is possible to maintain a much higher concentration of growing polymer chains in an ionic reaction. That is, because termination in a free-radical polymerization reaction occurs by the reaction of the active endgroups of two growing polymer chains, in order to prepare high molecular weight polymers, the concentration of growing polymer chains must be maintained at a very low level, approximately 10^{-8} to 10^{-9} M. In anionic or cationic polymerizations, on the other hand, there is no tendency for two polymer chain endgroups of like ionic charge to react, and much higher concentrations of growing polymer chains may be maintained without penalty to the molecular weights produced. For this reason, concentrations of carbanion or carbonium ion growing polymer chains in homogeneous polymerization reactions may easily reach 10^{-2} to 10^{-3} M, and because of these high concentrations, the rates of ionic polymerization reactions can be 10^4–10^5 times higher than that of a free-radical polymerization reaction of the same monomer, even though the activation energies for propagation are comparable.

An important practical difference between free-radical and ionic polymerization reactions in general is the greater versatility of physical methods available for carrying out a polymerization reaction by free-radical initiation and growth. Free-radical polymerization reactions can be initiated effectively in gas, solid, and liquid phases, and for the latter, procedures involving bulk, solution, precipitation, suspension, and emulsion techniques have been applied. Each of these techniques has its own peculiar characteristics, advantages, and special applications. Ionic polymerization reactions in contrast, are limited experimentally almost entirely to solution or bulk methods, although crystalline, solid-state polymerization reactions have been observed in a number of cases. A wider variety of physical procedures is available for radical polymerization reactions in part because of the unreactivity of water toward free radicals. Suspension and emulsion systems are generally based upon the use of water as the continuous phase and a hydrophobic monomer as the discontinuous phase.

9.4. LIVING POLYMERS

The technique of emulsion polymerization applied to free-radical initiation overcomes to some degree the problem of high termination rates which occurs when attempts are made to increase the rate of a polymerization reaction by increasing the concentration of growing polymer chains. As will be discussed in detail in Chapter 11, the number of growing chains in an emulsion system is limited to either zero or one for a given reaction locus in the discontinuous phase, so that premature biradical termination is largely prevented.

A similar deterrent may also be effected in free-radical polymerization reactions initiated either in the gas phase or in the solid state, and in certain radical polymerization reactions which involve precipitation of the growing polymer chains in the reaction medium. For polymerization reactions initiated in the gas phase (that is, in the monomer vapor), it has been suggested that the fog formed very early in the reaction is composed of many fine droplets each containing only one active growing chain very much like that in an emulsion polymerization reaction. In a related manner, in solid-state polymerization reactions of crystalline monomers, termination is prevented by the presence of dislocations and grain boundaries within the crystals which prevent the radical endgroups of two growing polymer chains from coming into direct contact. Finally, in a precipitation polymerization, a radical endgroup can become protectively buried inside its own coiled-up polymer chain when the active polymer precipitates out of solution after reaching a certain molecular weight.

These four systems, emulsion, gas-phase, solid-state, and precipitation polymerization reactions, may, therefore, be considered to be free-radical counterparts of the living-polymer polymerization reactions observed in most anionic and some cationic polymerization reactions, which have no inherent termination step. Long-lived polymer chains with active endgroups are also observed in heterogeneous polymerization reactions involving surface catalysis. In these systems, the active, growing end of the polymer chain is attached to the surface of the catalyst, and the chain will remain alive as long as it is attached. If the metal–carbon bond at the surface is not one which undergoes either a facile hydride elimination (9-17) or an exchange reaction, then the active chain can have a very long lifetime.

9.5. POLYMER STRUCTURE

Comparisons of free-radical and ionic chain-growth polymerization mechanisms in the previous discussions were confined to addition polymerization reactions of monomers containing carbon–carbon double bonds. This limitation was imposed upon the discussion both because the polymerization of olefin monomers is by far the most important type of chain-growth mechanism, and because it is the only type of polymerization reaction broadly applicable to both radical and ionic mechanisms, even though many of the phenomena mentioned, such as living-polymer reactions, are also observed in the chain-growth polymerization of cyclic reactions, are also observed in the chain-growth polymerization of cyclic monomers. Nevertheless, the following discussion of polymer structure will also be limited mostly to consideration of polymers obtained from olefin monomers, although once again many of the points covered are applicable to other types of monomers, but even with this limitation it is difficult to arrive at a completely systematic classification of polymeric structures because so many variables exist.

Several rather arbitrary classifications of polymer structures are presently in use, the most common of which is the frequent reference to condensation versus addition polymers, as discussed in Chapter 1. Other trivial but less common classification schemes for differentiating polymer structures can also be found in the literature, including such combinations as hydrolyzable versus nonhydrolyzable polymers, polymers versus resins, and others.[4,5,6] Instead of basing structure classifications on broad generalizations of this type, an attempt is made here to achieve some semblance of continuity by considering two characteristics of polymer structure; these two are: (*1*) the architecture of the polymer chain, and (*2*) the stereochemistry of the repeating units.

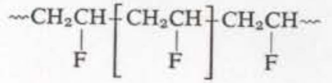
In the following discussion, the classification based on architecture of the polymer chain will consider variations in the number, diversity, and arrangement of the repeating units, while the classifications based on the stereochemistry of repeating units will include consideration of configuration, isomerism, and orientation of the molecular structures of each repeating unit and of sequence of units. Considering these structural characteristics as being the ones of primary importance, the following discussion is offered more as a descriptive treatment of the subject than as an attempt to establish a new classification scheme.

9.5.1. Polymer Chain Architecture

Synthetic polymers, although uniform in composition within a sample, invariably contain a distribution of chains having different numbers of repeating units, that is, different degrees of polymerization. To date, it has not been found possible to duplicate nature's feat of preparing high polymers in which all of the macromolecules are of exactly the same molecular weight. Instead, all known synthetic polymers, prepared either by step-growth or chain-growth reaction mechanisms, contain a distribution of molecular weights of the component macromolecules, as discussed in Chapter 2. Comments about polymer molecular weights, therefore, implicitly refer to average molecular weights of all macromolecules in the polymer sample.

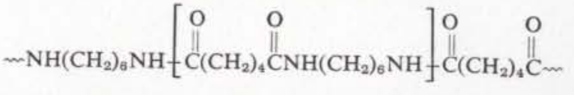
9.5.1.1. Diversity of Repeating Units. The diversity of repeating units in a given polymer depends mainly upon the number of different types of monomers present in the initial polymerization reaction, but extraneous units may be incorporated into the chains as a result of secondary reactions.

Polymers containing repeating units of only one chemical composition are termed homopolymers, while those with two or more chemically different types of repeating units in the same macromolecule are termed copolymers. Examples of typical chain-growth and step-growth homopolymers are poly(vinyl fluoride) (9-18) and poly(hexamethylene adipamide), nylon 66, (9-19), respectively. Both of these polymers as shown



$$\sim CH_2\underset{F}{CH}-\left[CH_2\underset{F}{CH}\right]-CH_2\underset{F}{CH}\sim$$

(9-18)

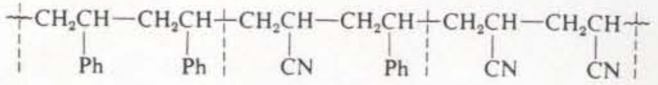


$$\sim NH(CH_2)_6NH-\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}NH(CH_2)_6NH\right]-\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}\sim$$

(9-19)

contain one and only one type of repeating unit, in brackets, although there are just two atoms in the backbone of the repeating unit of poly(vinyl fluoride) compared to 14 atoms in each repeating unit along the backbone of nylon 66.

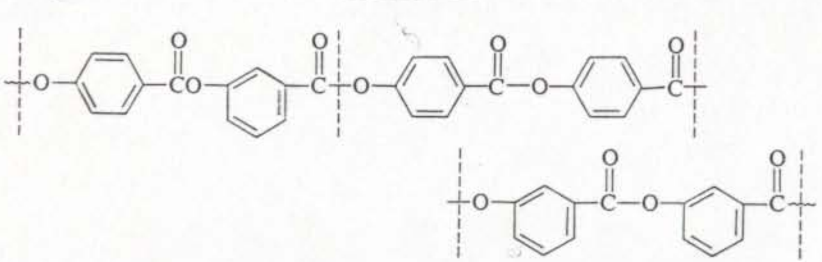
Chain-growth and step-growth copolymers are the products obtained from the concurrent polymerization reactions of two or more monomers, termed copolymerization. Typical of these is the copolymer of styrene and acrylonitrile (9-20) obtained by a chain-growth polymerization reaction



$$-CH_2\underset{Ph}{CH}-CH_2\underset{Ph}{CH}-CH_2\underset{CN}{CH}-CH_2\underset{Ph}{CH}-CH_2\underset{CN}{CH}-CH_2\underset{CN}{CH}-$$

(9-20)

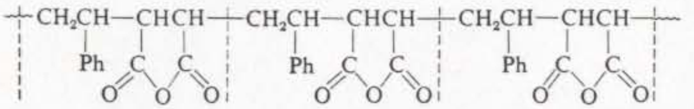
and the copolymer of *m*- and *p*-hydroxybenzoic acids (9-21) obtained by a step-growth polymerization reaction. These copolymers do not contain a simple repeating unit structure. Instead, many combinations of monomer residues, (9-20) and (9-21), exist along each polymer chain because the two



(9-21)

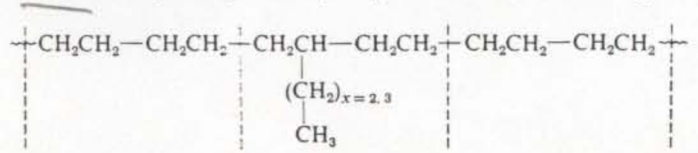
different monomers react more or less randomly during the copolymerization reactions.

Unfortunately, these definitions based on the structure of the polymer can be misleading to some extent, as is apparent from consideration of the product obtained by the copolymerization reaction of an approximately equimolar mixture of styrene and maleic anhydride. The copolymer so formed consists essentially of a perfectly alternating sequence of styrene and maleic anhydride units in each polymer chain (9-22), and this structure,



$$-\left[CH_2\underset{Ph}{CH}-CHCH\right]-\left[CH_2\underset{Ph}{CH}-CHCH\right]-\left[CH_2\underset{Ph}{CH}-CHCH\right]- \qquad (9\text{-}22)$$

based on the definitions above, is more appropriately considered to be a homopolymer having only one type of repeating unit, which contains both of the residues of the two monomers used in the polymerization reaction. In contrast, polyethylene prepared by free-radical initiation of ethylene under high pressure contains a number of randomly distributed 1-pentene and 1-hexene repeating units (9-23), which are formed by infrequent



$$-\left[CH_2CH_2-CH_2CH_2\right]-\left[CH_2\underset{\substack{|\\(CH_2)_{x=2,3}\\|\\CH_3}}{CH}-CH_2CH_2\right]-\left[CH_2CH_2-CH_2CH_2\right]- \qquad (9\text{-}23)$$

intramolecular chain transfer reactions during the polymerization reaction. By strict usage of the definitions given above, considering only the structure of the polymer, this polymer would have to be classed as a copolymer of ethylene, 1-pentene, and 1-hexene.

9.5.1.2. Arrangement of Repeating Units in Copolymers. Another important factor in polymer chain architecture is the arrangement of repeating units when more than one type of unit is present, and, for this characteristic, two structural arrangements are considered to be of primary importance; these are: (*1*) the extension in space of the polymer chains,

and (*2*) the stereochemistry of placement of different types of repeating units in a copolymer. The concept of extension in space pertains to the dimensional requirements of the atoms comprising the backbone of the copolymer chain; a linear chain is considered to have a one-dimensional backbone, a branched chain has a two-dimensional backbone, and a cross-linked or network polymer has a three-dimensional backbone. All three types of structures, linear, branched, or network copolymers, may contain a regular or irregular placement of repeating units. The most important general types of each class are the following:

A. One-Dimensional Copolymers

1. Regular placement of repeating units:

- *a. Block Copolymer.* Long, linear sequences of one monomer unit followed by long, linear sequences of another (9-24)

—B—B—A—A—A—A—A—A—A—B—B—B—B—B—B—A—A—A— (9-24)

- *b. Exactly Alternating Copolymer.* Equivalent in regularity to linear homopolymer, as discussed in the previous section (9-22).

2. Irregular placement of repeating units:

- *a. Random Copolymer.* Arrangement of monomer units in a statistically random placement along a linear chain (9-25)

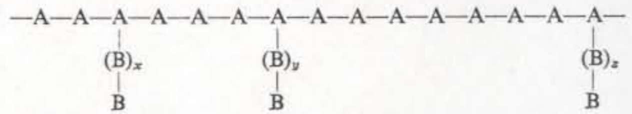
—A—B—B—A—B—A—A—A—B··A—B—B—A—B—B—B—B—A—A— (9-25)

- *b. Alternating Tendency.* Significant but nonperfect tendency toward alternation in placement of repeating units along linear chain.

B. Two-Dimensional Copolymers

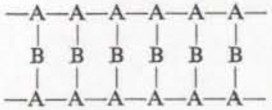
1. Branched Polymer. A polymer containing randomly placed forked structures at intervals along the chain (9-23). The primary and secondary chains may contain one or more types of repeating units.

2. Graft Copolymers. One homopolymer attached at various, generally random, points along the backbone of another homopolymer (9-26).



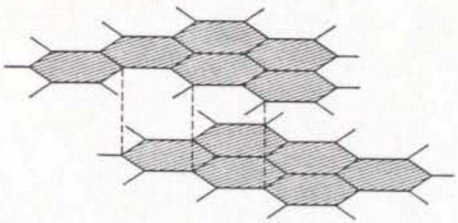
$$-A-A-\underset{\substack{|\\(B)_x\\|\\B}}{A}-A-A-\underset{\substack{|\\(B)_y\\|\\B}}{A}-A-A-A-A-A-A-A-\underset{\substack{|\\(B)_z\\|\\B}}{A}-A- \qquad (9\text{-}26)$$

3. Ladder Polymer. Two parallel polymer chains connected at frequent and generally regular intervals by short chains acting as rungs (9-27).



$$\begin{array}{c}-A-A-A-A-A-A-\\ \;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\\ \;\;B\;\;\;B\;\;\;B\;\;\;B\;\;\;B\;\;\;B\\ \;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\;\;\;\;|\\ -A-A-A-A-A-A-\end{array} \qquad (9\text{-}27)$$

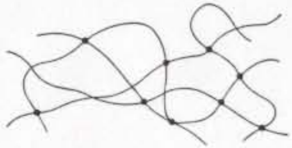
4. *Layer-Lattice Polymer*. Macromolecule with a sheet-like structure, as exemplified by graphite (9-28).



(9-28)

C. Three-Dimensional Copolymer

1. *Regular Placement*. No organic copolymer with this structure has been synthesized to date, but this type of architecture occurs in natural inorganic minerals and in diamond, for example.
2. *Irregular Placement*. Network structure of homopolymer or copolymer with randomly placed branched points (9-29).



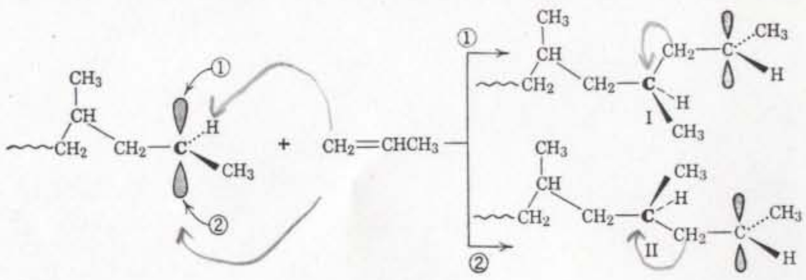
(9-29)

9.5.2. Stereochemistry of Repeating Units

The presence or absence of long-range order in the structures of polymer chains is the primary factor, but not the only factor, which determines whether or not a group of chains can pack into an ordered crystalline array in the solid state, as opposed to a disordered amorphous matrix. Long-range order can be disrupted by a number of structural irregularities, including: (*1*) nonuniformity in the configurations of dissymmetric atoms in successive repeating units; (*2*) the existence of isomeric molecular structures along the polymer chains; and (*3*) randomness in the head-and-tail orientation of adjacent repeating units. These imperfections, if extensive, will prevent regular packing and crystallization of polymer chains during either slow solidification from the melt or precipitation from solution.

9.5.2.1. Repeating Unit Configuration. The addition polymerization reaction of monomers containing carbon–carbon double bonds involves the formation of two new bonds at tetravalent carbon atoms as each new monomer is added onto the end of a growing polymer chain. The arrangement in space, or configuration, of the bonds formed at the active terminal carbon atom of the growing polymer chain is permanently established during the reaction and two distinguishable diastereomeric configurations are possible.[7] During the growth of the polymer, the regularity with which the two different configurations are established in the addition of each successive repeating unit will have a marked effect on the long-range order in the macromolecule.

For example, in the chain-growth polymerization (9-30) of propylene to form polypropylene, the opening of the double bond of the incoming monomer molecule and formation of a new single bond at the active carbon atom (indicated by bold-face type) on the end of the polymer chain will result in the formation of either one of two possible, mirror-image configurations, I or II, at this carbon atom. The active terminal carbon atom in the equation for this reaction (9-30) is represented in an sp^2 hybridization, which is believed to be the case for the structure of the active species in either a free-radical or a cationic polymerization reaction. However, the same type of equation (9-30) applies to an anionic polymerization reaction involving an sp^3 carbon atom if it is assumed that either rapid inversion of the carbanion or rapid rotation around the terminal carbon–carbon bond can occur. In either case, when the tetragonal carbon atom is firmly established in space as a result of the addition reaction (9-30), the substituents bonded to the previously active carbon atom will be set in one of two configurations, I or II, as mentioned.



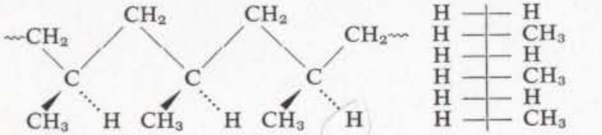
(9-30)

It may appear in this example that, after the addition of the next repeating unit, structures I and II will become equivalent, because two of the substituents on the tetragonal carbon atoms in question will be identical, as indicated by structures I′ and II′, Equation (9-31). That is, simple rotation of II′ through 180° in the plane of the paper seems to generate a structure identical in stereochemistry to I′, Equation (9-31), but, in fact, the difference between these two configurations, I′ and II′, is real

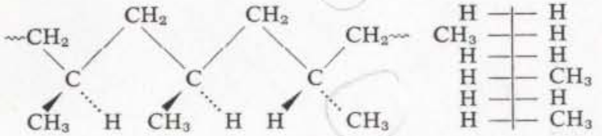
I′ II′ (9-31)

and a point of true dissymmetry is introduced into the polymer chain. The basis for this distinction is that, while structures I′ and II′ are neither asymmetric nor pseudoasymmetric, because no asymmetric atom exists on either side of the carbon atom in boldface type, the structures are dissymmetric because a set of three successive repeating units in the middle of a polymer chain (a triad) may exist in at least three possible combinations of configurations. This point is best illustrated graphically by depicting the carbon–carbon backbone of the polymer chain as existing in an extended zigzag conformation in the plane of the paper, and the pendant substituents will then lie either above or below the plane of the paper as shown for polypropylene by Structures (9-32)–(9-34) with the equivalent Fischer projections.[8,9] The three basic triads for polypropylene in this example are those with: (*1*) all methyl groups on one side, either above (9-32) or below; (*2*) two neighboring substituents above and the third below (9-33) or vice versa; and (*3*) the first and third substituents above and second below (9-34) or vice versa.

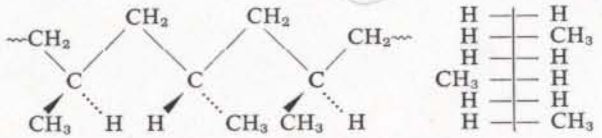
dissymetric
≡
chiral



(9-32)



(9-33)

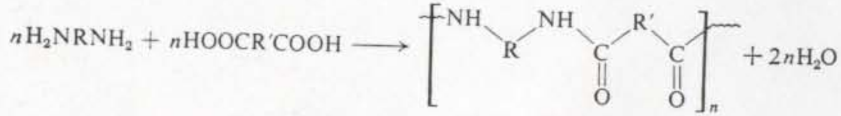


(9-34)

If more than one of these triads are present in significant amounts and are randomly dispersed along the polymer chain, the polymer will not contain long-range order and will generally be incapable of packing into a regular crystalline lattice. On the other hand, if one of the triads is repeated for extended lengths along the polymer chain, then groups of chains having these blocks of the same triad will be capable of packing into an ordered alignment. These crystalline high polymers, like their low molecular weight counterparts, will exhibit crystalline melting points and well-defined x-ray diffraction patterns and, most important, considerably different physical properties than those of the same polymer in an amorphous state.

Most crystalline polyolefins have ordered chain structures consisting of either the triad of Structure (9-32) or the triad of Structure (9-34). A polymer containing principally repeating units with identical configurations, triad Structure (9-32), is termed an isotactic polymer, while a polymer containing principally units of exactly alternating configurations, triad Structure (9-34), is termed a syndiotactic polymer. A chain which shows no regular order of repeating unit configurations is termed an atactic polymer.

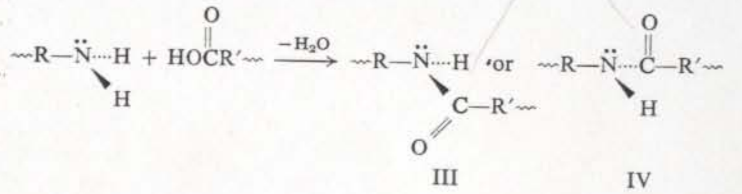
Not all polymerization reactions involve the type of bond formation in which specific configurations are unequivocally established. Reactions in which only divalent or trivalent atoms are involved in bond formation generally do not have to face this stereochemical dilemma, and polymers formed by such reactions are free of structural complexity arising from the formation of dissymmetric centers occurring in the polymerization reaction. As an example, an amidation reaction (9-35) involves bond formation



$$nH_2NRNH_2 + nHOOCR'COOH \longrightarrow \left[NH-R-NH-\underset{\underset{O}{\|}}{C}-R'-\underset{\underset{O}{\|}}{C} \right]_n + 2nH_2O$$

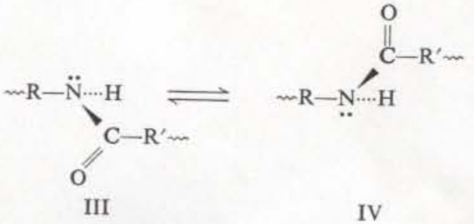
(9-35)

between a trigonal active carbon atom and a trivalent nitrogen atom, and although apparently either of two configurations, III or IV, may be formed (9-36), at the nitrogen atom, these two configurations are equivalent because of the ease of racemization by inversion (9-37) of the trivalent nitrogen



$$\sim R-\ddot{N}\cdots H\,(-H) + HO\overset{O}{\overset{\|}{C}}R'\sim \xrightarrow{-H_2O} \sim R-\ddot{N}\cdots H\,(-C(=O)-R'\sim) \text{ or } \sim R-\ddot{N}\cdots\overset{O}{\overset{\|}{C}}-R'\sim\,(-H)$$

III IV (9-36)



$$\sim R-\ddot{N}\cdots H\,(-C(=O)-R'\sim) \rightleftharpoons \sim R-\underset{\cdot\cdot}{N}\cdots H\,(-\overset{O}{\overset{\|}{C}}-R'\sim)$$

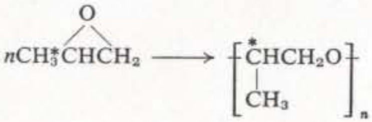
III IV (9-37)

atoms in such molecules. The absence of configurational complexity is one of the most valuable assets of this type of polymerization reaction. The resulting simplicity in polymer stereochemistry is the reason why step-growth polymerization reactions and many ring-opening chain-growth polymerization reactions which produce linear polymers, generally produce crystalline, or at least crystallizable, polymers.

9.5.2.2. Repeating Unit Isomerism. The principal types of repeating unit isomerism, other than configurational isomerism just discussed, are (*1*) optical isomerism, (*2*) geometrical isomerism, and (*3*) substitutional isomerism.

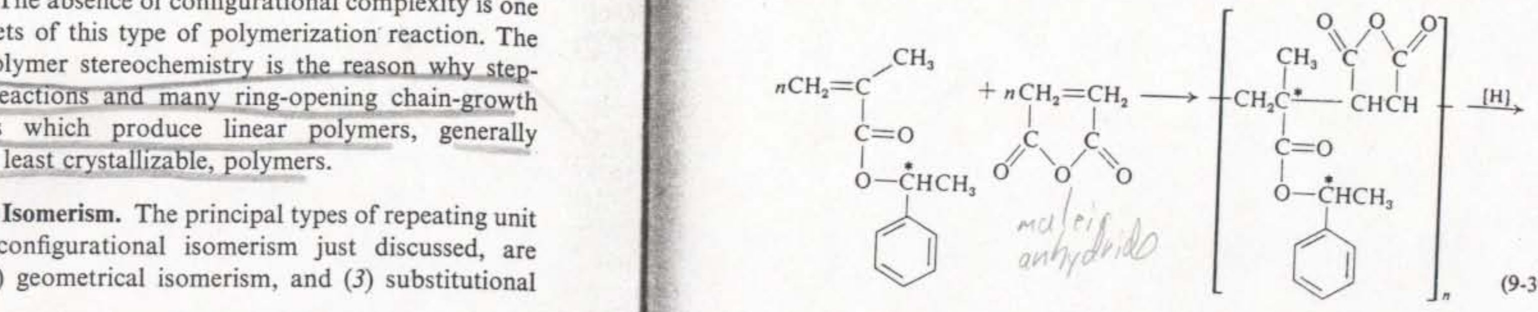
(*1*) *Optical Isomerism.* As discussed in the previous section, the homopolymerization reaction of olefin monomers does not generally produce structures containing optical isomers because asymmetric centers are not generated in the reaction (assuming that the role of endgroups is negligible in this regard). Isotactic polymers (9-32) are formed with dissymmetric centers, but they contain a plane of symmetry at every carbon atom, while syndiotactic polymers (9-34) possess a plane of symmetry at every other carbon atom in the backbone. However, a number of chain-growth polymerization reactions are known in which the polymers produced are optically active because of the presence of a center of asymmetry at atoms in the backbone of the chain.[7] In these cases, the optical activity is derived either: (*1*) as a result of the presence of a center of asymmetry in the monomer which is carried over undisturbed to the polymer, or (*2*) as a result of asymmetric induction in the polymerization reaction.

Examples of the former are the chain-growth polymerization reactions of optically active monomers, such as propylene oxide, Equation (9-38),

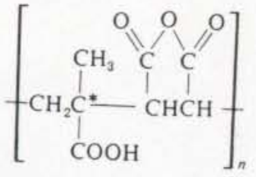


$$n\,\mathrm{CH_3^{*}}\overset{\mathrm{O}}{\mathrm{CHCH_2}} \longrightarrow \left[\underset{\mathrm{CH_3}}{\overset{*}{\mathrm{C}}}\mathrm{HCH_2O}\right]_n \tag{9-38}$$

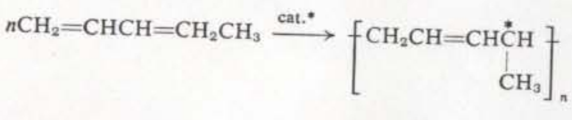
and *N*-carboxy amino acid anhydrides, as discussed in Chapter 14.[8] Examples of asymmetric induction are the free-radical copolymerization reaction (9-39) of (−)-1-phenylethyl methacrylate with maleic anhydride[10] and the polymerization (9-41) of 1,3-pentadiene initiated by an optically active heterogeneous catalyst.[11] The occurrence of asymmetric induction in the copolymerization reaction (9-39) with the resulting formation of a center of asymmetry in the backbone of the polymer chain was shown by reductive removal of the optically active ester groups in the polymer, Equation (9-40), to form an optically active copolymer completely free of active pendant groups. This copolymer and the optically active polymer from 1,3-pentadiene, Equation (9-41), unlike polymers from vinyl monomers, contain in every repeating unit a carbon atom with four different substituents which is a true center of asymmetry.



(9-39)

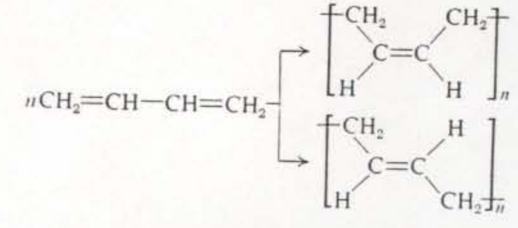


(9-40)



$$n\mathrm{CH_2{=}CHCH{=}CH_2CH_3} \xrightarrow{\text{cat.*}} \left[\mathrm{CH_2CH{=}CH}\underset{\mathrm{CH_3}}{\overset{*}{\mathrm{C}}}\mathrm{H}\right]_n \tag{9-41}$$

(*2*) *Geometrical Isomerism.* The most important type of geometrical isomerism is that encountered in the chain-growth polymerization of conjugated dienes. The addition reaction across the 1,4 positions of a conjugated diene may form either a *cis*, Equation (9-42), or a *trans*, Equation (9-43), repeating unit. The random variation in *cis* and *trans* contents within a diene polymer chain will again result in a significant variation in the long-range order of the polymer in the solid state. Furthermore, when long-range order does exist, the type of isomer present will determine the resulting physical properties, as illustrated by comparing an

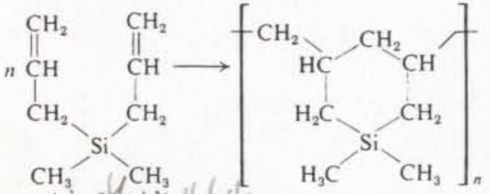


(9-42)

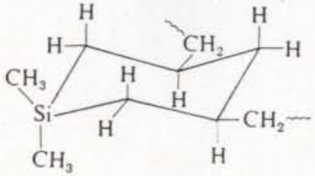
(9-43)

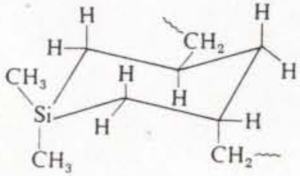
all *cis*-polyisoprene, which has a crystalline melting point of 22°C, to an all *trans* polymer with a melting point of 70–75°C. A random mixture of the two types of repeating units in the same backbone prevents the polymer from achieving crystallinity.

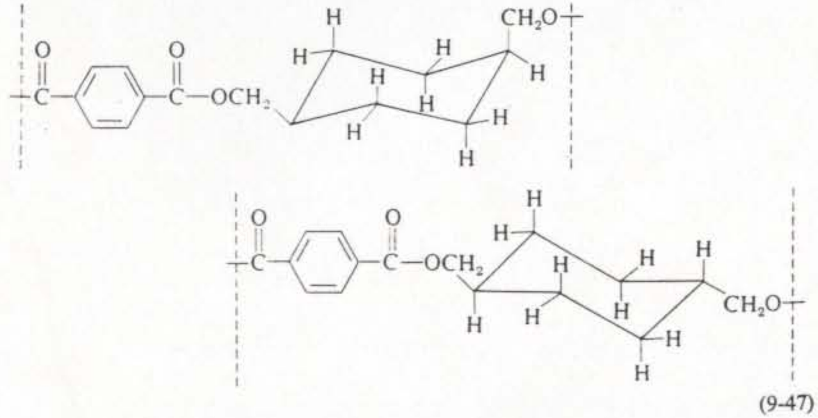
A different type of *cis-trans* isomerism is found in polymers containing alicyclic repeating units as exemplified by the polymer prepared by the cyclopolymerization (9-44) of dimethyldiallylsilane which is composed of repeating units containing 1,3-disubstituted cyclohexane rings.[12] The methylene groups connecting these rings may be present as either *cis* (9-45) or *trans* (9-46) configurations on the ring. This type of isomerism is also encountered in the structure of the polyester of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane (9-47), and the crystalline melting point undergoes a continuous increase from approximately 250°C for the all *cis* polyester to approximately 325°C for the all *trans* polyester.


(9-44)

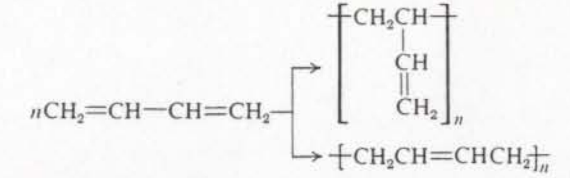
dimethyldiallylsilane


(9-45)

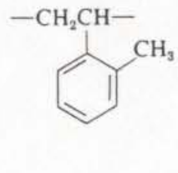

(9-46)

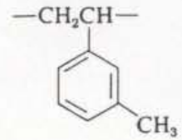

(9-47)

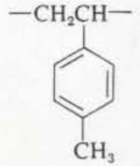
(*3*) *Substitutional Isomerism*. Substitutional isomerism is encountered in a variety of polymers, but probably the best known example of this type of isomerism is the 1,2 versus 1,4 polymerization of conjugated dienes. Butadiene, as a case in point, is capable of polymerizing either as a vinyl monomer by a 1,2-addition reaction (9-48) or as a diene monomer by a 1,4-addition reaction (9-49). Generally, both modes of addition are realized with the relative amounts of each depending upon the polymerization initiator and condition used. Another example of substitutional isomerism is the existence of three possible polyvinyltoluene homopolymers, which differ in *ortho* (9-50), *meta* (9-51), or *para* (9-52) substitution of the vinyl group relative to the methyl group on the benzene ring.


(9-48)

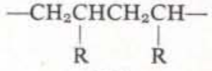
(9-49)


(9-50)


(9-51)


(9-52)

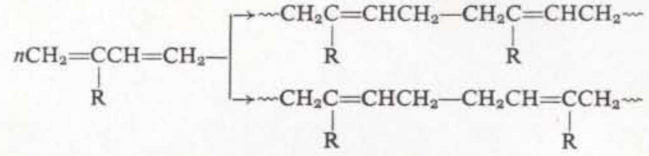
9.5.2.3. Repeating Unit Orientation. The repeating units of most olefin polymers formed by chain-growth polymerization reactions are unsymmetrical simply because most olefin monomers of interest are unsymmetrically substituted to begin with. As a result, adjacent repeating units can be connected in either a head-to-tail arrangement (9-53) or a head-to-head arrangement (9-54). In these designations the substituted end of the double bond is arbitrarily designated as the head. However, with the exception of the polymerization of unsymmetrical dienes, Reaction (9-55),


$-CH_2\underset{R}{CH}CH_2\underset{R}{CH}-$

(9-53)


$-CH_2\underset{R}{CH}\underset{R}{CH}CH_2-$

(9-54)


(9-55)

this type of structural complexity has never been observed to occur to any important extent for either vinyl or vinylidene monomers, that is for monomers containing substituents on only one side of the double bond: $CH_2 = CHR$ or $CH_2 = CR_2$.

. vinyl vinylidene

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10

Fundamental Reactions of Organic Free Radicals

Organic molecules containing an unpaired electron are termed either free radicals or radicals, and radicals are generally considered to be unstable species because of their very short lifetimes in the liquid or gaseous states. These short lifetimes, however, are only a reflection of the facility with which free radicals react with one another either by combination or by disproportionation, as discussed in the previous chapter. The instability of free radicals is, therefore, a kinetic rather than a thermodynamic property.

Free radicals can undergo four general types of reactions including: (*1*) transfer or abstraction, (*2*) elimination, (*3*) addition, and (*4*) combination or coupling. These reactions can be illustrated by considering the products obtained from the pyrolysis of ethane in the gas phase which is clearly a free-radical reaction.[1] The principal products of this reaction are hydrogen, methane, ethylene, ethane, propane, and butane, all formed from the initial homolytic decomposition (10-1) of ethane into two methyl radicals.

$$CH_3{-}CH_3 \longrightarrow 2\cdot CH_3 \tag{10-1}$$

Methane could result from a hydrogen-atom transfer reaction (10-2) between a methyl radical and ethane, which would also yield an ethyl radical.

$$\cdot CH_3 + H{-}CH_2CH_3 \longrightarrow H_3C{-}H + \cdot CH_2CH_3 \tag{10-2}$$

This radical transfer or abstraction reaction is closely analogous to bimolecular displacement reactions, such as the S_N2 or acid-base reactions, well known in ionic systems.

The ethyl radical formed by the transfer reaction (10-3), could eliminate a hydrogen atom directly to form ethylene, but this is an energetically unfavorable reaction, and hydrogen atom removal more likely occurs by attack at the β-position by another ethyl radical, Reaction (10-4). The latter

$$\cdot CH_2{-}CH_2{-}H \longrightarrow CH_2{=}CH_2 + H\cdot \tag{10-3}$$

$$\cdot CH_2{-}CH_2{-}H + \cdot CH_2CH_3 \longrightarrow CH_2{=}CH_2 + H{-}CH_2CH_3 \tag{10-4}$$