Chapter 3
Free-Radical Chain-Growth Polymerization

3.1 Free-Radical Chain-Growth Polymerization Process

Polymerizations by free-radical mechanism are typical free-radical reactions. That is to say, there is an ***initiation***, when the radicals are formed, a ***propagation***, when the products are developed, and a ***termination***, when the free-radical chain reactions end. In the polymerizations, the propagations are usually chain reactions. A series of very rapid repetitive steps follow each single act of initiation, leading to the addition of thousands of monomers.

This process of polymerization of vinyl monomers takes place at the expense of the double bonds, $-C{=}C- \rightarrow -C{-}C-$. Table 3.1 illustrates the steps in this process.

Formation of initiating radicals is the rate-determining step in the initiation reaction. The formation of initiating radicals can result, as shown in Table 3.1, from cleavages of compounds, such as peroxides, or from other sources. Actually, many reactions lead to formations of free radicals. The initiating radicals, however, must be energetic enough to react with the vinyl compounds. A linear correlation exists between the affinities of some radicals for vinyl monomers and the energy (calculated) required to localize a π electron at the β-carbon of the monomer [1]. By comparison to other steps in the polymerization process, initiation is a slow step and requires high energy of activation.

3.1.1 *Kinetic Relationships in Free-Radical Polymerizations*

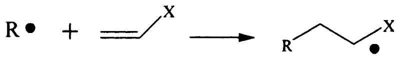
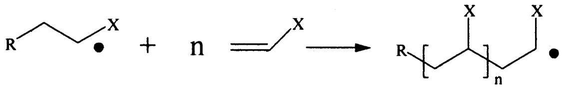
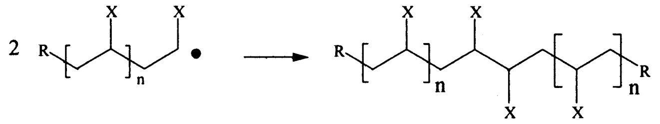
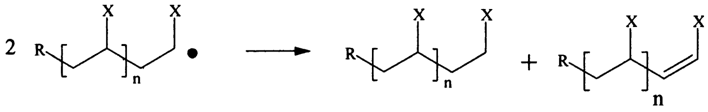
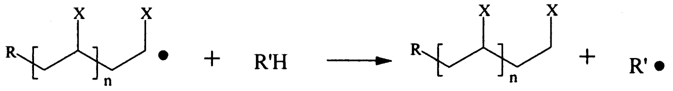
A kinetic scheme for typical free-radical polymerizations is pictured as follows [2]; the rate of propagation R_p is equal to the rate of polymerization R_{pol}, as all the monomer molecules (except one) are consumed during this step.

Initiation	$I \xrightarrow{k_d} 2R$	$d[R\bullet]/dt = R_i = 2k_d[I]$
	$R\bullet + M \xrightarrow{k_i} RM\bullet$	$-\,d[R\bullet]/dt = k_I[R\bullet][M]$
Propagation	$RM\bullet + nM \xrightarrow{k_p} {\sim}P_{n+1}\bullet$	$R_P = k_P[\sum RM_n\bullet][M]$
Termination	${\sim}P_{n+1}\bullet + {\sim}\,P_{m+1}\bullet \xrightarrow{k_t}$ polymer	$-\,d[P\bullet]/dt = 2k_t[P\bullet]^2$
Transfer	${\sim}P_n\bullet + S \xrightarrow{k_{tr}} P_n + S\bullet$	
	$S\bullet + nM \rightarrow SM_n\bullet$	

In the above shown kinetic scheme, M stands for the monomer concentration, I is the concentration of the initiator, and [R•] and [P•] mean the concentration of primary and polymer radicals,

A. Ravve, *Principles of Polymer Chemistry*, DOI 10.1007/978-1-4614-2212-9_3,

Table 3.1 Illustration of a free radical polymerization

1. Initiation	$\mathrm{R{-}R} \longrightarrow 2\mathrm{R}\bullet$ 
2. Propagation	
3. Termination	
a. By combination	
b. By disproportionation	
c. By transfer	

respectively. S stands for the chain transferring agent. R_I denotes the decomposition rate of the initiator and R_P the rate of polymerization. The rate constants, for the initiator decomposition is k_d, for the initiation reaction is k_I, for the propagation k_P, and for the termination is k_T. The above is based on an assumption that k_P and k_I are independent of the sizes of the radicals. This is supported by experimental evidence that shows that radical reactivity is not affected by the size, when the chain length exceeds dimer or trimer dimensions [3]. The reactions involved in a typical free-radical polymerization process, as stated above, are illustrated in Table 3.1

The equation for the rate of propagation, shown above in the kinetic scheme, contains the term [M•]. It designates radical concentration. This quantity is hard to determine quantitatively because its concentration is usually very low. A ***steady state*** assumption is, therefore, made to simplify the calculations. It is assumed that while the radical concentration increases at the very start of the reaction, it reaches a constant value almost instantly. This value is maintained from then on, and the rate of change of free-radical concentration is assumed to quickly become and remain zero during the polymerization. At steady state, the rates of initiation and termination are equal, or $R_i = R_t = 2k_i[\mathrm{M}\bullet]$ [4]. This assumption makes it possible to solve for [M•] and can then be expressed as:

$$[\mathrm{M}\bullet] = (k_d[\mathrm{I}]/k_t)^{1/2}$$

The rate of propagation is

$$R_P = k_P[\mathrm{M}](k_d[\mathrm{I}]/k_t)^{1/2}$$

The rate of propagation is approximately equal to the total rate of polymerization. The total rate can be designated as R_{pol}. Because all but one molecule are converted during the step of propagation, we can write:

$$R_P = k_P\left[\sum\nolimits_n \mathrm{RM_n}\right](\mathrm{M})$$

This rate of propagation applies if the kinetic chain length is large and if the transfer to monomer is not very efficient. The rate of monomer disappearance can be expressed as

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = R_i + R_p$$

Because many more molecules of the monomer are involved in the propagation than in the initiation step, a very close approximation is

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = R_\mathrm{p}$$

The average lifetime, τ, of a growing radical under steady state conditions can then be written as follows [3, 5],

$$\tau = k_P[M]/2k_t(R_P)$$

Not all primary radicals that form attack the monomer. Some are lost to side reactions. An initiator efficiency factor, f, is, therefore, needed. It is a fraction of all the radicals that form and can be expressed as:

$$f = \text{ initiating radicals/total number radicals that form.}$$

The rate of initiator decomposition and the rate equation can be expressed as

$$R_\mathrm{I} = 2fk_\mathrm{d}[\mathrm{I}] = k_\mathrm{i}\left[\sum \mathrm{RM_n}\bullet\right]^2$$

$$R_\mathrm{P} = k_\mathrm{P}[\mathrm{M}](k_\mathrm{d}[\mathrm{I}]f/k_\mathrm{t})^{1/2} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t$$

According to the kinetic scheme, chain transfer does not affect the rate of polymerization but alters the molecular weight of the product. Also, it is important to define the average number of monomer units that are consumed per each initiation. This is the ***kinetic chain length***, and it is equal to the rate of polymerization per rate of initiation:

$$\text{kinetic chain length} = v = k_\mathrm{P}/k_\mathrm{i}$$

At steady state conditions, ν is also equal to $k_\mathrm{p}/k_\mathrm{t}$. The kinetic chain length can also be expressed as:

$$v = k_\mathrm{p}[\mathrm{M}]/2k_\mathrm{t}[\mathrm{M}\bullet]$$

By substituting the expression for [M•] the equation becomes:

$$v = k_\mathrm{P}[\mathrm{M}]/2(fk_\mathrm{d}k_\mathrm{t}[\mathrm{I}])^{1/2}Z$$

The ***number average degree of polymerization***, **DP**, is equal to 2 v, if the termination takes place by coupling. It is equal to v, if it takes place by disproportionation. (Terminations by coupling or disproportionation are discussed in the section on the termination reactions) Above kinetic relationships apply in many cases. They fail, however, to apply in all cases [2]. To account for it, several mechanisms were advanced. They involve modifications of the initiation, termination, or propagation steps. These are beyond the discussions in this book.

At steady state conditions,

$$R_\mathrm{i} = f\,\mathrm{I}[\mathrm{M}] = R_\mathrm{t} = k_\mathrm{t}\left[\sum\nolimits_\mathrm{n} \mathrm{RM_n}\bullet\right]^2$$

3.2 Reactions Leading to Formation of Initiating Free Radicals

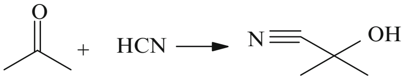
Initiating free radical can come from many sources. Thermal decompositions of compounds with azo and peroxy groups are common sources of such radicals. The radicals can also come from "redox" reactions or through various light induced decompositions of various compounds. Ionizing radiation can also be used to form initiating radicals.

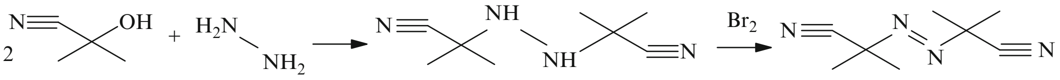
3.2.1 *Thermal Decomposition of Azo Compound and Peroxides*

The azo compound and peroxides contain weak valence bonds in their structures. Heating causes weak bonds in these compounds to cleave and to dissociate into free radicals as follows:

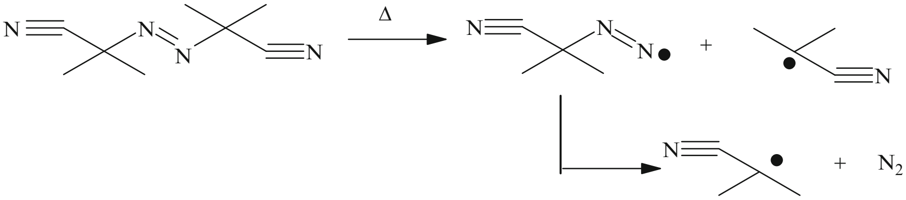
$$\text{R-N=N-R} \xrightarrow{\Delta} 2\text{R}\bullet + \text{N}_2$$

For many azo compounds such dissociations occur at convenient elevated temperatures. One commonly used azo compound is α,α′-azobisisobutyronitrile. An original synthesis of this compound was reported to be as follows [3, 4]:





The final products of decomposition of this compound are two cyanopropyl radicals and a molecule of nitrogen:



As stated earlier, not all free radicals that form, however, initiate polymerizations. Some are lost to side reactions. Thus, for instance, some free radicals that form can recombine inside or outside the solvent cage, where the decompositions take place, to yield either tetramethylsuccinonitrile or a ketenimine [4, 5]:

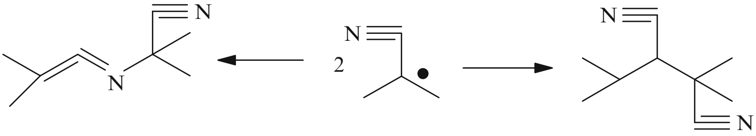


Table 3.2 Decomposition rates of some azonitrile initiators[a]

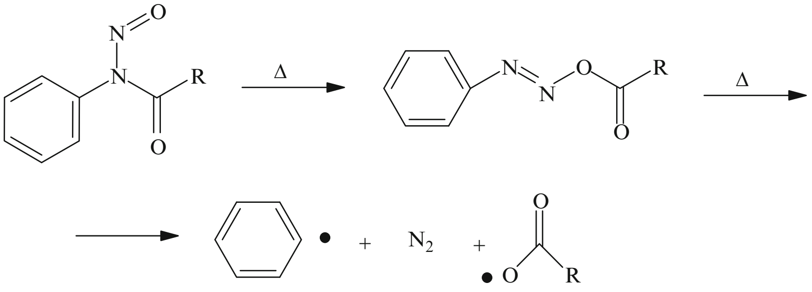
Compound	Solvent	T(°C)	$K_d{}^b(s^{-1})$
2,2′-azobisisobutyronitirle	Benzene	78.0	8×10^{-5}
2,2′-azobis-2-ethylpropionitrile	Nitrobenzene	100.0	1.1×10^{-3}
2,2′-azobis-2-cyclopropylpropionitrile	Toluene	50.0	8.2×10^{-5}
1,1′-azobiscyclohexanenitrile	Toluene	80.0	6.5×10^{-6}
2,2′-azobis-2-cyclohexylpropionitrile	Toluene	80.0	8.3×10^{-6}
1,1′-azobiscyclooctanenitrile	Toluene	45.0	1.5×10^{-4}

[a] From ref. [13], and from other sources in the literature

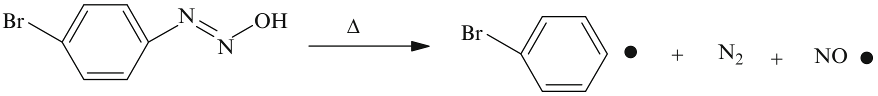
[b] $K_c = Ae^{(-E_a/RT)}$

Examples of other, fairly efficient, azo initiators include the following:

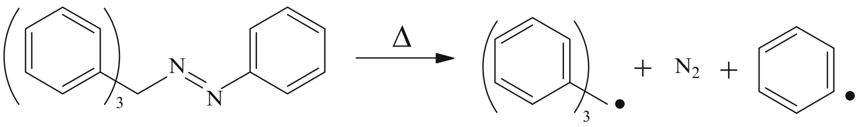
1. *N*-Nitrosoacylanilides,



2. Bromobenzenediazohydroxide,



3. Triphenylazobenzene,



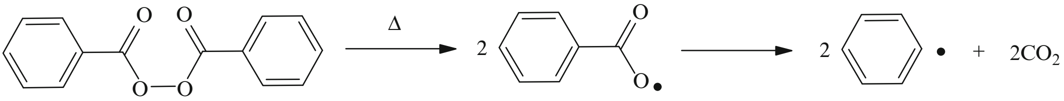
The triphenylmethyl radical shown above is resonance stabilized and unable to initiate polymerizations. The phenyl radical, on the other hand is a hot radical. It initiates polymerizations readily. Decomposition rates of some azonitrile initiators are listed in Table 3.2. There are also many peroxides available for initiating free-radical polymerizations. These can be organic and inorganic compounds. There are, however, many more organic peroxides available commercially than are the inorganic ones. The organic ones include dialkyl and diaryl peroxides, alkyl and aryl hydroperoxides, diacyl peroxides, peroxy esters, and peracids. Hydrogen peroxide is the simplest inorganic peroxide.

Syntheses, structures, and chemistry of various peroxides were described thoroughly in the literature [5]. Here will only be mentioned some properties of peroxides and their performance as they pertain to initiations of polymerizations. Decompositions of peroxides, such as the azo compounds, are also temperature dependent [6]. This means that the rates increase with temperature. The rates are also influenced by the surrounding medium, such as the solvents that imprison or "cage" the produced pairs of free radicals. Before undergoing a net translational diffusion out of the cage, one

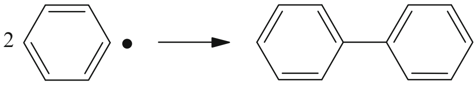
Table 3.3 Effect of substituents on decomposition of dibenzoylperoxide in benzene [10, 11]

Substituent	$K_i \times 10^3$	log K_1/K	$\sigma_i + \sigma_0$
p,p′-dimethoxy	7.06	0.447	0.536
p-methoxyy	4.54	0.255	0.268
p,p′-dimethyl	3.68	0.164	0.340
p,p′-di-*t*-butyl	3.65	0.161	0.394
Parent compound	2.52	0.000	0.000
p,p′-dichloro	2.17	−0.065	+0.454
m,m′-dichloro	1.58	−0.203	+0.746
m,m′-dibromo	1.54	−0.215	+0.782
p,p′-dicyano	1.22	−0.314	+1.300

or both of the radicals may or may not expel a small molecule. For instance, benzoyl peroxide can and often does decompose into a phenyl radical and carbon dioxide, as follows:



The resultant phenyl radicals can combine and yield new and completely inactive species:



The above-described recombination reactions of free radicals are some of the causes of inefficiency among initiators. The average time for recombination of free radicals inside a solvent cage and also the time for their diffusion out of the cage is about 10^{-10} s [7]. In addition, the efficiency of the initiator is affected by the monomer and by the solvent. It was shown that the viscosity of the medium is inversely proportional to the initiator efficiency because the more viscous the solution, the greater the cage-effect [8, 9].

Numerous lists are available in the literature that give the decomposition temperatures or the half-lives at certain elevated temperatures of many initiators [6]. Decompositions of peroxides may proceed via concerted mechanisms [10, 11] and the rates are structure dependent. This can be illustrated on benzoyl peroxide. The benzoyl groups, the two halves of this molecule, are dipoles. They are attached, yet they repel each other. Rupture of the peroxide link releases the electrostatic repulsion between the two dipoles. Presence of electron donating groups in the *para* position increases the repulsion, lowers the decomposition temperature, and increases the decomposition rate. The opposite can be expected from electron attracting groups in the same position [6]. The effect of substituents on the rate of spontaneous cleavage of dibenzoyl peroxide was expressed [11] in terms of the Hammett equation, $\log (K/K_O) = \rho\,\sigma$. This is shown in Table 3.3.

In addition, peroxides can cleave in two ways, ***heterolytically*** and ***homolytically***. Heterolytic cleavage of peroxides results in formation of ions,

$$R^{\oplus} + :^{\ominus}O\text{-}O\text{-}R' \rightleftharpoons R\text{-}O\text{-}O\text{-}R' \rightleftharpoons R\text{-}O\text{-}O:^{\ominus} + R'^{\oplus}$$

but homolytic cleavage results in formation of radicals:

$$R\text{-}O\text{-}O\text{-}R' \rightleftharpoons R\text{-}O\bullet + \bullet O\text{-}R'$$

Table 3.4 Decomposition of benzoyl peroxide in various solvents at 79.8°C [15]

Solvent	Approximate% decomposition in 4 h
Anisole	43.0
Benzene	50.0
Carbon tetrachloride	40.0
Chlorobenzene	49.0
Chloroform	44.0
Cyclohexane	84.0
Cyclohexene	40.0
Ethyl acetate	85.0
Ethylbenzene	46.0
Methyl benzoate	41.0
Methylene chloride	62.0
Nitrobenzene	49.0
Tetrachloroethylene	35.0
Toluene	50.0

In the gaseous phase, the cleavage is usually homolytic because it requires the least amount of energy [12]. In solution, however, the dissociation may be either one of the two, depending upon the nature of the R groups. Heterolytic cleavage may be favored, in some cases, if the two groups, R and R′, differ in electron attraction.

The same is true if the reaction solvent has a high dielectric constant. Solvation of the ions that would form due to heterolytic cleavage is also a promoting influence for such a cleavage:

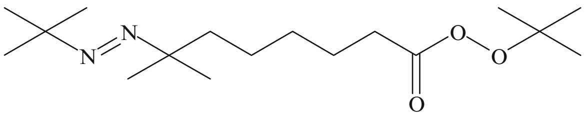
$$\mathrm{A{:}B} + 2\mathrm{S} \rightarrow \mathrm{SA{:}}^{\ominus} + \mathrm{BS}^{\oplus}$$

where, S represents the solvent.

In sum total, the types and the amounts of side reactions that can take place are a function of the structures of the peroxides, the stability of the formed radicals, the solvent, and the monomer that is being polymerized. The stability of the radicals that form can also affect the amount of radicals being captured by the monomers. Also, it was reported that while generally the character of free radicals is neutral, some of them are electrophilic (such as chloro) and others are nucleophilic (such as *t*-butyl). This tendency, however, is relatively slight when compared with positive and negative ions [15].

There is much information in the literature on the rates and manner of decomposition of many peroxides in various media. Beyond that, diagnostic tests exist that can aid in determining the decomposition rates of a particular peroxide in a particular media [13]. Table 3.4 is presented to show how different solvents affect the rate of decomposition of benzoyl peroxide into radicals.

Some initiators can function as both, thermal and photoinitiators. Such an initiator, for instance, is 2,2′-azobisisobutyronitrile. Also, Engel and coworkers [16] reported synthesis of an initiator that can function both as a thermal free radical initiator and a photoinitiator (see Sect. 3.2.4). It can be illustrated as follows:



The claimed advantage of this initiator is that it can be used to form block copolymers.

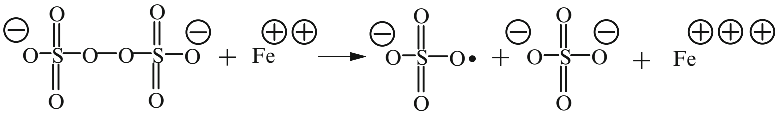
3.2.2 Bimolecular Initiating Systems

Decompositions of peroxides into initiating radicals are also possible through bimolecular reactions involving electron transfer mechanisms. Such reactions are often called ***redox*** initiations and can be illustrated as follows:

$$\underset{\text{electron donor}}{A} + \underset{\text{electron acceptor}}{\text{R-O-O-R}'} \longrightarrow A^{\oplus} + RO\bullet + {}^{\ominus}OR'$$

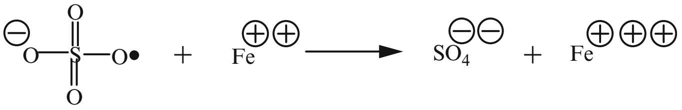
where, A is the reducing agent and ROOR′ is the peroxide.

The above can be illustrated on a decomposition of a persulfate (an inorganic peroxide) by the ferrous ion:



electron acceptor electron donor initiating ion-radical

Side reactions are possible in the presence of sufficient quantities of reducing ions:



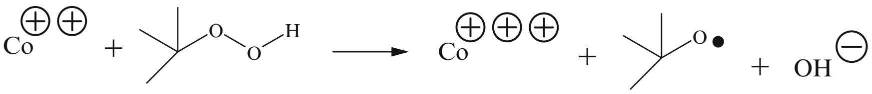
A redox reaction can also take place between the peroxide and an electron acceptor:

$$\text{R-O-O-H} + Ce^{\oplus\oplus\oplus\oplus} \longrightarrow \text{R-O-O}\,\bullet + Ce^{\oplus\oplus\oplus} + H^{\oplus}$$

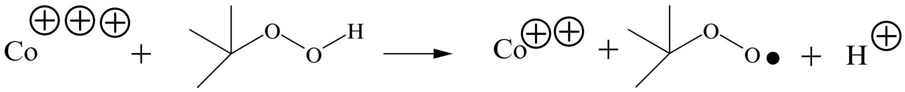
Side reactions with an excess of the ceric ion can occur as well:

$$\text{R-O-O}\,\bullet + Ce^{\oplus\oplus\oplus\oplus} \longrightarrow R^{\oplus} + O_2 + Ce^{\oplus\oplus\oplus}$$

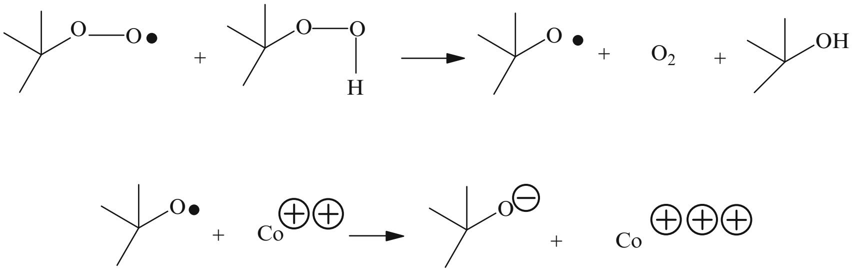
Another example is a redox reaction of *t*-butyl hydroperoxide with a cobaltous ion [17]:
The cobaltic ion that forms can act as an electron acceptor:



The cobaltic ion that forms can act as an electron acceptor:

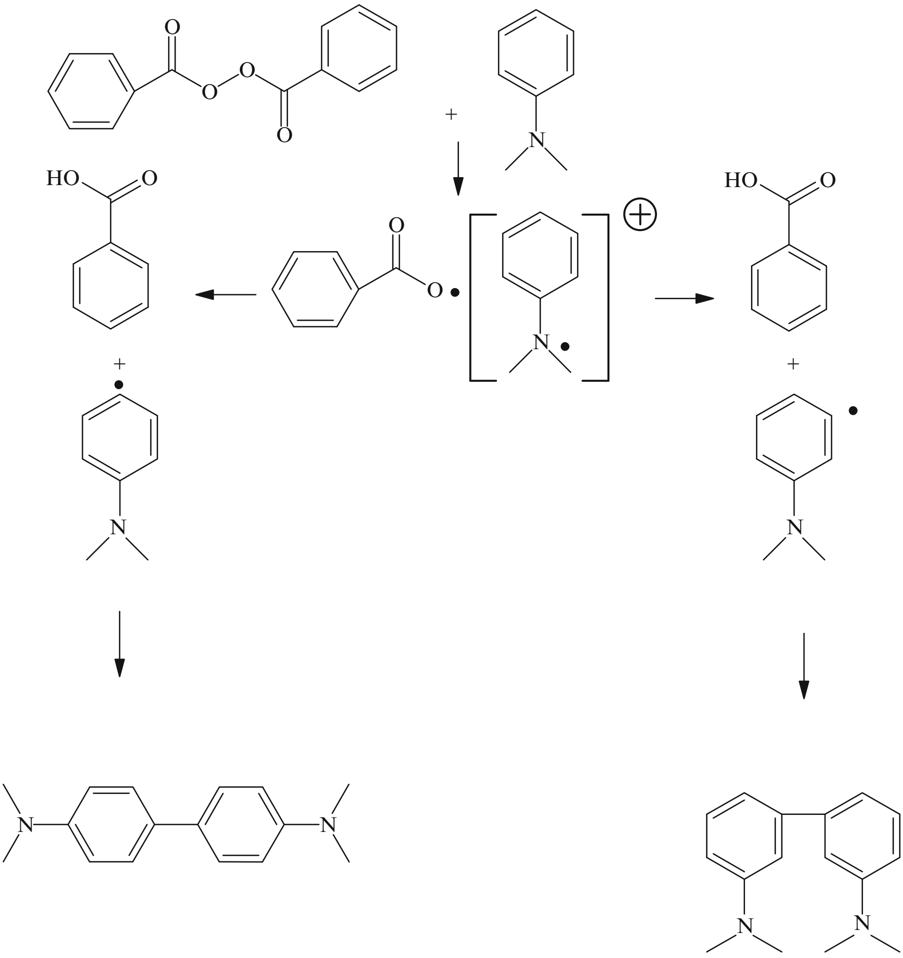


Side reactions can occur here too, such as:

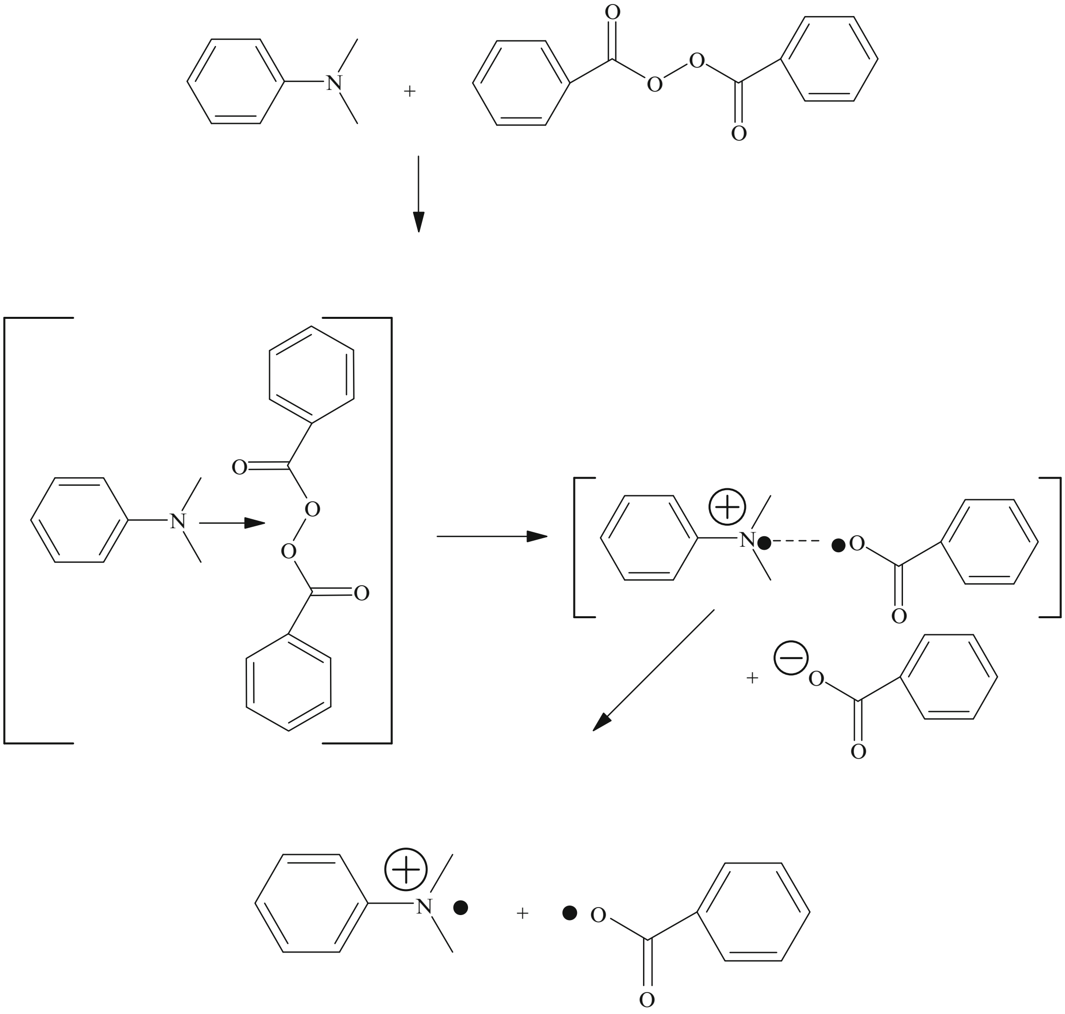


Nevertheless, cobaltous ions form efficient redox initiating systems with peroxydisulfate ions [18].

Tertiary aromatic amines also participate in bimolecular reactions with organic peroxides. One of the unpaired electrons on the nitrogen atom transfers to the peroxide link, inducing decomposition. No nitrogen, however, is found in the polymer. It is, therefore, not a true redox type initiation and the amine acts more like a *promoter* of the decomposition [19]. Two mechanisms were proposed to explain this reaction. The first one was offered by Horner et al. [19]:



A second mechanism, proposed by Imoto and Choe [20] shows the complex as an intermediate step:

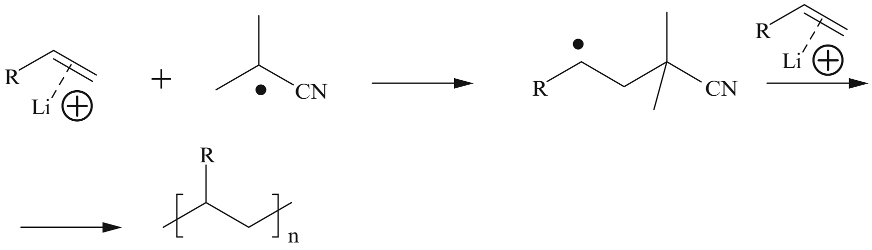


The dimethyl aniline radical-cation, shown above, undergoes other reactions than addition to the monomer. The benzoyl radical is the one that initiates the polymerizations.

Presence of electron-releasing substituents on diethyl aniline increases the rate of the reaction with benzoyl peroxide [21]. This suggests that the lone pair of electrons on nitrogen attack the positively charged oxygen of the peroxide link [22].

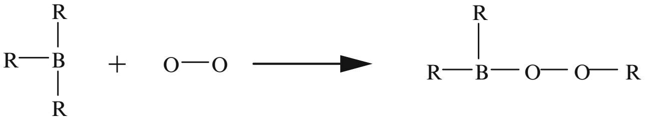
By comparison to peroxides, the azo compounds are generally not susceptible to chemically induced decompositions. It was shown [23], however, that it is possible to accelerate the decomposition of α,α′-azobisisobutyronitrile by reacting it with bis(-)-ephedrine-copper (II) chelate. The mechanism was postulated to involve reductive decyanation of azobisisobutyronitrile through coordination to the chelate [23]. Initiations of polymerizations of vinyl chloride and styrene with α,α′-azobisisobutyronitrile coupled to aluminum alkyls were investigated [24]. Gas evolution measurements indicated some accelerated decomposition. Also, additions of large amounts of tin tetrachloride to either α,α′-azobisisobutyronitrile or to dimethyl-α,α′-azobisisobutyrate increase the decomposition rates [25]. Molar ratios of $[SnCl_4]/[AIBN] = 21.65$ and $[SnCl_4]/[MAIB] = 19.53$ increase the rates by factors of 4.5 and 17, respectively. Decomposition rates are also enhanced by donor solvents, such as ethyl acetate or propionitrile in the presence of tin tetrachloride [25].

A bimolecular initiating system, based in 2,2′-azobisisobutyronitrile was reported by Michl and coworkers [26]. It consists of weakly solvated lithium in combination with the cyanopropyl radical (from AIBN). The combination can initiate polymerizations of olefins. The reaction was illustrated as follows:

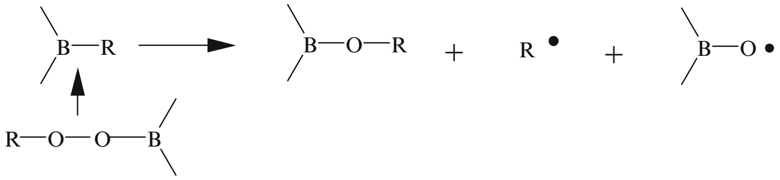


3.2.3 *Boron and Metal Alkyl Initiators of Free-Radical Polymerizations*

These initiators were originally reported a long time ago [27–29]. Oxygen plays an important role in the reactions [30, 31]. It reacts with the alkyl boride under mild conditions to form peroxides [32, 33]:



Initiating radicals apparently come from reactions of these peroxides with other molecules of boron alkyls [34, 35]. One postulated reaction mechanism can be illustrated as follows [35]:



Another suggested reaction path is [36]:

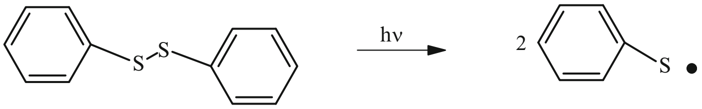
$$R_2B\text{-}O\text{-}O\text{-}R + 2R'_3B \rightarrow 2R\bullet + R'_2B\text{-}O\text{-}BR'_2 + R'_2B\text{-}O\text{-}R$$

Catalytic action of oxygen was observed with various organometallic compounds [35]. One example is dialkylzinc [37] that probably forms an active peroxide [38]. The same is also true of dialkylcadmium and of triethylaluminum [38]. Peroxide formation is believed to be an important step in all these initiations. Initiating radicals, however, do not appear to be produced from mere decompositions of these peroxides [35].

3.2.4 *Photochemical Initiators*

This subject is discussed in greater detail in Chap. 10, in the section on photo-cross-linking reactions of coatings and films. A brief explanation is also offered here because such initiations are used, on a limited scale, in a few conventional preparation of polymers.

Many organic compounds decompose or cleave into radicals upon irradiation with light of an appropriate wavelength [38, 39]. Because the reactions are strictly light and not heat induced, it is possible to carry out the polymerizations at low temperatures. In addition, by employing narrow wavelength bands that only excite the photoinitiators, it is possible to stop the reaction by merely blocking out the light. Among the compounds that decompose readily are peroxides, azo compounds, disulfide, ketones, and aldehydes. A photodecomposition of a disulfide can be illustrated as follows:



Today, many commercially prepared photoinitiators are available. Some consists of aromatic ketones that cleave by the Norrish reaction or are photoreduced to form free radicals. There are also numerous other two and three component photoinitiating systems. There are also those that decompose by irradiation with visible light and make it possible to initiate the reactions with longer wavelength light (see Chap. 10) Some examples of various photoinitiators are given in Chap. 10. Many others can be found in the literature.

As an example can be sited the work by Barner-Kowollik and coworkers studied the photoinitiation process in methyl methacrylate polymerization, using high-resolution electro spray-mass spectrometry [40]. The polymerization was conducted using a pulsed laser at temperatures ≤0°C in the presence of the photoinitiators 2,2-dimethoxy-2-phenylacetophenone, benzoin, benzil, benzoin ethyl ether, and 2,2-azobisisobutylnitrile. They identified the termination products, both combination and disproportionation with high accuracy. Both the benzoyl and acetal fragments generated as a result of 2,2-dimethoxy-2-phenylacetophenone photocleavage were found to initiate and highly likely terminate the polymerization. Both the benzoyl and ether fragments produced as a result of benzoin photocleavage were found to act as initiating and probable terminating species, indicating that the ether radical fragment does not act exclusively as a terminating species.

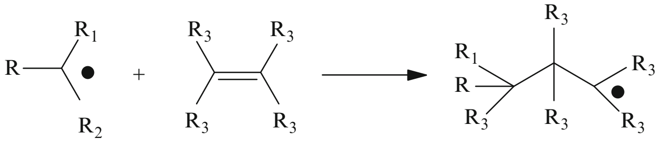
3.2.5 *Initiation of Polymerization with Radioactive Sources and Electron Beams*

Different radioactive sources can initiate free-radical polymerizations of vinyl monomers. They can be emitters of gamma rays, beta rays, or alpha particles. Most useful are strong gamma emitters, such as ^{60}Co or ^{90}Sr. Electron beams from electrostatic accelerators are also efficient initiators. The products from irradiation by radioactive sources or by electron beams are similar to but not identical to the products of irradiation by ultraviolet light. Irradiation by ionizing radiation causes the excited monomer molecules to decompose into free radicals. Ionic species also form from initial electron captures. No sensitizers or extraneous initiating materials are required. It is commonly accepted that free radicals and ions are the initial products and that they act as intermediate species in these reactions. There is still insufficient information, however, on the exact nature of all of these species [38, 39]. The polymerizations are predominantly by a free-radical mechanism with some monomers and by an ionic one with others [38, 39].

3.3 Capture of Free Radicals by Monomers

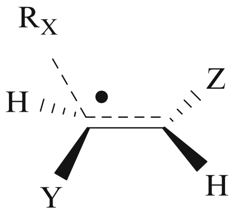
Once the initiating radical is formed, there is competition between addition to the monomer and all other possible secondary reactions. A secondary reaction, such as a recombination of fragments, as shown above, can be caused by the cage effect of the solvent molecules [41]. Other reactions can take place between a radical and a parent initiator molecule. This can lead to the formation of different initiating species. It can, however, also be a dead end as far as the polymerization reaction is concerned.

After the initiating radical has diffused into the proximity of the monomer, the capture of the free radical by the monomer completes the step of initiation. This is a straightforward addition reaction, subject to steric effects:



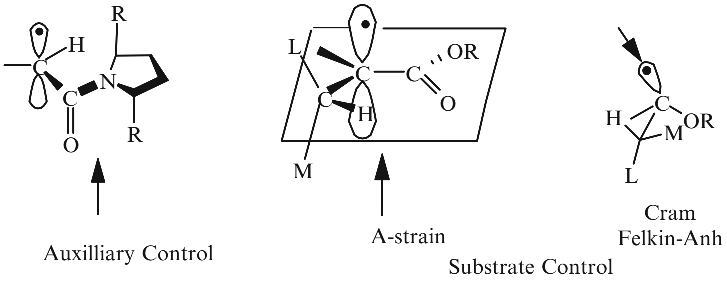
The unpaired electron of the radical is believed to be in the pure p-orbital of a planar, sp^2, carbon atom. Occasionally, however, radicals with sp^3 configuration appear to form [42–44].

Using quantum chemical calculations it was demonstrated that nucleophilic and electrophilic alkyl or aryl radicals attack alkenes following a tetrahedral trajectory [45, 46]:



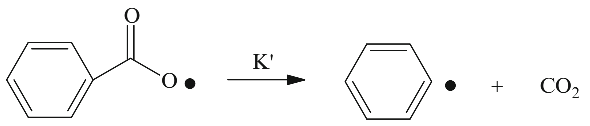
This means that only substituents Y at the attacked olefinic carbon exert large steric effects [47]. In addition to the steric effects, the rates of addition of strongly nucleophilic or electrophilic radicals are governed mainly by polar effects of the substituents R_x, Y, and Z [48]. In borderline cases, however, the stabilities of the adducts and products tend to dominate [47].

Also, it was demonstrated that acyclic radicals can react with high stereoselectivity [45]. In order for the reactions to be stereoselective, the radicals have to adopt preferred conformations where the two faces of the prochiral radical centers are shielded to different extents by the stereogenic centers. Giese and coworkers [49] demonstrated with the help of Electron Spin Resonance studies that ester-substituted radicals with stereogenic centers in β-positions adopt preferred conformations that minimize allylic strain [49] (shown below). In these conformations, large (L) and medium sized substituents (M) shield the two faces. The attacks come preferentially from the less shielded sides of the radicals. Stereoselectivity, because of A-strain conformation, is not limited to ester-substituted radicals [50]. The strains and steric control in reactions of radicals with alkenes can be illustrated as follows [50]:

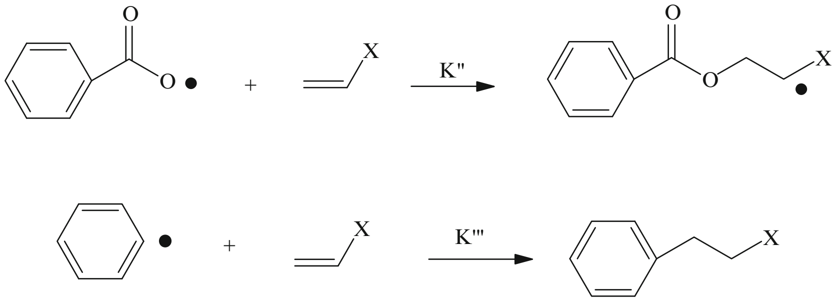


The above considerations can be illustrated on initiation by benzoyl peroxide, a commonly used initiating compound. The half-life of the initial benzoyloxy radicals from decompositions of benzoyl peroxide is estimated to be 10^{-4} to 10^{-5} s. Past that time, they decompose into phenyl radicals and carbon dioxide [49]. This is sufficient time for the benzoyloxy radicals to be trapped by fast-reacting monomers. Slow-reacting monomers, however, are more likely to react with the phenyl radicals that form from the elimination reaction. In effect, there are two competing reactions [50]:

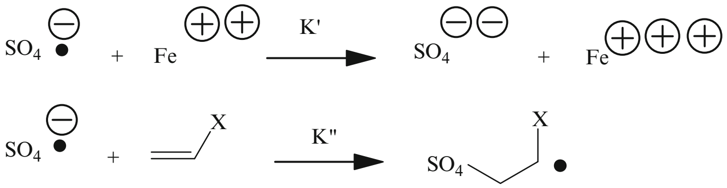
1. Decomposition of the free radical:



2. Two types of radicals can add to the monomer (where x represents any typical substituent of vinyl monomers, such as halogens, or esters, or aromatic groups, or nitriles, etc.):



The ratio of the rates of the two reactions, K''/K', (or K'''/K') depends upon the reactivity of the monomers. It is shown in Table 3.5 [51, 52]. The benzoyloxy radical is used in this table as an illustration. A similar comparison is possible for a redox initiating system. An initiating sulfate radical ion from a persulfate initiator can react with another reducing ion or add to the monomer:

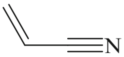
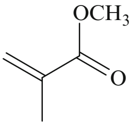
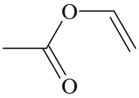
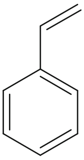
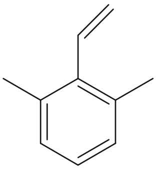


In Table 3.6 are shown the relative reaction rates of SO_4• ⊖ with some monomers at 25°C [53–57]. As explained, the rate of addition of a radical to a double bond is affected by steric hindrance from bulky substituents. Polar effect, such as dipole interactions also influence the rate of addition.

Forbes and Yashiro studied the addition of the initiating radials to methyl methacrylate in liquid supercritical carbon dioxide [58]. They demonstrated that the rate of addition of the initiating radicals to the monomers, k_{add} values, can be measured in liquid CO_2.

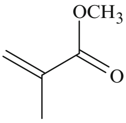
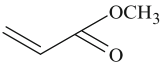
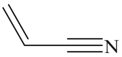
Phenyl or methyl groups located on the carbon atom that is under a direct attack by a free radical can be expected to interfere sterically with the approach. For instance, due to steric hindrance, *trans*-β-methylstilbene is more reactive toward a radical attack than is its *cis* isomer [58]. Yet, the *trans* isomer is more stable of the two. While 1,1-disubstituted olefins homopolymerize readily, the 1,2-disubstituted olefins are hard to homopolymerize [59]. Some exceptions are vinyl carbonate [61] and maleimide derivatives [62]. Also, perfluoroethylene and chlorotrifluoroethylene polymerize readily. Table 3.6 shows the relative reaction rates of SO_4• ⊖ with some monomers at 25°C [50].

Table 3.5 Relative reactivities of the benzoyloxy radical at 60°C

Monomer	Structure	K'/K'' (mol/L)
Acrylonitrile		0.12
Methyl methacrylate		0.30
Vinyl acetate		0.91
Styrene		2.50
2,5-dimethylstyrene		5.0

Addition to monomer/decomposition rates [51, 52]

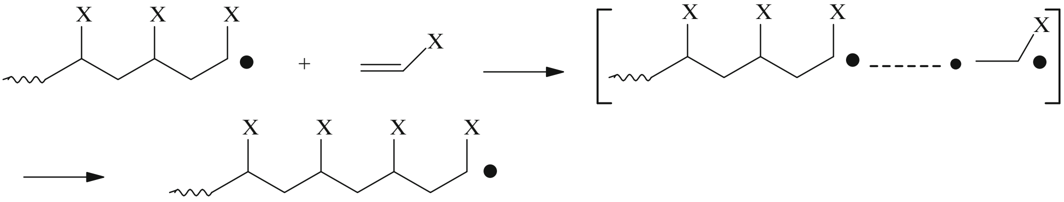
Table 3.6 Relative rates of reactions of the sulfate ion-radical with some monomers [51, 52]

Monomer	Structure	Relative rates K''/K'
Methyl methacrylate		7.7×10^{-3}
Methyl acrylate		1.1×10^{-3}
Acrylonitrile		3.9×10^{-4}

Homopolymerizations of diethyl fumarate by free-radical mechanism were reported [63]. The M_n was found to be 15,000. The same is true of homopolymerizations of several other dialkyl fumarates and also dialkyl maleates [64–66]. The polymerization rates and the sizes of the polymers that form decrease with increases in the lengths of linear alkyl ester groups. There is, however, an opposite correlation if the ester groups are branched. Also, the maleate esters appear to isomerize to fumarates prior to polymerization [66].

3.4 Propagation

The transition state in a propagation reaction can be illustrated as follows:



In the above transition state, the macroradical electron is localized on the terminal carbon. Also, the two π electrons of the double bond are localized at each olefinic carbon. Interaction takes place between p-orbital of the terminal atom in the active polymer chain with associated carbon of the monomer. This results in formation of σ-bonds [67].

The rate of the propagation reaction depends upon the reactivity of the monomer and the growing radical chain. Steric factors, polar effects, and resonance are also important factors in the reaction.

Another factor that can affect the rate of propagation is interaction between propagating radicals. Siegmann and Beuermann [60] studied the rate of propagation of 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate and compared it to the rate of propagation of methyl methacrylate. They observed that k_p for 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl methacrylate polymerization is 1.9 times that of k_p for methyl methacrylate. They concluded that this higher rate is due to less interactions occurring between the propagating macroradicals.

Bowman and coworkers studied the impact of intermolecular and intramolecular interactions on the polymerization kinetics of monoacrylates [69]. They carried out polymerization studies in the presence of extensive amounts of solvent. This was an attempt to elucidate the effects of intermolecular interactions, such as bulk medium polarity, π–π stacking, and hydrogen bonding and characterize the contribution of intramolecular conformational effects to monomer reactivity. Solution polymerization kinetics of various monomers were measured in the presence of 95 wt% 1,4-dioxane. The results were compared to bulk polymerization kinetics. The studies revealed that aliphatic acrylates such as hexyl acrylate exhibit approximately two to threefold reduction in reactivity upon dilution. Monomers characterized by only hydrogen-bonding features such as hydroxyethyl acrylate exhibit an 8- to 12-fold reduction upon dilution. Monomers possessing only aromatic ring stacking interactions such as phenyl acrylate exhibit approximately a five to tenfold reduction upon dilution under similar conditions. Even at a concentration of 5 wt% monomer in 1,4-dioxane, there were approximately two to fivefold differences in reactivity observed between various acrylates. Bowman and coworkers attributed these reactivity differences between various acrylates, upon extensive dilution, solely to intramolecular interactions [69].

3.4.1 Steric, Polar, and Resonance Effects in the Propagation Reaction

The steric effects depend upon the sizes of the substituents. The resonance stabilization of the substituents has been shown to be in the following order [70]:

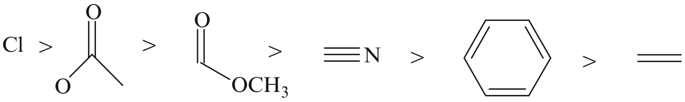
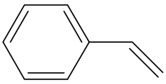
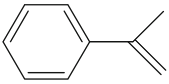
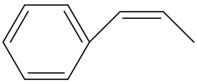
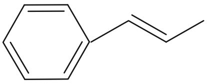
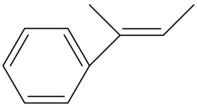
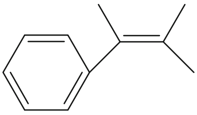
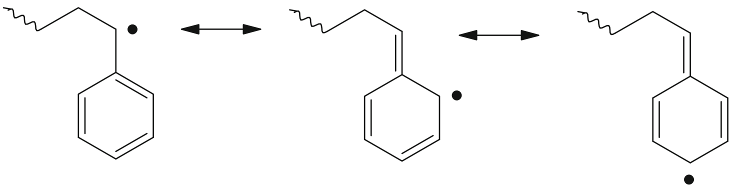


Table 3.7 Affinity of methyl radical for olefins[a] [56, 57, 67]

Monomer	Structure	Methyl affinity
Styrene		792
α-methyl styrene		92.6
cis-β-methyl styrene		40
Trans-β-methyl styrene		92.5
α,β-dimethyl styrene		66
α,β,β′-trimethyl styrene		20

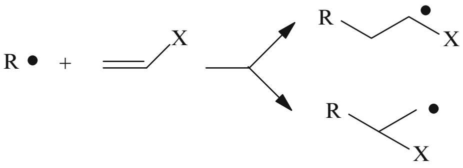
[a] From Carrick, Szwarc, Leavitt, Levy, and Stannett, by permission of American Chemical Society

The reactivities of the propagating polymer-radicals, however, exert greater influence on the rates of propagation than do the reactivities of the monomers. Resonance stabilization of the polymer-radicals is a predominant factor. This fairly common view comes from observations that a methyl radical reacts at a temperature such as 60°C approximately 25 times faster with styrene than it does with vinyl acetate [72]. In homopolymerizations of the two monomers, however, the rates of propagation fall in an opposite order. Also, poly(vinyl acetate)-radicals react 46 times faster with *n*-butyl mercaptan in hydrogen abstraction reactions than do the polystyrene-radicals [71]. The conclusion is that the polystyrene radicals are much more resonance stabilized than are the poly (vinyl acetate)-radicals. Several structures of the polystyrene-radicals are possible due to the conjugation of the unpaired electrons on the terminal carbons with the adjacent unsaturated groups. These are resonance hybrids that can be illustrated as follows:

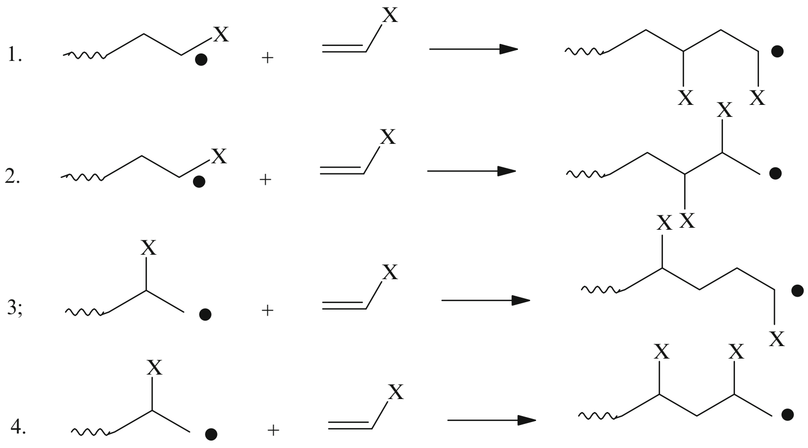


There is not such opportunity, however, for resonance stabilization of the poly(vinyl acetate) radicals because oxygen can accommodate only eight electrons. The effect of steric hindrance on the affinity of a methyl radical is illustrated in Table 3.7 [56, 57].

In vinyl monomers, both olefinic carbons are potentially subject to free-radical attack. Each would give rise to a different terminal unit:



The newly formed radicals can again potentially react with the next monomer in two ways. This means that four propagation reactions can occur:

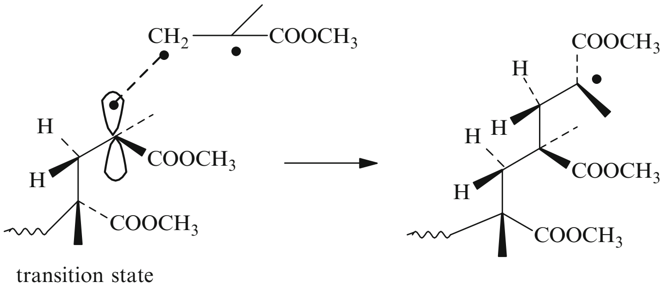


Contrary to the above shown four propagation modes, a “head to tail” placement shown in (3.1), strongly predominates. This is true of most free radical vinyl polymerizations. It is consistent with the localized energy at the α-carbon of the monomer. Also, calculations of resonance stabilization tend to predict head to tail additions [68].

The free-radical propagation reactions that correspond to conversions of double bonds into single bonds are strongly exothermic. In addition, the rates increase with the temperature. It is often assumed that the viscosity of the medium, or change in viscosity during the polymerization reaction does not affect the propagation rate or the polymer growth reaction. This is because it involves diffusion of small monomer molecules to the reactive sites. Small molecules, however, can also be impeded in their process of diffusion. This can impede the growth rate [50].

During chain growth, the radical has a great deal of freedom with little steric control over the manner of monomer placement. Decrease in the reaction temperature, however, lowers mobility of the species and increases steric control over placement. This is accompanied by an increase in stereoregularity of the product [70, 71]. The preferred placement is ***trans–trans***, because of lower energy required for such placement. As a result, a certain amount of syndiotactic arrangement is observed in polymerizations at lower temperatures [72]. *Trans–trans* configurations (with respect to the carbon atoms in the chains) yield zigzag backbones. This was predicted from observations of steric effects on small molecules [74, 75]. It was confirmed experimentally for many polymers, such as, for instance, in the formation of poly(1,2-polybutadiene) [74] and poly(vinyl chloride) [72]. Also, in the free-radical polymerizations of methyl methacrylate, syndiotactic placement becomes increasingly dominant at lower temperatures. Conversely, the randomness increases at higher temperatures [74]. The same is true in the free-radical polymerization of halogenated vinyl acetate [75].

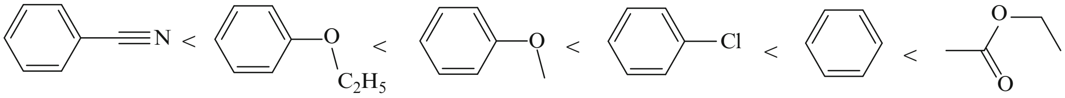
One proposed mechanism for the above is as follows. The least amounts of steric compression within macromolecules occur during the growth reactions if the ultimate and the penultimate units are *trans* to each other. Also, if the lone electrons face the oncoming monomers during the transition states [80, 81], as shown below, syndiotactic placement should be favored:



While the above model explains the formation of syndiotactic poly(methyl methacrylate), possible interactions between the free radicals on the chain ends and the monomers are not considered. Such interactions, however, are a dominant factor in syndiotactic placement, if the terminal carbons are sp^2 planar in structures [75].

3.4.2 *Effect of Reaction Medium*

There were some early reports that reaction media influences the polymerizations of vinyl chloride in aliphatic aldehydes at 50°C [80, 81]. This was not confirmed in subsequent studies [82–84]. Subsequently, the rate of polymerization was shown to be influenced by the pH of the reaction medium in polymerizations of monomers such as methacrylic acid (MAA) [85, 88]. Also, the rate of polymerization and solution viscosities increase in polymerizations of acrylamide and acrylic acid with an increase in water concentration [83]. It is not quite clear whether this is due to increases in the speeds of propagations or due to decreases in the termination rates. In the free-radical polymerization of vinyl benzoate, the rate of propagation varies in different solvents in the following order [88, 89]:



Similarly, the rate of photopolymerization of vinyl acetate is affected by solvents [88]. In most cases, however, the rate of polymerization is proportional to the square root of the initiator concentration and to the concentration of the monomer [5].

De Sterck and coworkers [90] studied solvent effect on tacticity of methyl methacrylate in free-radical polymerization. They observed that solvents CH_3OH and $(CF_3)_3COH$, which are H-bonded with the carbonyl oxygens and are located on the same side of the backbone of the growing polymer radical hinder the formation of isotactic poly(methyl methacrylate) to some extent. Methanol is less effective in reducing the isotacticity because of its small size and also because of the relatively loose hydrogen bonds with the carbonyl oxygens.

There is a controversial suggestion that the solvent affects the propagation step in some reactions by forming "hot" radicals [91]. These radicals are supposed to possess higher amounts of energy. At the moment of their formation, they obtain surplus energy from the heat of the reaction and from the activation energy of the propagation reaction. This is claimed to provide the extra energy needed to activate the next chain propagation step. The surplus energy may affect the polymerization kinetics if the average lifetime of the hot radicals is sufficient for them to react with the monomer molecules. This surplus energy is lost by the hot radicals in collisions with monomer and solvent molecules.

There is a difference in the rate constants of propagation for hot and ordinary radicals so two different reaction schemes were written [91]:
Propagation by ordinary radicals:

$$\mathrm{R\bullet + M \rightarrow RM\bullet} \quad (k_2)$$

Propagation by hot radicals:

$$\mathrm{R^* + M \rightarrow RM^*} \quad (k_2{}^*)$$

Energy transfer processes:

$$\mathrm{R^* + Solvent \rightarrow R\bullet + Solvent} \quad (k_3'{}^*)$$

where, R* is the symbol for hot radicals.

The rate expression for the polymerization is then written as follows [92]:

$$-\,\mathrm{d[M]}/\mathrm{d}t = K_\mathrm{X} X^{0.5}[\mathrm{M}] \times [\mathrm{I} + 1/(\gamma + \gamma' + \mathrm{S}/[\mathrm{M}])]$$

where, $K_\mathrm{x} = k_2(2k_1f/k_4)^{1/2}$, $\gamma = k_1{}^*/k_2{}^*$ and $\gamma' = k_3{}^*/k_2{}^*$, S = solvent, [M] = monomer

In comparing free-radical polymerizations of ethyl acrylates in benzene and in dimethyl formamide at 50°C [218] the rates were found to be proportional to the square roots of the initiator concentration. They were not proportional, however, to the concentrations of the monomer. This was interpreted in terms of hot radicals [93].

Similar results, however, were interpreted by others differently. For instance, butyl acrylate and butyl propionate polymerizations in benzene also fail to meet ideal kinetic models. The results, however, were explained in terms of termination of primary radicals by chain transferring (see Sect. 3.5 for explanation of chain transferring).

3.4.3 Ceiling Temperature

For most free-radical polymerization reactions, there are some elevated temperatures at which the chain-growth process becomes reversible and depropagation takes place:

$$\mathrm{M_{n+1}} \xrightarrow{k_{\mathrm{dp}}} \mathrm{M_n\bullet + M}$$

where, $k_{\mathrm{d\cdot p}}$ is the rate constant for depropagation or depolymerization. The equilibrium for the polymerization–depolymerization reaction is temperature dependent. The reaction isotherm can be written:

$$\Delta F = \Delta F^0 + RT\ln K$$

In the above equation ΔF^0 is the free energy of polymerization of both, monomer and polymer, in appropriate standard states [88]. The standard state for the polymer is usually solid (amorphous or partly crystalline). It can also be a one molar solution. The monomer is a pure liquid or a one molar solution. The relationships of monomer concentration to heat content, entropy, and free energy are shown by the following expression. This applies over a wide range of temperatures [5].

$$\ln[\mathrm{M}] = \Delta H^0{}_{\mathrm{P}}/RT_{\mathrm{c}} - \Delta S^0{}_{\mathrm{P}}/R$$

In the above equation, T_c is the ***ceiling temperature*** for the ***equilibrium monomer concentration***. It is a function of the temperature of the reaction. Because the heat content is a negative quantity, the concentration of the monomer (in equilibrium with polymer) increases with increasing temperatures. There are a series of ceiling temperatures that correspond to different equilibrium monomer concentrations. For any given concentration of a monomer in solution, there is also some upper temperature at which polymerization will not proceed. This, however, is a thermodynamic approach. When there are no active centers present in the polymer structure, the material will appear stable even above the ceiling temperature in a state of metastable equilibrium.

The magnitude of the heat of polymerization of vinyl monomers is related to two effects: (1) Steric strains that form in single bonds from interactions of the substituents. These substituents, located on the alternate carbon atoms on the polymeric backbones, interfere with the monomers entering the chains. (2) Differences are in resonance stabilization of monomer double bonds by the conjugated substituents [70].

Most 1,2 disubstituted monomers, as stated earlier, are difficult to polymerize. It is attributed to steric interactions between one of the two substituents on the vinyl monomer and the β-substituent on the ultimate unit of the polymeric chain [94]. A strain is also imposed on the bond that is being formed in the transition state.

The propagation reaction usually requires only an activation energy of about 5 kcal/mol. As a result, the rate does not vary rapidly with the temperature. On the other hand, the transfer reaction requires higher activation energies than does the chain-growth reaction. This means that the average molecular weight will be more affected by the transfer reaction at higher temperature. When allowances are made for chain transferring, the molecular weight passes through a maximum as the temperature is raised. At temperatures below the maximum, the product molecular weight is lower because the kinetic chain length decreases with the temperature. Above the maximum, however, the product molecular weight is also lower with increases in the temperature. This is due to increase in the transfer reactions. The above assumes that the rate of initiation is independent of the temperature. The relationship of the kinetic chain length to the temperature can be expressed as follows [5]:

$$\mathrm{d}\ln v/\mathrm{d}T = (E_{\mathrm{P}} - 1/2E_{\mathrm{T}} - 1/2E_{\mathrm{I}})/RT^2$$

where, E_{P}, E_{T}, and E_{I} are energies of propagation, termination, and initiation, respectively. A large E_{I} means that if the temperature of polymerization is raised, the kinetic chain length decreases. This is affected further by a greater frequency of chain transferring at higher temperatures. In addition, there is a possibility that disproportionation may become more significant.

3.4.4 Autoacceleration

When the concentrations of monomers are high in solution or bulk polymerizations, typical autoaccelerations of the rates can be observed. This is known as the ***gel effect*** or as the ***Trammsdorff effect***, or also, as the ***Norrish–Smith effect*** [66]. The effect has been explained as being caused by a decrease in the rate of termination due to increased viscosity of the medium. Termination is a reaction that requires two large polymer-radicals to come together and this can be impeded by viscosity. At the same time, in propagation the small molecules of the monomer can still diffuse for some time to the radical sites and feed the chain growth.

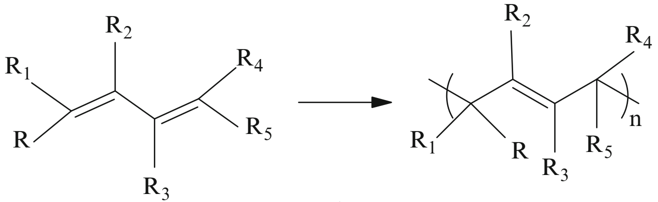
One should not mistake an acceleration of the polymerization reaction due to a rise in the temperature under nonisothermal conditions for a true gel effect from a rise in viscosity. The gel effect can occur when the temperature of the reaction is kept constant.

A critical analysis of the gel effect suggests that the situation is complicated. In some polymerizations, three different stages appear to be present when $R_P/[M][I]^{1/2}$ is plotted against conversion or against time [95]. The plot indicates that during the first stage there is either a constant or a declining rate and during the second stage there is autoacceleration. During the third stage, there is again a constant or a declining rate [95].

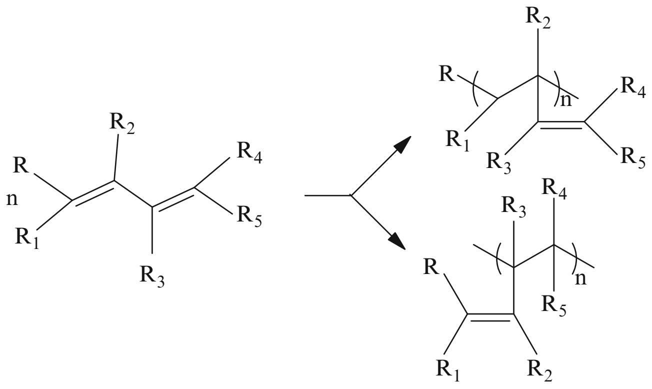
Numerous publication made a substantial case for associating and/or attributing the gel effect to entanglement of polymerizing chain radicals, resulting in a marked reduction in the termination rate parameter, k_T. This was often done by using the assumption that in the neighborhood of the gel effect k_T is controlled by polymer self-diffusion, which in turn exhibits entangled polymer dynamics. O'Neil et al. [96], however, argued against that opinion. They carried out a series of experiments involving bulk polymerizations of methyl methacrylate and styrene and feel that their data contradicts this widely held belief that the gel effect onset is related to the formation of chain entanglements. The experimental conditions used were such that they tended to delay or eliminate the formation of chain entanglement. These conditions were high initiator and/or chain transferring agent concentrations and additions of low molecular weight polymers prior to the reactions. The results indicated that the gel effect occurs readily in the absence of entanglement and that delaying the onset of entanglements does not necessarily delay the onset of the gel effect. Also, critical examination of the molecular weights produced in these experiments indicated values that were too low for entanglement formation in solution (polymer plus monomer) and sometimes even in bulk polymer, not only at the onset but also throughout the gel effect [96]. O'Neil et al. [96], found that even under conditions where entanglements are likely to exist, the gel effect onset does not correlate with polymer molecular weight of the chains produced in a manner consistent with entanglement arguments. Whether the kinetics during the gel effect may be affected by entanglements was left uncertain.

3.4.5 Polymerization of Monomers with Multiple Double Bonds

Polymerizations of monomers with multiple double bonds yield products that vary according to the locations of these bonds with respect to each other. Monomers with conjugated double bonds, such as 1,3-butadiene and its derivatives, polymerize in two different ways. One way is through one of the double bonds only. Another way is through both double bonds simultaneously. Such 1,4 propagation is attributable to the effect of conjugation and hybridization of the C_2–C_3 bond that involves *sp*^{2} hybrid orbitals [97]. All three modes of propagation are possible in one polymerization reaction so that the product can, in effect, be a copolymer. The 1,4, 1,2, and 3,4, placement in propagations can be illustration as follows:



1,4-placement

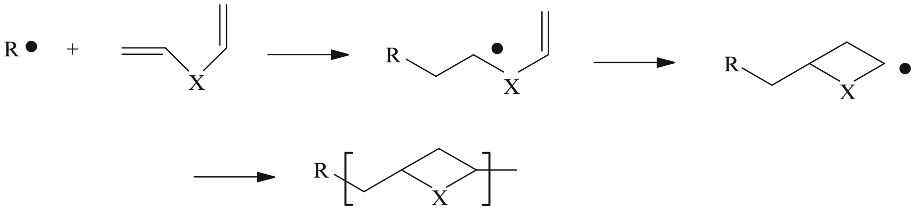


1,2 and 3,4 placements

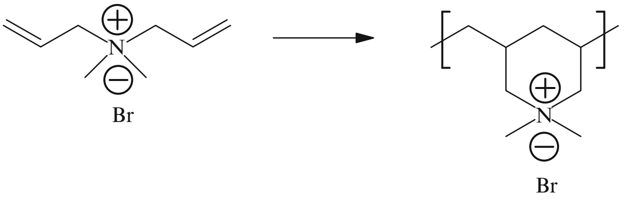
The polymerizations and copolymerizations of various conjugated dienes are discussed in Chap. 6.

3.4.5.1 Ring Forming Polymerization

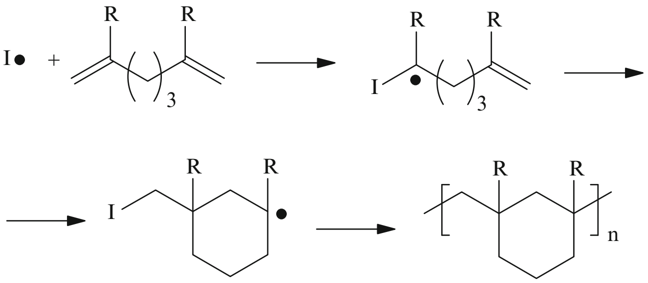
Propagation reactions of unconjugated dienes can proceed by an intra-intermolecular process. This usually results in ring formation or in ***cyclopolymerization***. It can be illustrated as follows:



where, X can designate either a carbon or a heteroatom. An example of such a polymerization is a free-radical polymerization of quaternary diethyldiallylamine [98]:

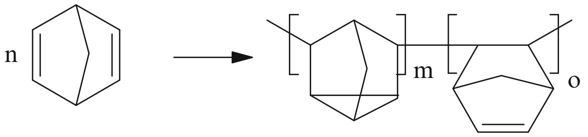


Another example is a polymerization of 2,6-disubstituted 1,6-heptadiene [103]:

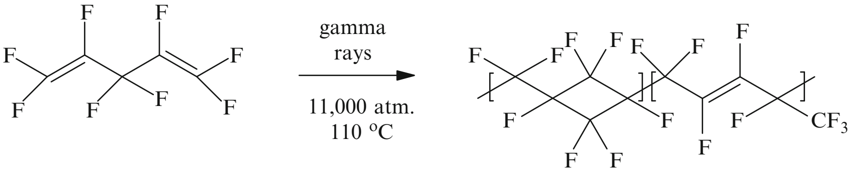


where, R=$COOC_2H_5$, $COOCH_3$, or COOH.

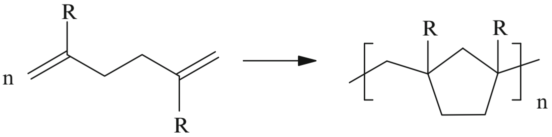
The intra-intermolecular propagations can result in ring structures of various sizes. For instance, three-membered rings can form from ***transanular*** polymerizations of bicycloheptadiene [100, 101]:



Four-membered rings form in free-radical polymerization of perfluoro-1,4-pentadiene [103]. The size of the ring that forms depends mainly on the number of atoms between the double bonds:



Formation of many five-membered rings is also known. One example is a polymerization of 2,3-dicarboxymethyl-1,6 hexadiene [98]:

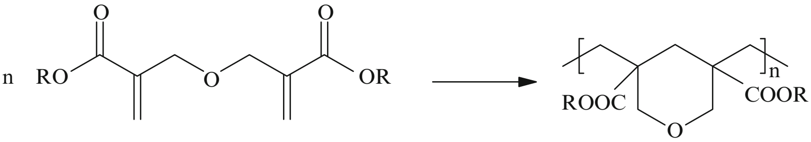


where, R=$COOCH_3$.

The polymer that forms, shown above, is cross-linked, but spectroscopic analysis shows that 90% of the monomer placement is through ring formation [104]. Formations of six-membered rings are also well documented. Two examples were shown above in the polymerization of a quaternary diethyldiallylamine and in the polymerization of 2,6 disubstitued, 1,6-heptadiene. Many other 1,6-heptadienes yield linear polymers containing six-membered rings [105].

This tendency to propagate intra-intermolecularly by the unconjugated dienes is greater than can be expected from purely statistical predictions [106]. Butler suggested that this results from interactions between the olefinic bonds [107–109]. Ultraviolet absorption spectra of several unconjugated diolefins does show bathochromic shifts in the absorption maxima relative to the values calculated from Woodward's rule [102, 104]. This supports Butler's explanation [107, 109].

A RAFT type of controlled/living polymerization (see Sect. 3.14.4) was applied to cyclopolymerization of *t*-butyl (hydroxyethyl) acrylate ether dimer [108]. The polymerizations, carried out in xylene at 70°C, yielded polymers with six-membered tetrahydropyran repeat units:



3.5 The Termination Reaction

The termination process in free-radical polymerization is caused, as was shown early in this chapter, by one of three types of reactions: (1) a second order radical-radical reaction, (2) a second order radical-molecule reaction, and (3) a first order loss of radical activity.

The first reaction can be either one of combination or of disproportionation. In a combination reaction, two unpaired spin electrons, each on the terminal end of a different polymer-radical, unite to form a covalent bond and a large polymer molecule. In disproportionation, on the other hand, two polymer-radicals react and one abstracts an atom from other one. This results in formation of two inactive polymer molecules. The two differ from each other in that one has a terminal saturated structure and the other one has a terminal double bond. Usually, the atom that is transferred is hydrogen.

It was suggested [111] that a basic rule of thumb can be applied to determine which termination reaction predominates in a typical homopolymerization. Thus, polymerizations of 1,1-disubstituted olefins are likely to terminate by disproportionation because of steric effects. Polymerizations of other vinyl monomer, however, favor terminations by combination unless they contain particularly labile atoms for transferring. Higher activation energies are usually required for termination reactions by disproportionation. This means that terminations by combination should predominate at lower temperatures.

For a polymer radical that simply grows by adding monomeric units and still possesses an active center after the growth, the number of monomeric units (r) added to a radical center during the time interval t, according to Tobita [112], conforms to the following Poisson distribution:

$$p(r) = \mathrm{e}^{-\theta}\theta^{r}/r$$

where θ is the expected number of monomeric units added to a radical center, given by

$$\theta = k_{\mathrm{p}}[\mathrm{M}]t$$

where k_{p} is the propagation rate coefficient and [M] is the monomer concentration. If the number of the added monomeric units, r, is large enough, one can approximate that $r \cong \theta$. For bimolecular termination reactions that are independent of chain length, the required time for bimolecular termination between a particular radical pair is also given by the following most probable distribution [112]:

$$p_{\mathrm{t}}(\theta_{\mathrm{t}}) = \xi \exp\left(-\xi\theta_{\mathrm{t}}\right)$$

where $\xi = k_{\mathrm{t}}/(k_{\mathrm{p}}[\mathrm{M}]vN_{\mathrm{A}})$, and k_{t} is the bimolecular termination rate coefficient. The imaginary time for chain stoppage by bimolecular termination must be considered for all radical pairs that exist in the reaction medium [112].

The third type of a termination reaction is chain transferring. Premature termination through transferring results in a lower molecular weight polymer than can be expected from other termination reactions. The product of chain transferring is an inert polymer molecule and, often, a new free radical capable of new initiation. If, however, the new radical is not capable of starting the growth of a new chain, then this is ***degenerative chain transferring***. It is also referred to as a ***first-order termination reaction***. The molecules that accept the new radical sites (participate in chain transferring) can be any of those present in the reaction medium. This includes solvents, monomer molecules, inactive polymeric chains, and initiators.

The ease with which chain transferring takes place depends upon the bond strength between the labile atoms that are abstracted and the rest of the molecule to which they are attached. For instance, chain transferring in methyl methacrylate polymerization to the solvent occurs in the following order [115]:

$$\text{benzene} < \text{toluene} < \text{ethyl benzene} < \text{cumene}$$

The rate of a chain transferring reaction is,

$$R_{\mathrm{tr}} = k_{\mathrm{tr}}[\mathrm{M}\bullet][\mathrm{XA}]$$

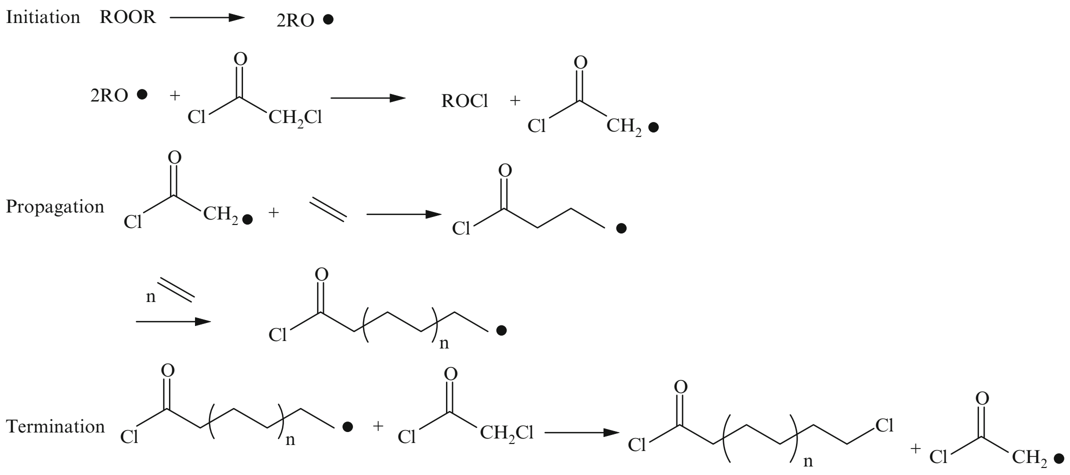
where, k_{tr} is the chain transferring constant in a reaction:

$$M\bullet + X - A \xrightarrow{K_{tr}} M - X + A\bullet$$

Examples of molecules that have particularly labile atoms and contribute readily to chain-transferring are mercaptans and halogen compounds, such as chloroform, carbon tetrachloride, etc.

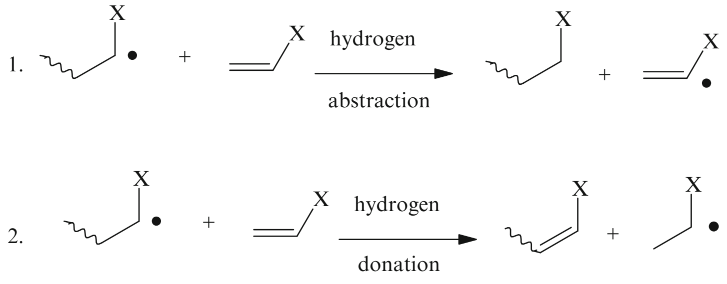
A polymer that was prematurely terminated in its growth by chain transferring may be a ***telomer***. In most cases of telomer formation, the newly formed radical and the monomer radical are active enough to initiate new chain growth. Thus, the life of the kinetic chain is maintained.

An illustration of a ***telomerization reaction*** can be free-radical polymerization of ethylene in the presence of chloroacetyl chloride:

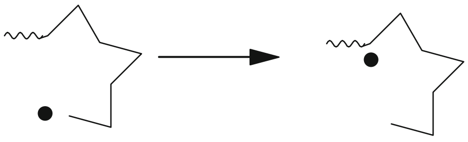


Chain transferring is affected by temperature but not by changes in the viscosity of the reaction medium [115]. When a transfer takes place to a monomer, it is independent of the polymerization rate [116, 117]. When, however, transfer takes place to the initiator, the rate increases rapidly [118].

A chain transferring reaction to a monomer can be illustrated as follows:



A transfer reaction can also occur from the terminal group of the polymer-radical to a location on the polymeric backbone. This is known as ***backbiting***:



The new free-radical site on the polymer backbone starts chain growth that results in formation of a branch. The same reaction can take place between a polymer-radical and a location on another polymer chain. In either case, fresh chain growth results in formation of a branch.

Whether chain transferring can take place to an initiator depends upon the initiator's chemical structure. It was believed in the past that chain transferring to α,α′-azobisisobutyronitrile does not occur. Later it was shown that chain transferring to this initiator does occur as well, at least in the polymerizations of methyl methacrylate [118, 119].

The amount of chain transferring that takes place to monomers is usually low because the reaction requires breaking strong carbon-hydrogen bonds. Monomers, however, such as vinyl chloride and vinyl acetate have fairly large chain transferring constants. In the case of vinyl acetate, this is attributed to the presence of an acetoxy methyl group. This explanation, however, cannot be used for vinyl chloride.

The chain transferring constants, are usually defined as:

$$C_M = k_{tr,M}/k_p \quad \text{for monomers}$$

$$C_S = k_{tr,S}/k_p \quad \text{for solvents}$$

$$C_I = k_{tr,I}/k_P \quad \text{for initiators,}$$

The values can be found in handbooks and other places in the literature. Presence of chain transferring agents in a polymerization reaction requires redefining the degree of polymerization to include the chain termination terms. The number average degree of polymerization has to be written as follows:

$$\overline{DP} = \frac{R_p}{(R_t/2) + k_{tr,M}[M\bullet][M] + k_{tr,s}[M\bullet][S] + k_{tr,I}[M\bullet][I]}$$

It can also be expressed in terms of the chain transferring constants as follows:

$$1/\overline{DP} = 2R_P/R_I + C_M + C_S[S]/[M] + C_I[I]/[M]$$

This can also be written in still another form:

$$1/\overline{DP} = k_t R_P/k_P{}^2[M]^2 + C_M + C_S[S]/[M] + C_I k_t R_P{}^2/k_P{}^2 f k_d[M]^3$$

When a polymerization reaction is conducted in a concentrated solution, or in complete absence of a solvent, the viscosity of the medium increases with time, (unless the polymer precipitates out). This impedes all steps in the polymerization process, particularly the diffusions of large polymer-radicals [54]. The decreased mobility of the polymer-radicals affects the termination process. It appears that this is common to many, though not all, free-radical polymerizations. All molecular processes in the termination reactions are not fully understood, particularly at high conversions [119] This is a complex process that consists of three definable steps. These can be pictured as follows. First, two polymer radicals migrate together by means of translational diffusion. Second, the radical sites reorient toward each other by segmental diffusion. Third, the radicals overcome the small chemical activation barriers and react. The termination reaction is, therefore, diffusion controlled. At low concentrations, this will be segmental diffusion while at medium or high concentrations it will be translational diffusion.

Present theories of terminations suggest that at intermediate conversions, terminations are dominated by interactions between short chains formed by transfer and entangled long chains [121].

When terminations are diffusion controlled, most termination events involve two highly entangled chains whose ends move by the “reaction-diffusion” process [119]. In this process, terminations occur because of the propagation-induced diffusion of the chain ends of growing macroradicals. This means that the rates of terminations depend upon the chain lengths [113].

Diffusion theories have been proposed that relate the rate constant of termination to the initial viscosity of the polymerization medium. The rate-determining step of termination, the segmental diffusion of the chain ends, is inversely proportional to the microviscosity of the solution [123]. Yokota and Itoh [124] modified the rate equation to include the viscosity of the medium. According to that equation, the overall polymerization rate constant should be proportional to the square root of the initial viscosity of the system.

The number average termination rate constants in a methyl methacrylate polymerization were measured with an in-line ESR spectrometer. This was done by observing the radical decay rates [120]. The results are in disagreement with the concept of termination by propagation-diffusion that is expected to be dominant at high conversion rates. Instead, the termination rate constants decrease dramatically in the posteffect period at high conversions. Actually, a fraction of the radicals were found trapped during the polymerization. Thus, there are two types of radicals in the reaction mixture, trapped and free radicals. In the propagations and termination reactions, the two types of radical populations have very different reactivities [120].

Shipp and coworkers [120] described a method for analyzing the chain length dependence of termination rate coefficients of the reacting radicals in low conversion free radical polymerizations. Their method involves comparing experimental molecular weight distributions of polymers formed in pulsed laser photolysis experiments with those predicted by kinetic simulation. The method is enabled by direct measurements of the concentration of radicals generated per laser pulse. Knowledge of the radical concentrations should mean that the only unknowns in the simulations are the termination rate coefficients. They concluded that the analysis demonstrates the need for chain length dependent termination rate constants in describing polymerization kinetics.

Free-radical photopolymerizations (see Chap. 10) of multifunctional acrylic monomers result in cross-linked polymeric networks. The kinetic picture of such polymerizations varies from ordinary linear polymerization because the diffusion of free radicals and functional groups becomes severely restricted. This causes growing polymer chains to rapidly cyclize and cross-link into clusters (microgels). The clusters become linked up into networks. Many free radicals become trapped, but terminations take place by combinations and by chain transferring. The cumulative chain length in such polymerizations can be calculated from the following equation [125]:

$$v = \frac{x n_{\mathrm{m0}}}{n_{\mathrm{rg}}}$$

where, χ is the conversion of functional groups and n_{m0} is the initial number of functional groups and n_{rg} is the total number of radicals generated.

3.6 Copolymerization

If more than one monomer species is present in the reaction medium, a copolymer or an interpolymer can result from the polymerization reaction. Whether the reaction products will consist of copolymers or just a mixture of homopolymers of both, however, depends largely upon the reactivity of the monomers. A useful and a simplifying assumption in kinetic analyses of free-radical copolymerizations is that the reactivity of polymer radicals is governed entirely by the terminal monomer units [52]. For instance, a growing polymer radical that contains a methyl methacrylate terminal unit, is

Table 3.8 Some reactivity ratios [132, 136]

Monomer 1	Monomer 2	r_1	r_2
Styrene	Butadiene	0.78	1.39
Styrene	Methyl methacrylate	0.52	0.46
Styrene	Vinyl acetate	55.0	0.01
Vinyl acetate	Vinyl chloride	0.23	1.68
Methyl acrylate	Vinyl chloride	9.00	0.083

considered, in terms of reactivity, as a poly(methyl methacrylate) radical. This assumption although not always adequate [52] can be used to predict satisfactorily the behavior of many mixtures of monomers. Based on this assumption, the copolymerization of a pair of monomers involves four distinct growth reactions and two types of polymer radicals.

3.6.1 Reactivity Ratios

In a reaction of two monomers, designated as M_1 and M_2, four distinct reactions can be written as follows:

$$1.\ \sim M_1\bullet + M_1 \xrightarrow{k_{11}} \sim M_1M_1\bullet$$

$$2.\ \sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_1M_2\bullet$$

$$3.\ \sim M_1\bullet + M_2 \xrightarrow{k_{21}} \sim M_1M_2\bullet$$

$$4.\ \sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim M_2M_2\bullet$$

The ratios of k_{11}/k_{12} and k_{22}/k_{21} are called ***monomer reactivity ratios***. They can be written as follows:

$$r_1 = k_{11}/k_{12} \quad r_2 = k_{22}/k_{21}$$

The relationship can be express in terms of the ratio of the monomers, $[M_1]/[M_2]$ that end up in the formed polymer, R_p:

$$R_p = R_m(r_{12}R_m + 1)/(r_{21} + R_m)$$

where, R_m is equal to $[M_1]/[M_2]$. Table 3.8 illustrates a few typical reactivity ratios taken from the literature. Many more can be found [128].

These reactivity ratios represent the relative rates of reactions of polymer radicals with their own monomers vs. that with the comonomers. When $r_1 > 1$, the radical ~$M_1\bullet$ is reacting with monomer M_1 faster than it is with the comonomer M_2. On the other hand, when $r_1 < 1$, the opposite is true. Based on the ***r values***, the composition of the copolymers can be calculated from a ***copolymerization equation*** [52] shown below:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left[\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right]$$

In an ideal copolymerization reaction,

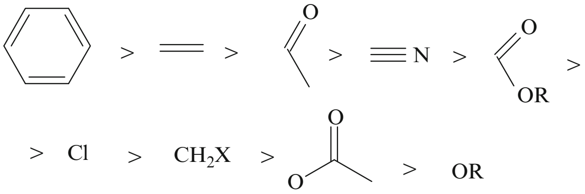
$$k_{11}/k_{12} = k_{22}/k_{21} \text{ and } r_1 r_2 = 1$$

If r_1 and r_2 values are equal to or approach zero, each polymer radical reacts preferentially with the other monomer. This results in an alternating copolymer, regardless of the composition of the monomer mixture. That is, however, a limiting case. In the majority of instances, $r_1 \times r_2$ is greater than zero and less than one. When the polymer radicals react preferentially with their own monomer, and $r_1 \times r_2 > 1$, then mainly a mixture of homopolymers forms and only some copolymerization takes place.

Reactivity of vinyl monomers is very often determined experimentally by studying copolymerizations. Values of many free-radical reactivity ratios have been tabulated for many different monomer pairs [126]. Also, the qualitative correlations between copolymerization data and molecular orbital calculations can be found in the literature [136].

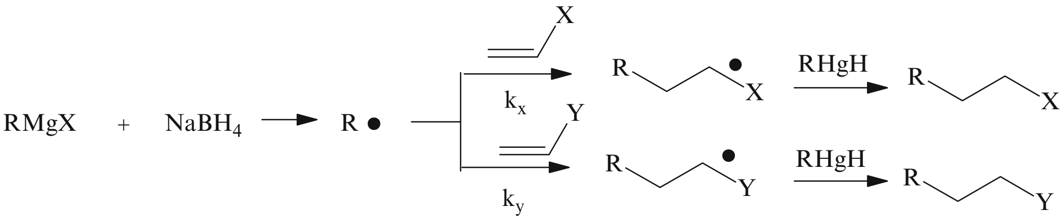
Some general conclusion about monomer reactivity toward attacking radicals was drawn by Mayo and Walling [130]:

1. The alpha substituents on a monomer have the effect of increasing reactivity in the following order.



2. The effect of a second alpha substituent is roughly additive.

Giese and coworkers [131–136] developed a special technique for studying the effects of the substituents upon the relative reactivity of vinyl monomers toward free radicals. Briefly it is as follows. Free radicals are produced by reducing organomercury halides with sodium borohydride. The radicals undergo competitive additions to pairs of various substituted olefins. The adducts are in turn trapped by hydrogen transfers from the formed organomercury hydrides. Relative quantities of each product are then determined



This method was applied in copolymerization of acrylonitrile and methyl acrylate [129]. It showed that the ratios of the rate constants for each of the two monomers are independent of their concentrations.

Copolymerization reactions are affected by solvents. One example that can be cited is an effect of addition of water or glacial acetic acid to a copolymerization mixture of methyl methacrylate with acrylamide in dimethyl sulfoxide or in chloroform. This causes changes in reactivity ratios [131]. Changes in r values that result from changes in solvents in copolymerizations of styrene with methyl methacrylate are another example [133, 134]. The same is true for styrene acrylonitrile copolymerization [132]. There are also some indications that the temperature may have some effect on the reactivity ratios [135], at least in some cases.

3.6.2 Q and e Scheme

Though molecular orbital calculations allow accurate predictions of reactivity ratios [133], many chemists also rely upon the Price–Alfrey ***Q–e* equations** [140]. These are based on: (1) the polarity of the double bonds of the monomers or measures of the propagating chain ends, (2) mesomerism of the substituents with the double bonds or with the chain ends, and (3) the steric hindrance of the substituents. This relationship is expressed in the following equation [149]:

$$\mathrm{K}_{12} = \mathrm{P}_1\mathrm{Q}_2^{-e_1 e_2}$$

it can also be written as follows:

$$\log \mathrm{K}_{12} = \log \mathrm{Q}_1 + \log \mathrm{Q}_2 - 0.4343 e_1 e_2$$

where K_{12} represents the rate constant for the reaction of the propagating radical ~M_1• with monomer M_2, P_1 represents the general reactivity of the polymer radical with the terminal unit of monomer M_1, Q_1 and Q_2 are the reactivities of the monomer M_1 and M_2, and e_1 and e_2 are measures the polar characters of the monomers.

It is possible to calculate the Q and e values from r_1 and r_2, or, conversely, r values can be obtained from the Q and e values. The relationship is as follows [136]:

$$r_1 = k_{11}/k_{12} = \mathrm{Q}_1/\mathrm{Q}_2 \exp[-e_1(e_1 - e_2)]$$

$$r_2 = k_{22}/k_{21} = \mathrm{Q}_2/\mathrm{Q}_1 \exp[-e_2(e_2 - e_1)]$$

The Q and e scheme is based on a semiempirical approach. Nevertheless, some attempts were made to develop theoretical interpretations. Thus, Schwann and Price [141] developed the following relationship:

$$Q = \exp(-q/RT)$$

$$e = \varepsilon/(\gamma DRT)^{\mathbf{1/2}}$$

In the above equation, q represents the resonance of stabilization (kcal/mol), ε is the electrical charge of the transition state, and γ is the distance between the centers of the charge of the radical and the monomer, D stands for the effective dielectric constant of the reaction field. The values of q and e are derived by calculation. In addition, more rigorous molecular orbital calculations [138] show a relationship between Q and the localized energy of a monomer, and between e and the electron affinity. Also, a scale of Q and e values was deduced from essentially molecular orbital considerations [143]. In addition, a Huckel treatment of the transition state for the monomer–radical reaction in a free-radical copolymerization was developed [142]. The resulting reactivity ratios compared well with those derived from the Q and e scheme. This scheme is regarded by some as a version of the molecular orbital approach [145]. Nevertheless, the scheme should only be considered as an empirical one. The precision of calculating Q and e values can be poor because steric factors are not taken into account. It is good, however, for qualitative or semiquantitative results.

A revised reactivity scheme was proposed by Jenkins, that he called U,V scheme [148]. It is claimed to be more accurate and also capable of application to both copolymerizations and to transfer reactions. The scheme retains much of the format of the Q and e scheme. In this one, the intrinsic radical reactivity is quantified by reference to the rate of reaction of the radical with styrene monomer.

The original approach for this scheme was based on copolymerizations of styrene with acrylonitrile and with other acrylic monomers [149]. In developing a more general approach, however, Jenkins concluded that while in principle, a general procedure involves fewer assumptions, in practice much of the utility is lost. He proposed that it is convenient in practice to employ k_{is}: from styrene copolymerizations.

In writing the original scheme for styrene copolymerization with acrylic monomers in benzene, Jenkins introduced the term "*S*" to denote styrene σ_p represents the Hammett sigma constant for a substituent in the *para* position. In his revised scheme, he still uses k_{is} and writes it as follows:

$$\log r_{12} = \log k_{1s} + u_2 + v_2$$

The term k_{11} is substituted from both sides of the equation to yield:

$$\log r_{12} = \log k_{1s} - u_2\sigma_1 - v_2$$

The above equation represents a postulate on the same bases as does the Q and e scheme. This scheme contains an assumption that the intrinsic reactivity of a radical is measured by the value of k_{1s} and its polarity σ_1 (or π_1). Thus,

$$\log r_{12} - \log k_{1s} = -u_2\sigma_1 - v_2$$

It follows that $r_{s2} = -v_2$ and $\sigma_1 = \pi_S = u_S = v_S = 0$. The final equation becomes:

$$\log r_{12} = \pi_1(u_1 - u_2) + (v_1 + v_2)$$

k_{is} represents the intrinsic reactivity of the styrene polymer radical (assuming that it is monomer 1)
v_2 represents the intrinsic reactivity of monomer 2
σ_1 represents the polarity of the polymer radical derived from monomer 1, and
u_2 represent polarity of monomer 2

Whether this scheme is applicable to general copolymerizations is not clear at this point.

3.6.3 Solvent Effect on Copolymerization

It was reported by Barb in 1953 that solvents can affect the rates of copolymerization and the composition of the copolymer in copolymerizations of styrene with maleic anhydride [145]. Later, Klumperman also observed similar solvent effects [145]. This was reviewed by Coote and coworkers [145]. A number of complexation models were proposed to describe copolymerizations of styrene and maleic anhydride and styrene with acrylonitrile. There were explanations offered for deviation from the terminal model that assumes that radical reactivity only depends on the terminal unit of the growing chain. Thus, Harwood proposed the "bootstrap model" based upon the study of styrene copolymerized with MAA, acrylic acid, and acrylamide [146]. It was hypothesized that solvent does not modify the inherent reactivity of the growing radical, but affects the monomer partitioning such that the concentrations of the two monomers at the reactive site (and thus their ratio) differ from that in bulk.

Hutchinson and coworkers investigated [147] effects of solvent on free-radical copolymer composition and propagation kinetics in copolymerizations of styrene with three methacrylates, 2-hydroxyethyl methacrylate, glycidyl methacrylate, and *n*-butyl methacrylate Three different solvents, *n*-butanol, toluene, and *N*,*N*-dimethylformamide were used. They found that all three solvents effected the composition of styrene-2-hydroxyethyl methacrylate copolymer. Liang and Hutchinson [147] also observed variations in monomer reactivity ratios with solvent polarity. Butanol was the only one that affected styrene butyl methacrylate copolymer composition. None of the solvents appeared to effect the composition of the styrene–glycidyl methacrylate copolymer.

3.7 Terpolymerization

A quantitative treatment of terpolymerization, where three different monomers are interpolymerized, becomes complex. Nine growth reactions take place [155]:

Reaction	Rate
$\sim M_1\bullet + M_1 \xrightarrow{K_{11}} \sim M_1M_1\bullet$	$R_{11} = k_{11}[M_1\bullet][M_1]$
$\sim M_1\bullet + M_2 \xrightarrow{k_{12}} \sim M_1M_2\bullet$	$R_{12} = k_{12}[M_1\bullet][M_2]$
$\sim M_1\bullet + M_3 \xrightarrow{k_{13}} \sim M_1M_3\bullet$	$R_{13} = k_{13}[M_1\bullet][M_3]$
$\sim M_2\bullet + M_1 \xrightarrow{k_{22}} \sim M_2M_1\bullet$	$R_{21} = k_{21}[M_2\bullet][M_1]$
$\sim M_2\bullet + M_2 \xrightarrow{k_{22}} \sim M_2M_2\bullet$	$R_{22} = k_{22}[M_2\bullet][M_2]$
$\sim M_2\bullet + M_3 \xrightarrow{k_{23}} \sim M_2M_3\bullet$	$R_{23} = k_{23}[M_2\bullet][M_3]$
$\sim M_3\bullet + M_1 \xrightarrow{k_{31}} \sim M_3M_1\bullet$	$R_{31} = k_{31}[M_3\bullet][M_1]$
$\sim M_3\bullet + M_2 \xrightarrow{k_{32}} \sim M_3M_2\bullet$	$R_{32} = k_{32}[M_3\bullet][M_2]$
$\sim M_3\bullet + M_3 \xrightarrow{k_{33}} \sim M_3M_3\bullet$	$R_{33} = k_{33}[M_3\bullet][M_3]$

There are six reactivity ratios in copolymerizations of three monomers [148]:

$$r_{12} = k_{11}/k_{12} \quad r_{13} = k_{11}/k_{13} \quad r_{21} = k_{22}/k_{21}$$

$$r_{23} = k_{22}/k_{23} \quad r_{31} = k_{33}/k_{31} \quad r_{32} = k_{33}/k_{32}$$

The rates of disappearance of the three monomers are given by

$$-\,\mathrm{d}[M_1]/\mathrm{d}t = R_{11} + R_{21} + R_{31}$$

$$-\,\mathrm{d}[M_2]/\mathrm{d}t = R_{12} + R_{22} + R_{32}$$

$$-\,\mathrm{d}[M_3]/\mathrm{d}t = R_{13} + R_{23} + R_{33}$$

By assuming steady state conditions for the three radicals, $M_1\bullet$, $M_2\bullet$, and $M_3\bullet$ it is possible to write:

$$R_{12} + R_{13} = R_{21} + R_{31}; \quad R_{21} + R_{23} = R_{12} + R_{32}; \quad R_{31} + R_{32} = R_{13} + R_{23}$$

An equation for terpolymer composition was developed from the rate expressions by expressing the steady state with the relationships [94]:

$$R_{12} = R_{21}; \quad R_{23} = R_{32}; \quad R_{31} = R_{13}.$$

$$\begin{aligned} d[M_1]/d[M_2]/d[M_3] = {} & [M_1]\{[M_1] + [M_2]/r_{12} + [M_3]/r_{13}\} \\ & /[M_2]r_{21}/r_{12}\{[M_1]/r_{21} + [M_2] + [M_3]/r_{23}\} \\ & /[M_3]r_{31}/r_{13}\{[M_1]/r_{31} + [M_2]/r_{32} + [M_3]\} \end{aligned}$$

It is claimed that this ***terpolymerization composition equation*** is often in good agreement with experimental results. Other, more complicated equations also exist, but apparently they yield results that are similar to those obtained from the above shown expression [94, 149].

One example of other equations is an early theoretical relationship for terpolymerization that was written by Alfrey and Goldfinger [150].

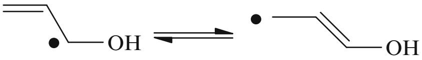
$$\frac{a}{b} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{B[(A/(r_{12}r_{31}) + B/(r_{12}r_{32}) + C/(r_{32}r_{13})][B + A/r_{21} + C/r_{23}]}.$$

$$\frac{a}{c} = \frac{A[A/(r_{31}r_{21}) + B/(r_{21}r_{32}) + C/(r_{31}r_{23})][A + B/r_{12} + C/r_{13}]}{C[A/(r_{13}r_{21}) + B/(r_{23}r_{12}) + C/(r_{13}r_{23})][C + A/r_{13} + B/r_{32}]}$$

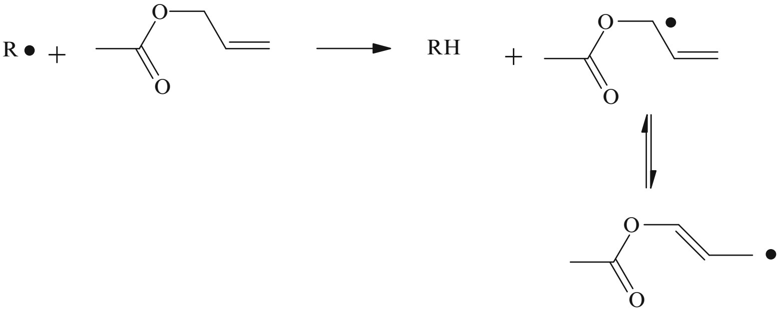
where a, b, and c are the quantities of each monomer found in the resultant terpolymer and A, B, and C are the quantities of the monomer in the feed system. Needless to say, a copolymerization of four or even more monomers becomes progressively more difficult to treat rigorously.

3.8 Allylic Polymerization

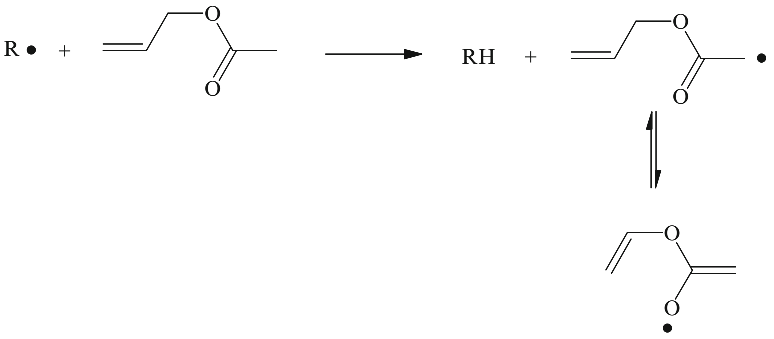
Compounds possessing allylic structures polymerize by free-radical mechanism only to low molecularweight oligomers. In some cases the products consist mostly of dimers and trimers. The DP for poly(allyl acetate), for instance, is only about 14. This is due to the fact that allylic monomer radicals are resonance-stabilized to such an extent that no extensive chain propagations occur. Instead, there is a large amount of chain transferring. Such chain transferring essentially terminates the reactions [151]. The resonance stabilization can be illustrated on an allyl alcohol radical:



The hydrogen transfer takes place from the allylic hydrogen, as shown on allyl acetate:



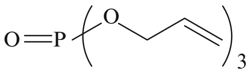
Hydrogen transfer can also take place to the acetate moiety:



The above described chain transferring is called ***degradative chain transferring***. Other monomers, such as methyl methacrylate and methacrylonitrile, also contain allylic carbon–hydrogen bonds. They fail to undergo extensive degradative chain transferring, however, and do form high-molecular-weight polymers. This is believed to be due to lower reactivity of the propagating radicals that form from these monomers [5].

Yamasaki et al. [152], reported that they successfully performed the radical polymerization of allylbiguanide hydrochloride in a concentrated, acid solution using either hydrochloric acid or phosphoric acid in the presence of a radical initiator at 50°C. The polymer was precipitated from the reaction solution through the addition of an excess amount of acetone. The molecular weight average of the product was 10,340–113,200, with a low polydispersity 1.04–1.68.

In spite of degradative chain transferring, polyallyl compounds can be readily polymerized by a free-radical mechanism into three-dimensional lattices. High DP is not necessary to achieve growth in three dimensions. An example of such polyallyl compounds is triallyl phosphate:



Many other polyallyl derivatives are offered commercially for use in cross-linked films and are described in the trade literature.

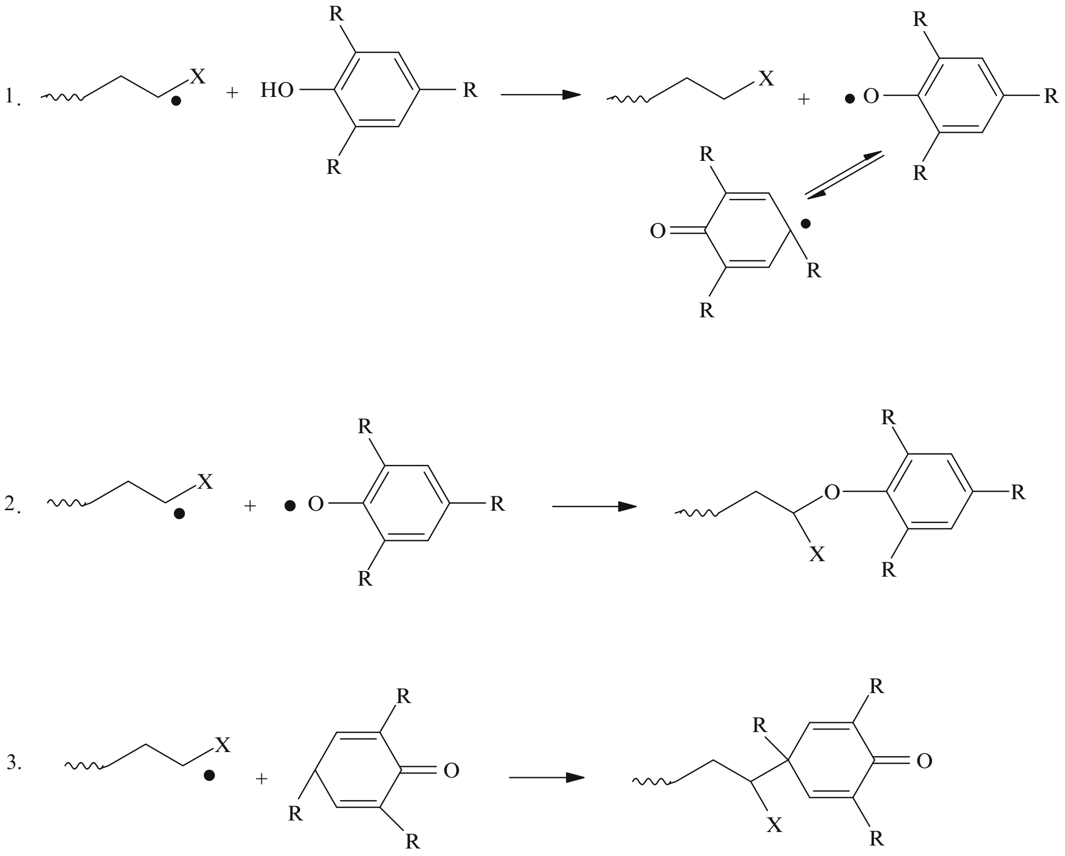
3.9 Inhibition and Retardation

Free-radical polymerizations are subject to inhibition and retardation from side reactions with various molecules [54]. Such polymerization suppressors are classified according to the effect that they exert upon the reaction. ***Inhibitors*** are compounds that react very rapidly with every initiating free radical as it forms. This prevents any polymerization reaction from taking place until the inhibitor is completely consumed in the process. The reactions of inhibitors with initiating radicals result in formations of new free radicals. The newly formed free radicals, however, are too stable to initiate chain growths. As a result, well-defined induction periods exist. After the inhibitors are used up, polymerizations proceed at normal rates.

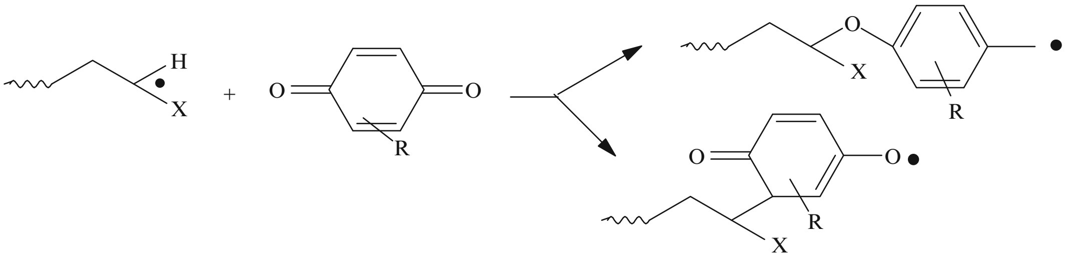
Retarders are compounds that also react with initiating radicals. They do not react, however, as energetically as do the inhibitors, so some initiating radicals escape and start chain growth. This affects the general rate of the reaction and slows it down. There is no induction period and retarders are active throughout the course of the polymerization.

The efficiency of an inhibitor depends upon three factors: (1) the chain transfer constant of an inhibitor with respect to a particular monomer, (2) the reactivity of the inhibitor radical that forms, (3) the reactivity of the particular monomer.

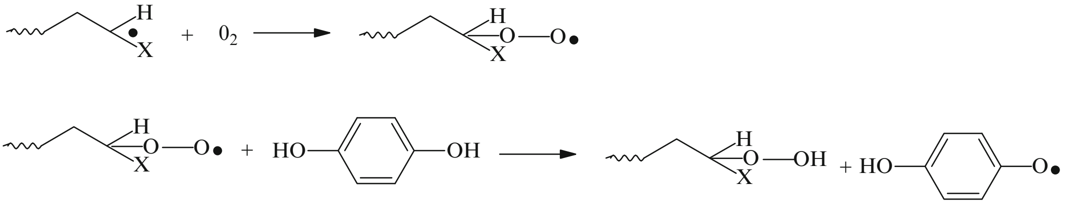
Phenols and arylamines are the most common chain transfer inhibitors. The reaction of phenols, though not fully elucidated, is believed to be as follows [153]



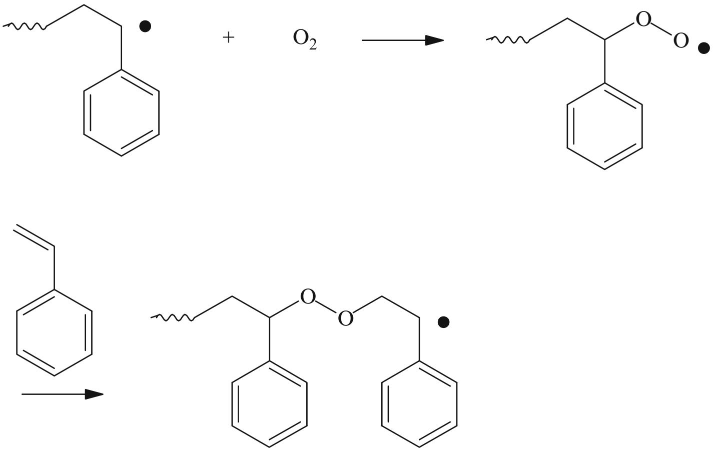
Quinones are effective inhibitors for many polymerization reactions. The reaction occurs either at an oxygen or at a ring carbon [153–156]:



The reaction, however, is not always strict inhibition. Thus, for instance, hydroquinone acts as an efficient inhibitor for the methyl methacrylate radical but only as a retarder for the styrene radical [155]. Hydroquinone is often employed as an inhibitor; it requires, however, oxygen for activity [156, 157]:



Oxygen, however, can also act as a comonomer in a styrene polymerization:



It causes marked retardation, however, in the polymerizations of methyl methacrylate [158]. The same is true of many other free-radical polymerizations.

The ability of phenols to inhibit free-radical polymerizations appears to increase with the number of hydroxyl groups on the molecules [157]. The locations of these hydroxyl groups on the benzene rings in relationships to each other is important. For instance, catechol is a more efficient inhibitor than is resorcinol [158].

Aromatic nitro compounds can act as strong retarders. Their effect is proportional to the quantity of the nitro groups per molecule [160, 161].

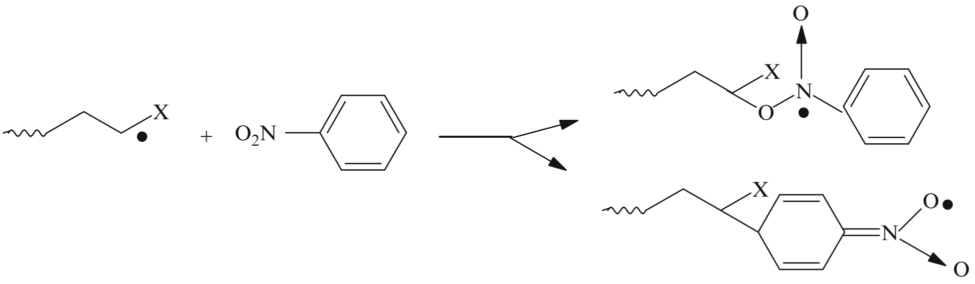


Figure 3.1 illustrates the effect of inhibitors and retarders on free-radical polymerization [162]. The equation that relates rate data to inhibited polymerizations is

$$2R_P{}^2k_t/k_P{}^2[M]^2 + R_P[Z]k_z/k_P[M] - R_i = 0$$

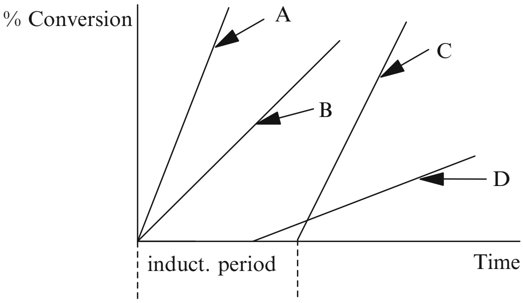


Fig. 3.1 Illustration of the effects of inhibitors and retarders. (A) Normal polymerization rate, (B) effect of a retarder, (C) effect of an ideal inhibitor, and (D) effect of a non ideal inhibitor. The time between A and C is the induction period caused by an ideal inhibitor

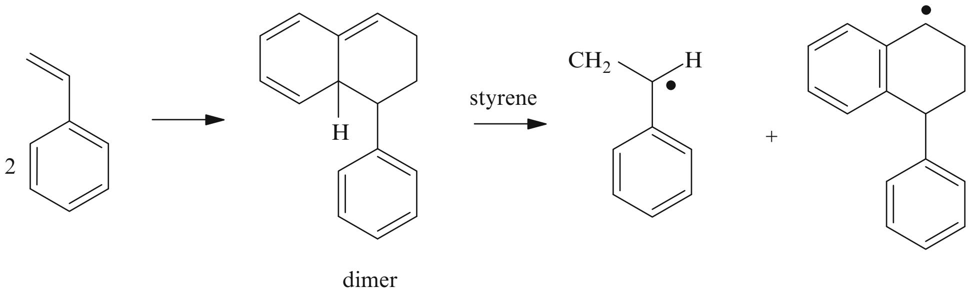
where Z is the inhibitor or the retarder in chain-growth termination:

$$\sim M_n\bullet + \mathrm{Z} \xrightarrow{k_Z} \sim M_n + \mathrm{Z}\bullet(\text{and/or} \sim M_n\mathrm{Z}\bullet)$$

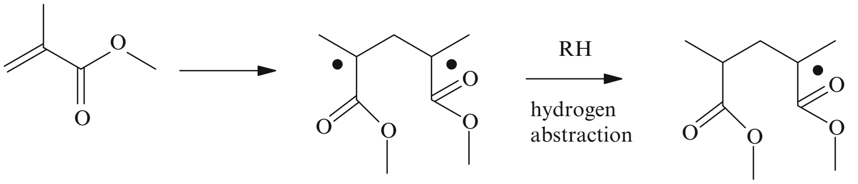
To simplify the kinetics it is assumed that Z• and ~M_nZ• do not initiate new chain growth and do not regenerate Z upon termination.

3.10 Thermal Polymerization

A few monomers, such as styrene and methyl methacrylate, will, after careful purification and presumably free from all impurities, polymerize at elevated temperatures. It is supposed that some ring-substituted styrenes act similarly. The rates of such thermal self-initiated polymerizations are slower than those carried out with the aid of initiators. Styrene, for instance, polymerizes only at a rate of 0.1% per hour at 60°C and only 14% at 127°C. The rate of thermal polymerization of methyl methacrylate is only about 1% of the rate for styrene [163, 164]. Several mechanisms of initiation were proposed earlier. The subject was reviewed critically [165]. More recently, the initiation mechanism for styrene polymerization has been shown by ultraviolet spectroscopy to consist of an initial formation of a Diels–Alder dimer. The dimer is believed to subsequently transfer a hydrogen to a styrene molecule and as in doing so form a free radical [166]:

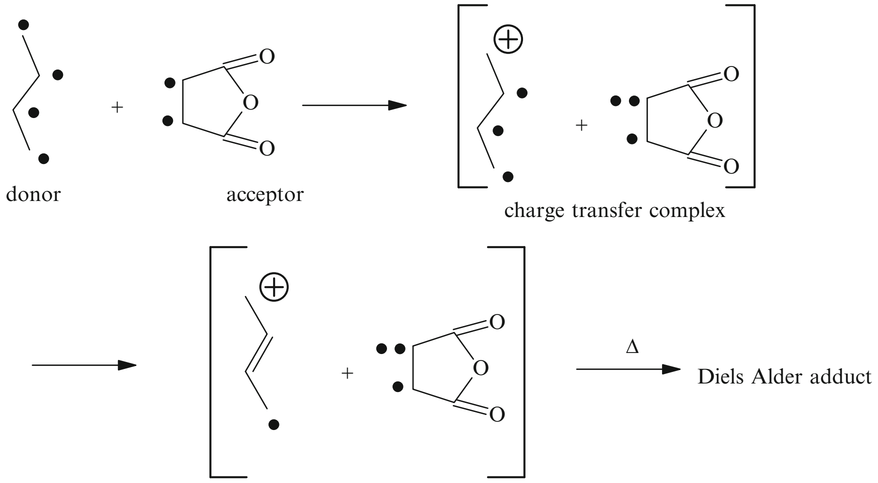


Thermal polymerization of methyl methacrylate, on the other hand, appears to proceed through an initial dimerization into a diradical [167]. This is followed by a hydrogen abstraction from any available source in the reaction mixture.

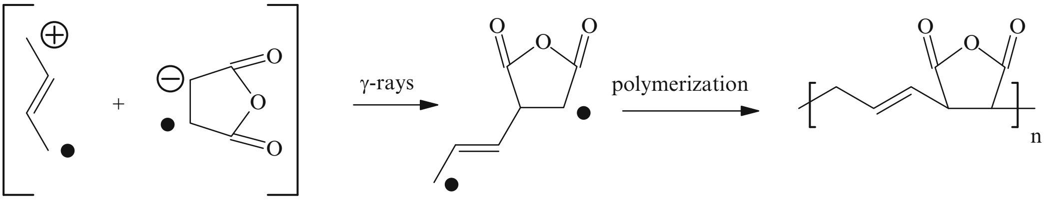


3.11 Donor–Acceptor Complexes in Copolymerization

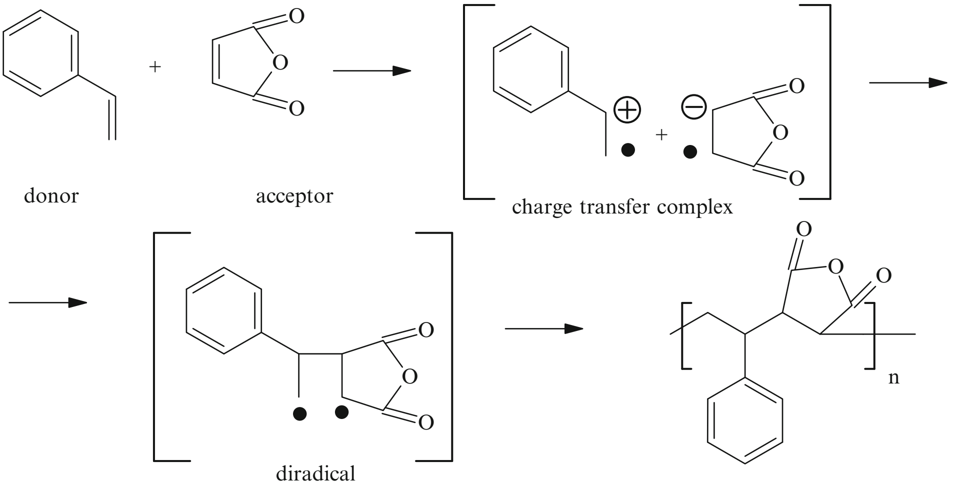
Polar interactions of electron donor monomers with electron acceptor monomers lead to strong tendencies toward formations of alternating copolymers. Also, some alternating copolymerizations might even result from compounds that by themselves are not capable of conventional polymerization. An example is copolymerization of dioxene and maleic anhydride. Two reaction mechanisms were proposed. One suggests that the interactions of donor monomers with acceptor radicals or acceptor monomers with donor radicals lead to decreased energies of activation for cross-propagations [168]. The transition state is stabilized by a partial electron transfer between the donor and acceptor species [169]. The second mechanism suggests that the interactions result in formations of charge-transfer complexes [170]. An electron is completely transferred from the donor monomer to the acceptor monomer. After the transfer, the complex converts to a diradical that subsequently polymerizes by intermolecular coupling. For instance, while many believe that the Diels–Alder reaction takes place by a concerted mechanism, the intermediate was postulated by some to be a charge-transfer complex. An electron is transferred from the donor to the acceptor and a charge-transfer complex forms [171]. This can be illustrated on a Diels–Alder reaction between butadiene and maleic anhydride:



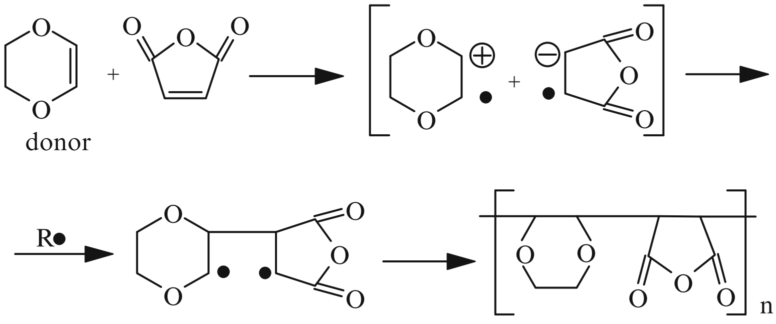
If the reaction mixture is irradiated with high energy radiation, such as gamma rays, instead of being heated, an alternating copolymer forms. The complex converts to a diradical [1, 171] that homopolymerizes:



Alternating copolymerization of styrene with maleic anhydride is also explained by donor acceptor interactions [171]. A charge-transfer complex is seen as the new monomer, a diradical, which polymerizes through coupling [171–174].



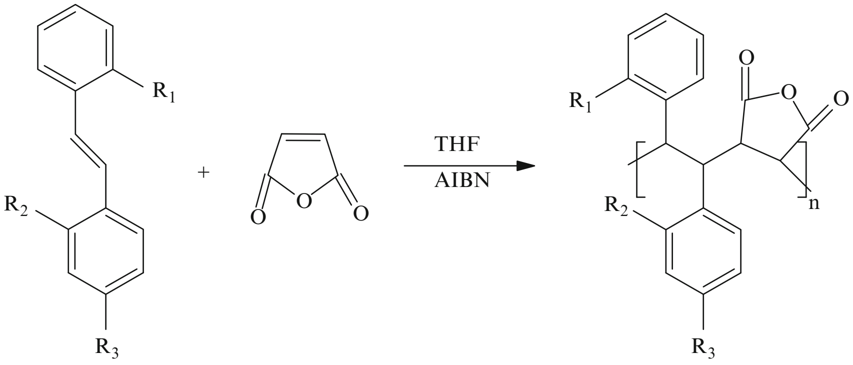
Charge-transfer complexes are also claimed to be the intermediates in free-radical alternating copolymerization of dioxene or vinyl ethers with maleic anhydride [176–179]:



where, R• is a polymerization-initiating radical. Here, a third monomer can be included to interpolymerize with the complex that acts as a unit. The product is a terpolymer [176, 177]. A diradical intermediate was also postulated in sulfur dioxide copolymerizations and terpolymerizations with bicycloheptene and other third monomers [173]. These third monomers enter the copolymer chain as block segments, while the donor–acceptor pairs enter the chains in a one-to-one molar ratio. This one-to-one molar ratio of the pairs is maintained, regardless of the overall nature of the monomer mixtures.

The propagation and termination steps in the above reactions are claimed [175, 181–183] to be related. As stated, an interaction and coupling between two diradicals is a propagation step. When such interactions result in disproportionations, however, they are termination steps. This means the charge-transfer mechanisms are different from conventional free-radical polymerizations. They involve interactions not only between growing polymer-radicals and monomers but also between polymer-radicals and complexes. In addition, the polymer radicals react with each other [175, 181–184].

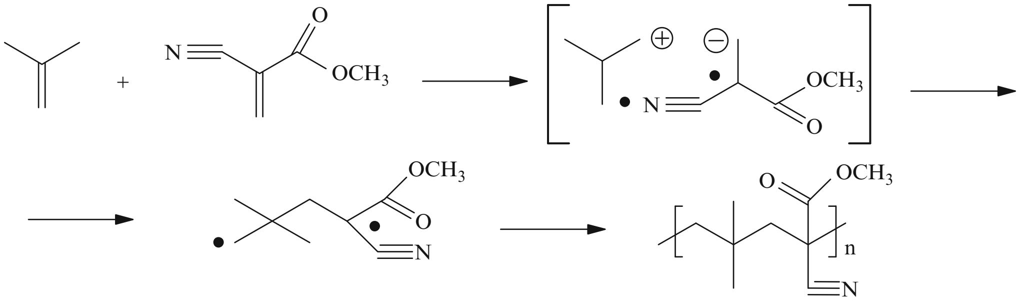
Li and Turner [185], reported copolymerization of maleic anhydride with *trans*-stilbene:



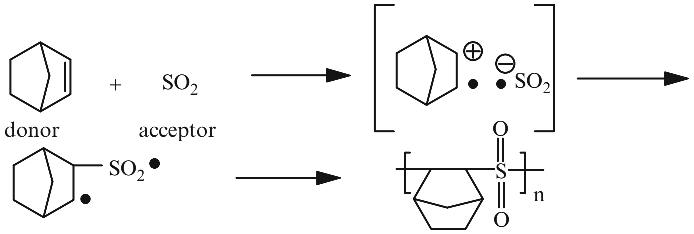
where, R_1, R_2, and R_3 are either methyl groups or hydrogens

The stability of charge-transfer complexes depends upon internal resonance stabilization. This degree of stabilization determines how easily the diradicals open up [183]. Consequently, the stability also determines how the copolymerization occurs. It can occur spontaneously, or under the influence of light or heat, or because of an attack by an initiating free radical.

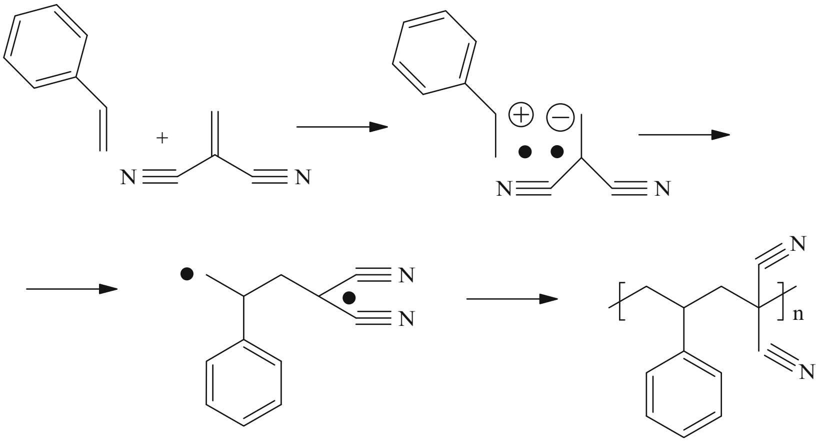
There are many examples of spontaneous reactions. When, for instance, isobutylene is added to methyl α-cyanoacrylate, a spontaneous copolymerization in a 1:1 ratio takes place at room temperature. This was explained by the following scheme [175, 181–183]:



The same happens when sulfur dioxide is added to bicycloheptene at −40°C [184].



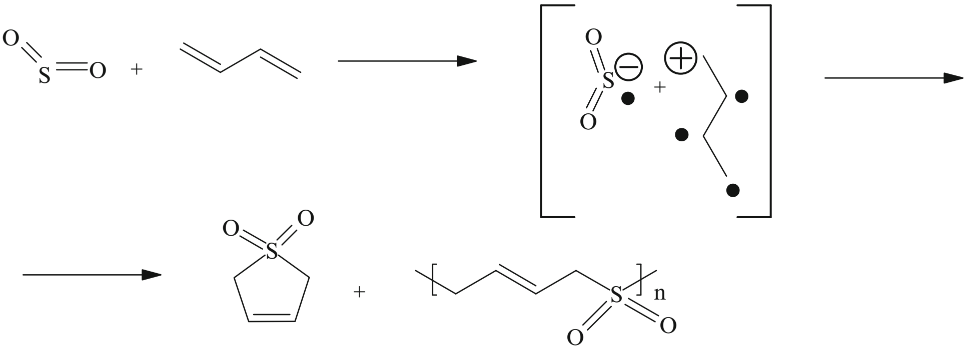
Another example is a room temperature 1:1 copolymerization of vinylidene cyanide with styrene [185]:



Still another example is a reaction of 1,3 dioxalene with maleic anhydride [183].

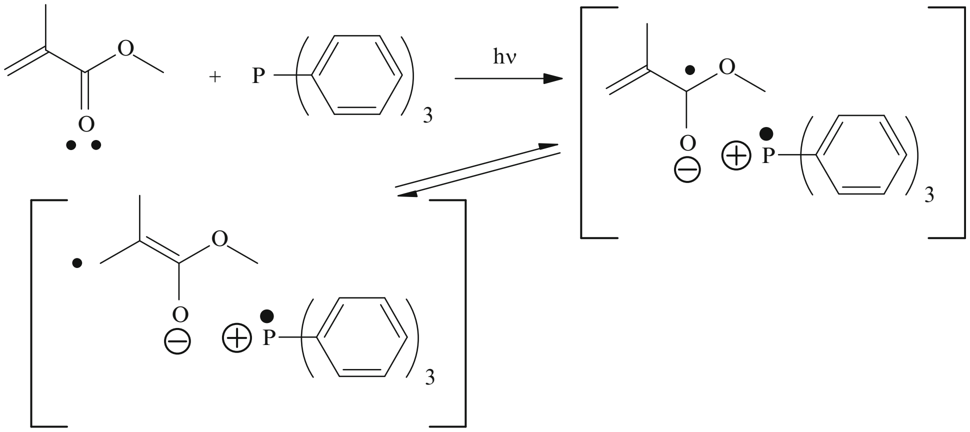
Examples of stable complexes are reactions of sulfur dioxide with styrene [175], or vinyl ethers with maleic anhydride [184], also α-olefins with maleic anhydride [179–181]. Also, a reaction of *trans*-stilbene with maleic anhydride [182], In these reactions charge-transfer complexes form. They are stable and their existence can be detected by spectroscopic means. Additional energy, such as heat or a free-radical attack, converts them to diradicals and polymerizes them into alternating copolymers [175, 185–191].

Examples of intermediates between the two extremes in stability are reaction products of sulfur dioxide with conjugated dienes [192]. In this case, the reaction results in formation of mixtures of alternating copolymers and cyclic adducts:



The yield of the polymer increases at the expense of the cyclic structure when heat or radiation is applied. A free-radical attack has the same effect [192].

If donor–acceptor interactions and subsequent polymerizations occur upon irradiation with ultraviolet light, the reactions can be very selective. An example is a triphenylphosphine interaction with acrylic monomers [193]:



This reaction does not occur, however, between triphenylphosphine and styrene or vinyl acetate [193].

The nature and the amount of solvent can influence the yield and the composition of the copolymers in these copolymerizations. Thus, copolymerization of phenanthrene with maleic anhydride in benzene yields a 1:2 adduct. In dioxane, however, a 1:1 adduct is obtained. In dimethyl formamide, no copolymer forms at all [193]. Another example is a terpolymerization of acrylonitrile with 2-chloroethyl vinyl ether and maleic anhydride or with *p*-dioxene-maleic anhydride. The amount of acrylonitrile in the terpolymer increases with an increase in the π-electron density of the solvent in the following order [194]:

$$\text{xylene} \gg \text{toluene} \gg \text{benzene} > \text{chlorobenzene} \gg \text{chloroform}.$$

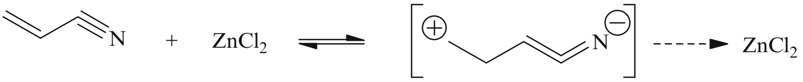
The ratio of maleic anhydride to the vinyl ether in the product remains, however, equimolar.

Whether the concept of charge-transfer complexes in copolymerizations is fully accepted is not certain. Much of the accumulated evidence, to date, such as UV and NMR spectroscopy, does support it in many systems [195]. Further support comes from the strong tendencies to form alternating copolymers over a wide range of feed compositions, and also from high reaction rates at equimolar feed compositions [171]. On the other hand, as shown above, it was claimed in the past that copolymerization of styrene with maleic anhydride involves charge-transfer complexes [171, 181–183]. This, however, is now contradicted in a publication of a study of radical copolymerization of maleic acid with styrene. The reaction was carried out in a dioxane solution at 70°C. The authors reported that UV spectroscopy fails to show presence of a charge transfer and formation of a complex between the two monomers in the copolymerization system [196].

3.12 Polymerization of Complexes with Lewis Acids

Some polar vinyl monomers such as methyl methacrylate or acrylonitrile interact and complex with Lewis acids. They subsequently polymerize at a faster rate and to a higher molecular weight than can be expected otherwise. The effective Lewis acids are $ZnCl_2$, $AlCl_3$, $Al(C_2H_5)_2Cl$, $AlCl_2(C_2H_5)$, $SnCl_4$, and some others [197–199]. Complexes can form on an equimolar basis and undergo homopolymerizations after application of heat. A free-radical attack or irradiation with ultraviolet light or with gamma rays is also effective [198].

It was proposed [198–201] that the greater reactivity is due to delocalization of the electrons of the complexed molecules:



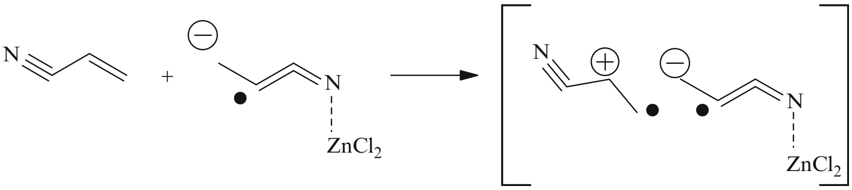
Molecular orbital calculations support this [200, 201]. Polymerizations can also be carried out with less than stoichiometric ratios of the Lewis acids to the monomers. As an illustration, coupling of an acrylic or a methacrylic monomer with a Lewis acid can be shown as follows [203, 204]

$$\mathrm{aM} + \mathrm{MeX}_n \rightleftharpoons (\mathrm{M})_\mathrm{a} ------\mathrm{MeX_n}$$

where, $\mathrm{MeX_n}$ represents a Lewis acid.

Vinyl pyridine and vinyl imidazole also form complexes with zinc chloride. Here, conjugation with the metal salt results in a super delocalizability and leads to spontaneous thermal polymerization [203, 204].

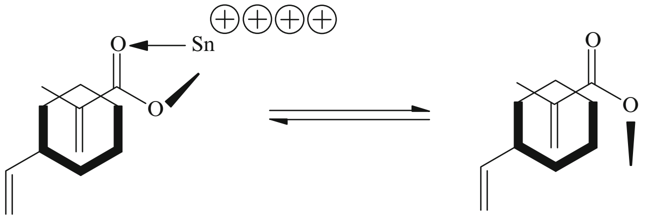
The increased reactivity toward polymerization by some monomers, even in the presence of less than equimolar amounts of Lewis acids, was suggested to be due to one of two possibilities. It may be due to greater reactivity of the portion of the monomer that complexes toward the growing chain end. It may also be due to formation of new complexes between uncomplexed monomer and complexed ones [171]:



The picture is more complicated when the Lewis acids are used in combinations with donor–acceptor monomers. The donor–acceptor complexes are believed to form first and then react with Lewis acids according to the following scheme [203, 204]:

$$a\mathrm{M}_1 + b\mathrm{M}_2 + \mathrm{MeX_n} \rightleftharpoons \left[a\left(\mathrm{M}_1\right) ----\mathrm{MeX}_n\right] + b\mathrm{M}_2 \rightleftharpoons \left[\mathrm{MeX_n}----b\left(\mathrm{M}_2\right)\right] + a\mathrm{M}_1$$

A structure of methyl methacrylate and styrene complexed with $\mathrm{SnCl_4}$ was shown to be as follows [204]:



In formations of ternary complexes, the acceptor vinyl compound must have a double bond conjugated to a cyano or to a carbonyl group. Such acceptors are acrylonitrile, methacrylonitrile, acrylic and methacrylic esters and acids, methyl vinyl ketone, acrylamide, etc. Donor monomers are styrene, α-methyl styrene, butadiene, 2–3-dimethyl butadiene, isoprene, chloroprene, etc.

One proposed mechanism [171, 204] is that such charge-transfer polymerizations are in effect homopolymerizations of the charge-transfer complexes $[\mathrm{D} \oplus \mathrm{A}\_ \ldots \mathrm{MeX}_n]$. In other words, the metal halide is complexed with the electron acceptor monomer and acts as an acceptor component.

The above opinion, however, is not universal. Others hold that the increased susceptibility to ultraviolet radiation or to initiating radicals [205] is due to increased reactivity of the propagating radicals of complexed monomers toward incoming uncomplexed ones.

Arguments against the ternary complex mechanism are as follows: (1) the physical evidence that proves the existence of the ternary molecular complexes is weak; (2) the ternary molecular complexes can have no bearing on the copolymerizations because the equilibrium concentration of the complexed monomers is low, compared to the uncomplexed ones [206].

A third opinion is that a complex of an acceptor monomer with a Lewis acid copolymerizes alternately with the donor monomer and with an uncomplexed acceptor monomer [207, 208]. This presumably takes place according to the conventional chain-growth polymerization scheme of radical copolymerization. The alternate placement of monomers is due to highly enhanced values of cross-propagation constants. It results from complexing acceptor monomers with Lewis acids. Such a mechanism fails to explain satisfactorily the completely alternating incorporation of monomers and the inefficiency of chain-transfer reagents. It also fails to explain the spontaneous initiation of alternating copolymerization.

Kabanov suggested [209] that during the primary free-radical formation of the Lewis acid–monomer complex, both the uncomplexed and the complexed monomers may participate in chain propagation. This would result in appearance of complexed propagating radicals besides the usual ones. In the complexed ones, the last unit carrying the valence is a ligand of coordination complex:

$$\sim\mathrm{M}\bullet \ldots\ldots \mathrm{MeX}_n$$

It excludes, however, all electron transfer reactions that may take place due to ultraviolet light irradiation.

3.13 Steric Control in Free-Radical Polymerization

In free-radical polymerization reactions, the propagating radical chain has a great amount of freedom. Atactic polymers, therefore, are usually formed. Some control that the reaction conditions exercise over the propagating species increases at lower temperatures due to lower mobilities. This leads to increased syndiotactic placement, as was discussed in the section on propagation. Special techniques, however, such as the use of canal complexes can be employed to form stereoregular polymers by free-radical mechanism. Urea and thiourea were used originally for such purposes [210, 211]. Monomers such as butadiene or others form complexes within the voids, or canals of the crystal lattices of these compounds. Brief exposure to high energy radiation initiates chain growth. In the canals, the monomer molecules are held in fixed positions, so chain growth is restricted in one direction only. Steric control is exercised because in these fixed positions the monomer molecules tend to align uniformly. It was suggested that in the canal complexes the monomers are not just lined up end to end, but packed in an overlapping arrangement. For molecules such as isobutylene or vinylidene chloride, it may be possible for the monomers to lie directly on top of each other, resembling a stack of coins. Such stacking greatly facilitates reactions between guest molecules [210, 211].

Polymerizations in thiourea canal complexes yields high melting crystalline *trans*-1,4 polybutadiene, 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, and 1,3-cyclohexadiene. Cyclohexadiene monoxide, vinyl chloride, and acrylonitrile also form stereoregular polymers. On the other hand, polymerizations of isobutylene and of vinylidene chloride fail to yield stereospecific polymers.

Sodium montmorillonite can also be used to polymerize polar monomers between the lamellae. Here too, the organization of monomer molecules within the monolayers influences the structure of the resultant polymers [212, 213]. Poly(methyl methacrylate) formed in sodium montmorillonite is composed of short, predominantly isotactic stereosequences [211]. The percentage of isotactic component increases with an increase in the ion exchanging population on the surface of the mineral and is independent of the temperature between 20 and 160°C. In this way, it is possible to vary the population of isotactic triads at will up to 50% composition [205].

Perhydrotriphenylene also forms channel-like inclusions with conjugated dienes. Polymerization of these dienes yields some steric control [216, 218].

Uemura and coworkers [217] carried out radical polymerizations of vinyl monomers (styrene, methyl methacrylate, and vinyl acetate) within various nanochannels of porous coordination polymers. They studied the relationships between the channel size and polymerization behaviors, such as monomer reactivity, molecular weight, and stereostructures. They reported that in these polymerization systems, the polymer-growing radicals were remarkably stabilized by efficient suppression of the termination reactions within the channels, resulting in relatively narrow molecular weight distributions. A significant nanochannel effect on the polymer stereoregularity was also seen, leading to a clear increase of isotactic placement in the resulting polymers.

There were attempts at controlling steric placement by a technique called ***template polymerization***. An example is methyl methacrylate polymerization in the presence of isotactic poly(methyl methacrylate) [208, 209]. Thus template polymerization is a process of polymerizing a monomer in the presence of a polymer, usually from a different monomer. The presence of template polymers, however, only results in accelerating the rates of polymerizations [219].

3.14 Controlled/"Living" Free-Radical Polymerization

Living polymerizations are chain-growth reactions where the propagating centers on the growing chains do not terminate and do not undergo chain transfer. Such polymerizations are noted for preparations of polymers with controlled molecular weights, desired end groups and low polydispersities. In addition, the preparations of polymers with predetermined molecular weights and narrow molecular weight distributions require fast initiations and fast exchanges between sites of variable activities and variable lifetimes. Such chain-growth reactions, ionic in nature, are discussed in Chap. 4. In typical homogeneous free radical polymerizations, however, bimolecular terminations between two growing radicals cannot be avoided and, therefore, typical living free radical polymerization cannot be fully realized. Also, in conventional free radical polymerizations, the initiations are slow, while high-molecular-weight polymers form shortly after the start of the reactions. As the reactions progress, polydispersities increase, while the molecular weights actually decrease. It is possible, however, to adjust conditions of some radical polymerizations in such a way that polymers with controlled molecular weights and relatively low polydispersities form [220, 221]. These are not true living polymerization as such because termination reactions do occur. They possess, however, some characteristics that are similar to living polymerizations and are referred to by many as ***controlled/"living"*** polymerizations. Such reactions yield polymers with controlled molecular weights, exhibit increase in molecular weight with conversion, yield narrow molecular weight distributions, and can be used to form copolymers. Some examples of such polymerizations include nitroxyl radical-mediated polymerizations of styrene [222–225], atom transfer polymerizations controlled by ruthenium-(II)/aluminum [226, 227] or by copper/bipyridine complexes [228], Co (II)-mediated polymerizations of methacrylates and acrylates [229], and polymerization of styrene using a degenerative transfer method [230], as well as others. Some features are unusual for radical processes and the radical nature of some of these reactions might be questioned, as for instance, polymerizations catalyzed by transition metals. Evidence has been presented, however, that strongly indicates radical nature in at least in atom transfer polymerizations [231]. The evidence, however, is not unambiguous.

Some initial attempts at producing “living” polymerizations made use of ***iniferters.*** This term appears to come from the word ***inifer***, a bifunctional compound that brings about both initiation and chain transfer. “Living” cationic polymerizations make use of inifers to form block copolymers. This is discussed in Chap. 9. The term iniferter was proposed by Otsu and Yoshida in 1982 [232]. Iniferters used in controlled/living free-radical polymerizations are sulfur-centered free radicals that can be generated from sulfur-containing molecules such as dithiocarbamates. The radicals react reversibly with growing polymeric chain ends, thereby controlling the concentration of the radical species. Many of these sulfur centered radicals, however, can also initiate new polymer chains. This can lead to uncontrolled growth. To overcome these difficulties, other approaches were also developed [233].

Deactivation of growing radicals with stable radicals can be carried out with the aid of various nitroxyl radicals, protected phenoxy radicals, dithiocarbamate, trityl, and benzhydryl derivatives. Growing radicals can also be deactivated with nonradicals in the presence of organometallic compounds that form stabilized hyper-coordinated radicals. The polymerizations with the aid of reversible degradative chain transferring are unique in that they requires very rapid and “clean” chain transfers without side reactions. The enhanced control of polymerization process relies on reduction in the ratio of the rate of termination to that of propagation, due to low instantaneous concentration of growing radicals. This means that initiation and propagation reactions must proceed at similar rates due to application of the initiators resembling polymer end groups in their dormant state. Also, in these polymerization reactions, there must be a low proportion of chains marked by uncontrolled termination and/or transfer due to relatively low molecular weights.

Homogenous controlled/“living” free radical polymerizations are based, therefore, on the reversible deactivations of growing radicals. Early, Matyjaszewski divided such polymerizations into three classes [240, 241]. These were:

1. Deactivations of growing radicals with stable radicals by reversible formations of dormant covalent species, followed by homolytic cleavages:

$$P\bullet + R\bullet \underset{\text{act.}}{\overset{\text{deact.}}{\rightleftarrows}} P\text{——}R$$

2. Reversible deactivations of growing radicals with “nonradical” species by formation of dormant persistent radicals:

$$P\bullet + X^{*} \underset{\text{act.}}{\overset{\text{deact.}}{\rightleftarrows}} (P\text{——}X)$$

3. Reversible degenerative transfers based on thermodynamically neutral exchange reactions between growing radicals and transfer agents:

$$P_n\bullet + P_1\text{——}R \overset{k_{tr}}{\rightleftarrows} P_1\bullet + P_n\text{——}R$$

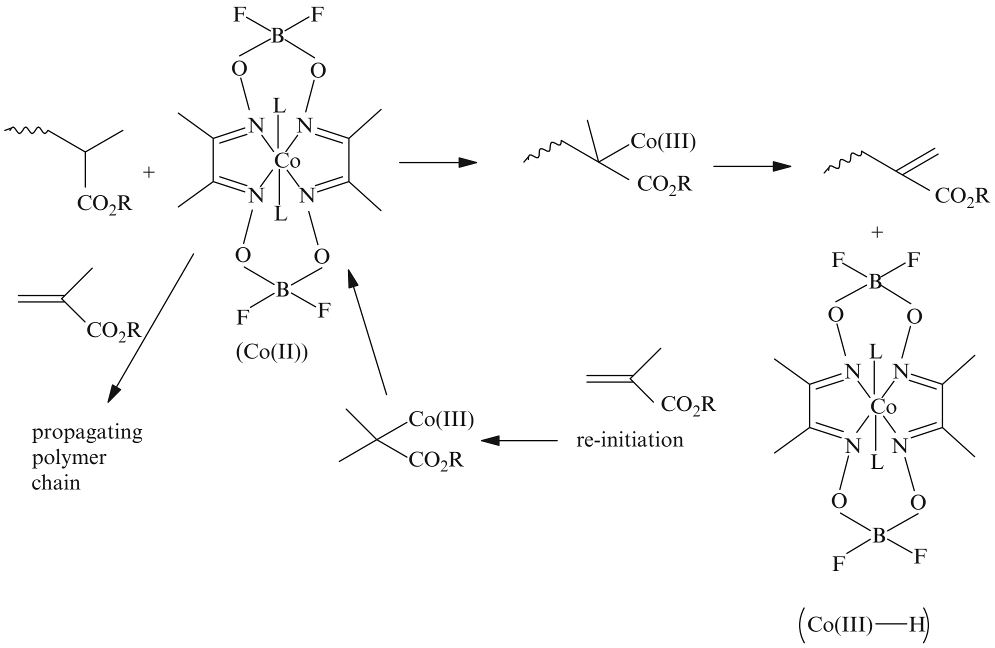


Fig. 3.2 Cobalt mediated controlled/“living” polymerization

3.14.1 Cobalt Mediated Polymerizations

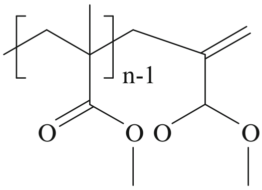
Catalytic chain transfer polymerizations can utilize metals such as low spin cobalt(II) compounds as chain transferring agents. The mechanism is believed to involve repeated disturbing of each propagating step by abstraction of hydrogen atoms from the propagating polymers. This yields chains with unsaturated terminal units and hydrogen transfer agent adducts, Co(III)–H. Subsequent transfers of hydrogens to the growing chains result in reinitiating the processes [241]. The β-hydrogen abstractions from the growing radicals and the formations of metal hydrides [229] can be illustrated as follows:

where Mt = Co

This catalytic cycle for a cobalt mediated polymerization, using bis-dimethyl-glyoximate cobalt boron fluoride catalyst was illustrated Haddleton et al. [233, 234]. A similar illustration of the process is shown in Fig. 3.2. The affinities of metals for hydrogen abstractions, and/or their abilities to lose electrons depend on their oxidation states and the nature of their ligands. Such reactions can, therefore, be suppressed. This can be done by choosing high oxidation state metals, ligands that protect the metal from the abstraction of the P–H atoms, and by controlling the position of the oxidation–reduction equilibrium.

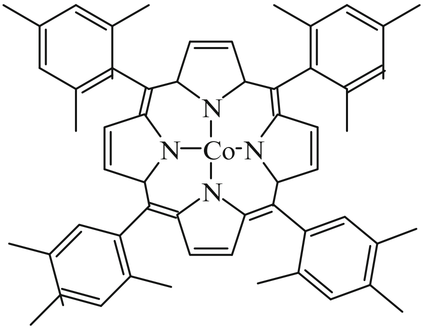
$$\mathrm{R}\text{—}\,\mathrm{Co}+++\mathrm{Ln} \rightleftharpoons \mathrm{R}\bullet+\bullet\mathrm{Co}++\mathrm{Ln}$$
$$\mathrm{RM_x}+\mathrm{Co}++\mathrm{Ln} \rightleftharpoons \mathrm{RM_x}\text{—}\mathrm{Co}+++\mathrm{Ln}$$

The metal cobalt(II) is usually chelated. This can be cobalt porphyrin, cobalt phthalocyanin, or cobalt oxime, as well as others. The polymer molecules that form have, as stated earlier, terminal double bonds and can be illustrated as follows,



The cobalt hydride in turn reacts with a new monomer molecules to regenerate the Co(II) [235].

One publication describes a chain transferring agents that can be used in controlled polymerization of methacrylate monomers where reductive elimination of cobalt hydride from the neighboring methyl group deflects further chain growth [236]. The agent was illustrated as follows:

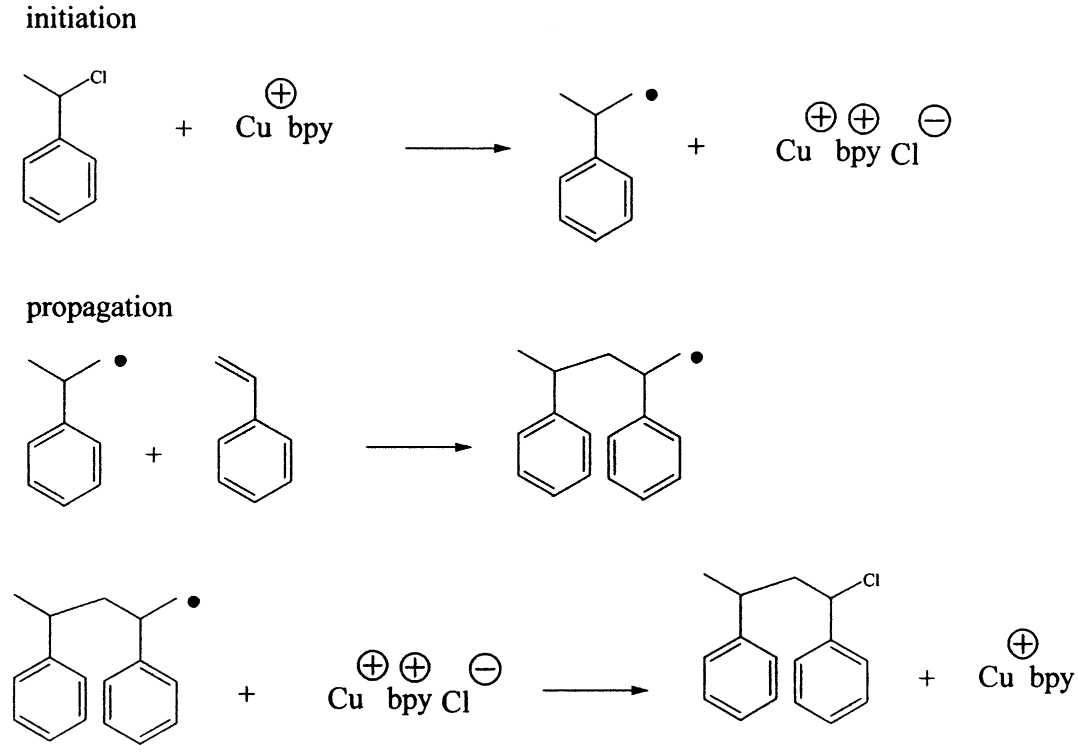


A described example is a reaction conducted at 60°C in deoxygenated benzene, using neopentylcobalt with tetramesityl-porphyrin ligand and methyl acrylate monomer [236]. A slow polymerization yields 66% conversion in 38 h. The product is a narrow molecular weight distribution polymer of $M_n = 144{,}000$. The polymerization is even slower with less hindered phenyl substituents on the porphyrin ligand. Both homopolymers and block copolymers can be formed.

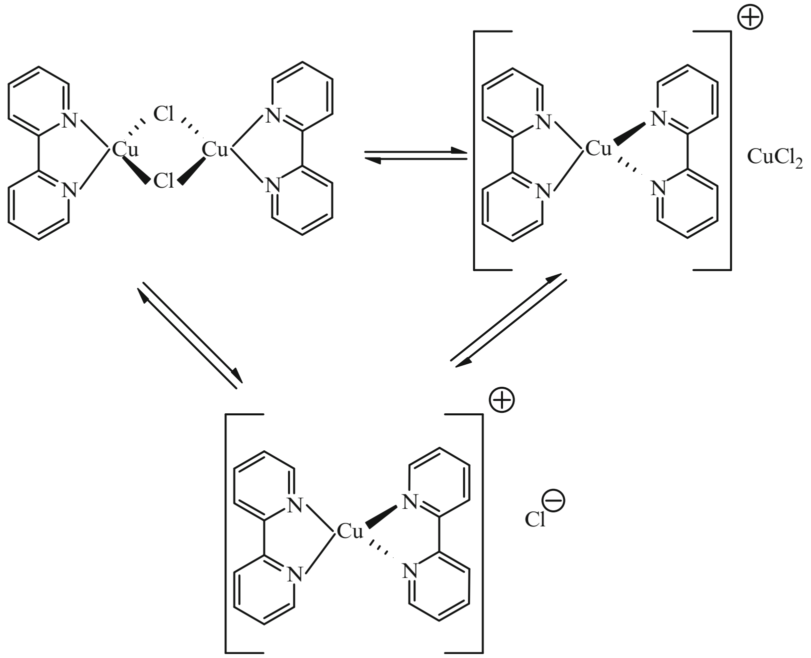
Catalytic chain transfer by a cobalt(ll) porphyrin in radical polymerization of MAA in water was studied by Wayland and coworkers [237]. Cobalt tetrasulfonatophenylporphyrin was found by them to be exceptionally effective in the catalytic chain transfer for the radical polymerization of MAA in water. A remarkable feature of this process is that the increase in the degree of polymerization, with conversion requires that more monomer be consumed in chain growth of the existing macromonomers than in initiation and propagation of new chains through chain transfer to monomer. Reinitiation of oligomer olefins and chain growth are significant inherent reactivity features of the cobalt^{++}-porphyrin catalyzed chain transfer process.

3.14.2 Atom Transfer Radical Polymerizations

Atom transfer radical polymerizations (ATRP) were reported simultaneously by two groups: (1) Matyjaszewski et al. [218] and (2) Sawamoto and coworkers [226]. Matyjaszewski et al. utilized a Cu/bipyridine complex as a ***halogen transfer agent*** that functions between dormant and active polymer chains. Formation of polymers with predetermined molecular weight of up to $M_n \approx 10$ [5] and polydispersity as narrow as 1.05 was reported [238, 239]. This type of polymerization appears to offer the possibility of preparing a broad range of polymeric materials [240–242]. The reactions proceed under conditions that could make the process commercially attractive. Thus, for instance, by using nonionic surfactants, such as poly(oxyethylene oleyl ethers) it is possible to prepare polymers from butyl methacrylate, methyl methacrylate, styrene, and butyl acrylate in aqueous emulsions. In addition, by using multidentate ligand such as tris[(2-dimethyl-amino)ethyl]amine the atom transfer polymerizations can be made to proceed rapidly at room temperature [242, 243]. The atom transfer polymerization reaction can be illustrated as follows:



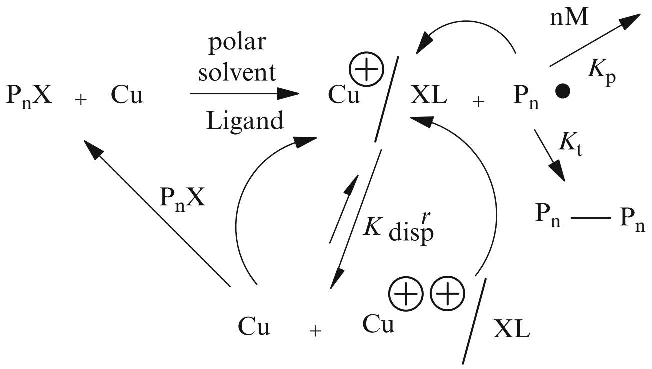
Polymerizations of styrene using 2,2′-dipyridyl as the ligand indicated that they proceed first order with respect to the concentration of initiator, and 0.4 and 0.6 orders with respect to the concentration of Cu(l) halide and ligand [218, 229]. The copper bipyridyl complexes mentioned above were pictured by Haddleton et al. [233, 234] as follows:



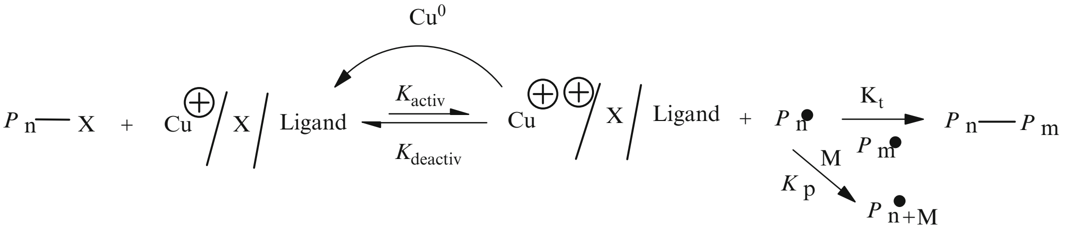
Recently, Matyjaszewski has summarized the mechanism of these polymerizations [245].

Matyjaszewski and coworkers [246–250] reported that small amounts of air present in the reaction mixture can be consumed by addition of sufficient amounts of an appropriate reducing agent, such as tin(II) 2-ethylhexanoate or ascorbic acid. In this process, the cuprous ions are initially oxidized by oxygen to the cupric ions, but then in turn reduced by the reducing agent. The cuprous ions activate the reaction. There is an induction period until all the oxygen is consumed. This is referred to as ***(ARGENT) ATRP***. Also, they have subsequently reported that polymerizations of 2-(dimethylamino)ethyl methacrylate does not require any addition of a reducing agent as the tertiary amine group presumably serves as an internal one [251].

In addition, Percec and coworkers [253] reported that polymerizations in polar solvents in conjunction with copper and appropriate ligands allow ultrafast syntheses of high-molecular-weight polymers at ambient temperature. The process is referred to as ***Single Electron Transfer-Living Radical Polymerization* (*SET-LRP*).** The mechanism proposed is based on disproportionation of cuprous ions to cupric ions and metallic copper. This is catalyzed by the polar solvents and the appropriate ligands. The proposed mechanism can be illustrated as follows:



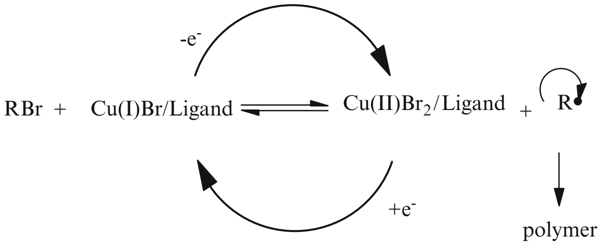
The work by Percec and coworkers included an investigation of various solvents and ligands for the catalyst activity and their ability to disproportionate the cuprous ion. They demonstrated that addition of 10 mol% of phenol as ligand leads to spontaneous disproportionation to metallic copper and cupric ions [253]. An alternative to the proposed Percec’s mechanism was proposed by Matyjaszewski [254]. According to this mechanism, metallic copper acts as a reducing agent for the cupric ions and yields active cuprous ions that catalyze the polymerization. This mechanism is similar to one proposed for the reactions that utilize ascorbic acid or tin based reagents to reduce cupric ions to cuprous ones [255, 256]. The mechanism can be illustrated as follows:



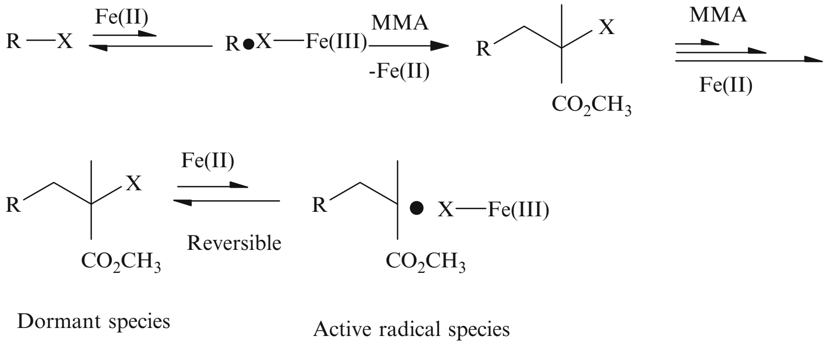
Haddleton and coworkers [256] investigated use of toluene as a solvent with phenol as an additive for use in living/controlled polymerizations. They demonstrated a direct relationship between the reaction time and the amount of phenol added. The optimum amount found by them is 20 equivalents of phenol with respect to the initiator. Their products were narrow molecular weight polymers with MWD ranging between 1.05 and 1.25.

Removal of copper from ATP products can sometimes be a problem [257]. Honigfort and coworkers reported that they found that when the ligands were supported on Janda Jel (see Chap. 10) resins, easy removal of the catalyst complex was possible from the reaction mixture. The Janda Jel ligands were used in ATRP of methyl methacrylate, styrene, and 2-(dimethylamino)ethyl methacrylate. The methyl methacrylate and 2-(dimethylamino)ethyl methacrylate polymerizations proceeded quickly to high conversion (>90%) and were well controlled. The styrene polymerization, however, was found by them to be sluggish and proceeded only to 63% conversion. After polymerizations were complete, the catalyst ligand complex was easily removed by filtration. Zhu and coworkers [257] claim to have a simple and effective method for purification of an ATP product using catalyst precipitation and microfiltration. The method relies on the precipitation of the Cu + Br ligand catalyst complex by the additions of $Cu{+}{+}Br_2$. The precipitate thus formed is effectively retained by a 0.14-µm PTFE filter, resulting in up to 99.9% of the catalyst being removed from the polymer. The resulting clear polymer filtrate contains little residual copper, down to 10 ppm.

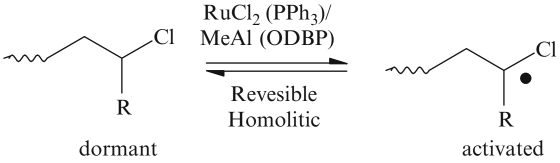
Matyjaszewski and coworkers developed a process [255] for an electrochemically mediated ATRP. They use applied voltage to drive the production of Cu + ions that catalyze the polymer formation. Because the rate of the reaction is controlled by a redox equilibrium between cuprous and cupric ions, electrochemistry permits the regulation of the concentration of each species.



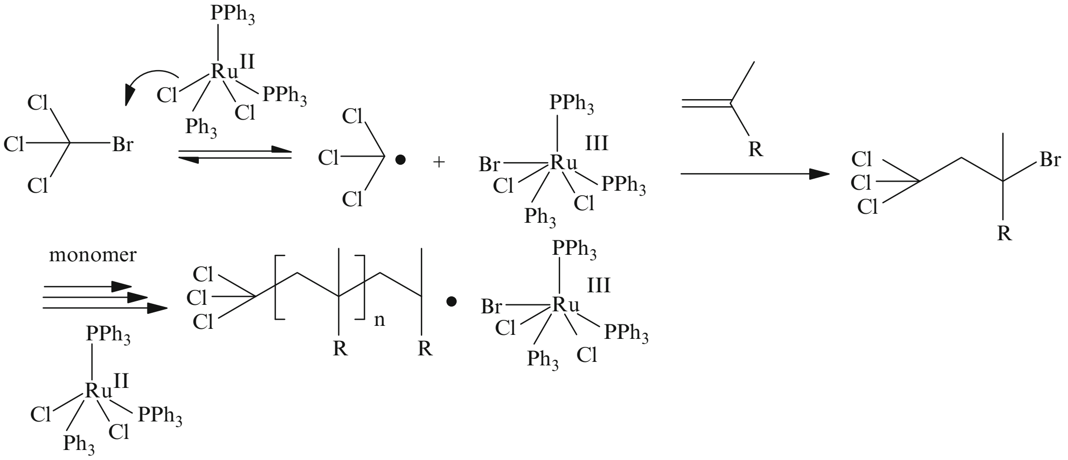
A similar ATP process is one that uses iron(II) bis(triphenylphosphine)-dichloride$[FeCl_2(PPh_3)_2]$. It induces “living” polymerization of monomers such as methyl methacrylate in conjunction with organic halides as initiators in the presence and in the absence of $Al(O^iPr)_3$ in toluene at 80°C. The molecular weight distributions of the products are 1.1–1.3 [269]. The following mechanism is visualized [269]:



The ATP process developed by Sawamoto and coworkers [226], uses an initiating system consisting of carbon tetrachloride, dichlorotri(triphenyl-phosphine)-ruthenium (II) and methylaluminum bis(2,6-di-*tert*-butylphenoxide) to polymerize methyl methacrylate [226]. The polymerization involves reversible and homolytic cleavages of carbon-halogen terminal groups assisted by transition metal complexes [226].



The ruthenium(II) complexes interact with CCl_4 and are oxidized in the process to become Ru(III) and radicals CCl_3• that add to molecules of methyl methacrylate. The polymerization proceeds via repetitive additions of methyl methacrylate molecules to the radical species that are repeatedly generated from the covalent species with carbon-halogen terminal groups [226]. Suwamoto also reported [226] that addition of a halogen donor, $Ph_3C–Cl$ aids the shift of the equilibrium balance to dormant species. The reaction of polymerization can be illustrated as follows:



Klumperman and coworkers [259] observed that while it is lately quite common to treat living radical copolymerization as being completely analogous to its radical counterpart, small deviations in the copolymerization behavior do occur. They interpret the deviations on the basis of the reactions being specific to controlled/living radical polymerization, such as activation—deactivation equilibrium in ATRP. They observed that reactivity ratios obtained from atom transfer radical copolymerization data, interpreted according to the conventional terminal model deviate from the true reactivity ratios of the propagating radicals.

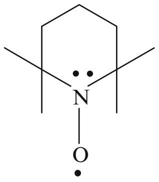
Velazquez and coworkers [260], developed a kinetic model incorporating effects of diffusion-controlled reactions on atom-transfer radical polymerization. The reactions considered to be diffusion-controlled are monomer propagation, bimolecular radical termination, chain transfer between propagating radicals and catalyst, and transfer to small molecules. Model predictions indicate that a diffusion-controlled propagation reduces the “living” behavior of the system, but a diffusion-controlled termination enhances its livingness. Also, diffusion-controlled transfer between chains and catalyst is the same in the forward and in the reverse directions. The “livingness” of the system is enhanced, but if one of them is kept unchanged the other is increased, and the “livingness” of the system is reduced. When diffusion-controlled termination is important, their simulations show that the overall effect of diffusion-controlled phenomena in ATRP is to enhance the livingness of the system.

Preparation of gradient copolymer of styrene and *n*-butyl acrylate was reported by the use of ATRP [261]. ***Gradient copolymers*** are copolymers with sequence distributions varying in a well-defined order as functions of chain lengths. It is suggested that gradient copolymers have the potential of outperforming block and alternating copolymers in some instances [261].

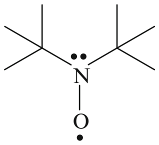
3.14.3 Nitroxide-Mediated Radical Polymerizations

A nitroxide mediated polymerization of styrene was first reported in 1985 [262]. This reaction, however, was studied extensively only since 1993. The monomer conversion rates vs. temperatures are much slower than they are in conventional styrene polymerization. Also, the polydispersities of the products are not as narrow as obtained in anionic polymerization but, generally, the polydispersities produced by this process are proportional to the molecular weights of the polymers produced. In fact, a linear relationship between polydispersity and the molecular weight of the polystyrene product was demonstrated [263].

After the initial nonstationary period, typical alkene polymerizations in the presence of alkoxyamines proceed according to the first order kinetics with the molecular weights increasing with conversion. The dispersity of the products and the contribution of the nonstationary periods depend upon the temperature, the particular initiating system and on the nature of the monomers. Styrene polymerizations can be carried out in the presence of stable nitroxyl radicals, such as the 2,2,6,6-tetramethylpiperydinyl-1-oxy radical, commonly referred to as ***TEMPO*** [264] or ditertiary butyl nitroxide, referred to as ***DTB N.***



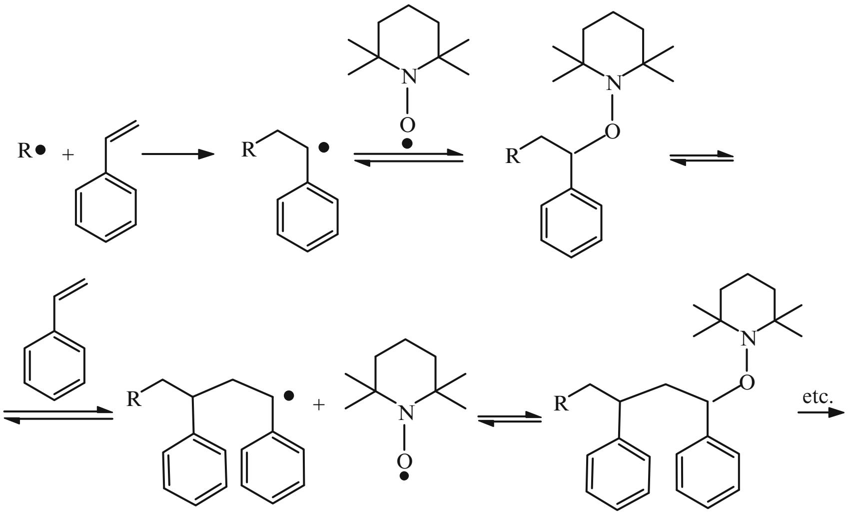
TEMPO



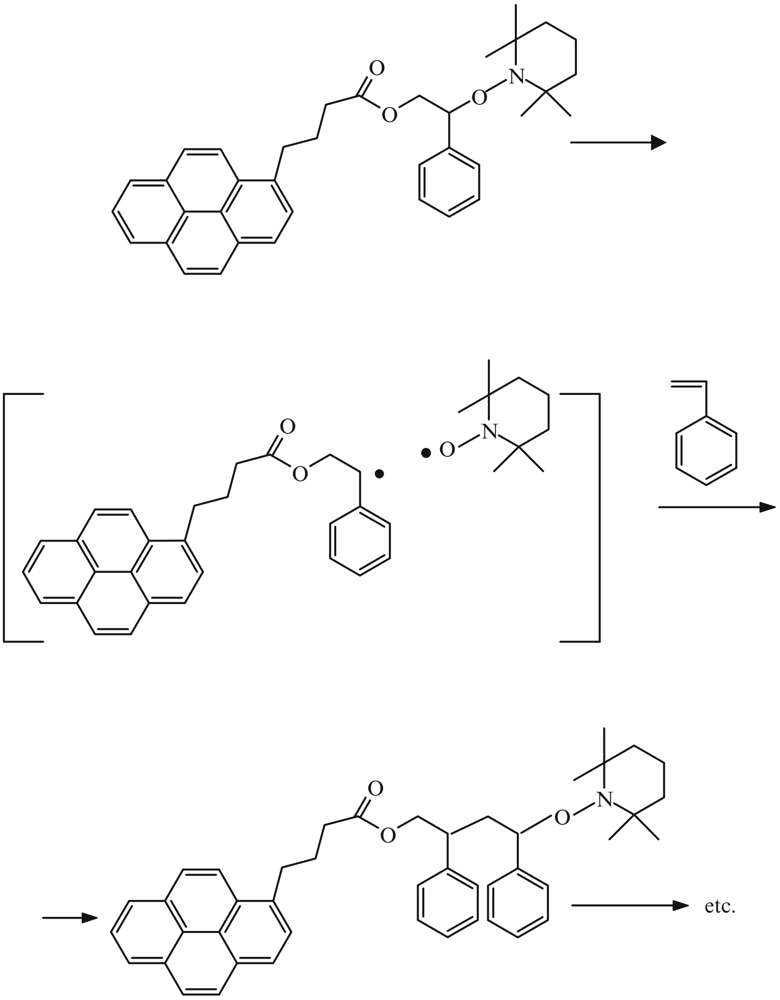
DTBN

Such radicals are incapable of initiating polymerizations by additions to the double bonds, but react selectively with growing radicals to form reversibly covalent species [265]. In addition, the reactions of growing radicals with dormant species occur via degenerative transfer:

The position of the equilibrium constant in reactions with TEMPO depends on the nature of the radical, the solvent and the temperature. These polymerizations can be initiated by either bimolecular initiators or by unimolecular ones. The bimolecular initiators utilize common free radical sources such as benzoyl peroxide or azobisisobutyronitrile to start the reaction. The carbon-centered initiating radicals that form in turn react with TEMPO. This can be illustrated as follows:



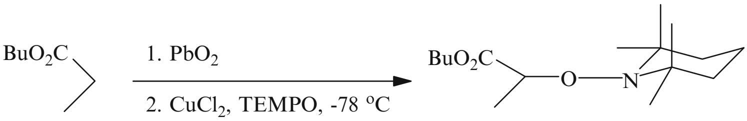
Various descriptions of different unimolecular initiators can be found in the literature. A presence of α-methyl groups on the alkoxyamines appears to be essential [266]. These compounds yield, upon dissociation, both stable radicals and initiating ones and can be shown as follows [267].



The optimal amount of the radical initiator depends on the efficiency of the initiation. Ideally the concentration of the radicals generated from the initiator should be slightly higher than the concentration of the scavenger.

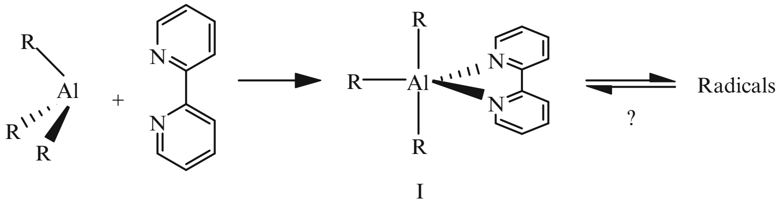
At higher temperatures, such as 120°C, the polymerizations of styrene tend to exhibit ideal behavior. Also, at higher temperatures narrower molecular weight distributions are obtained, indicating sufficiently high exchange rates.

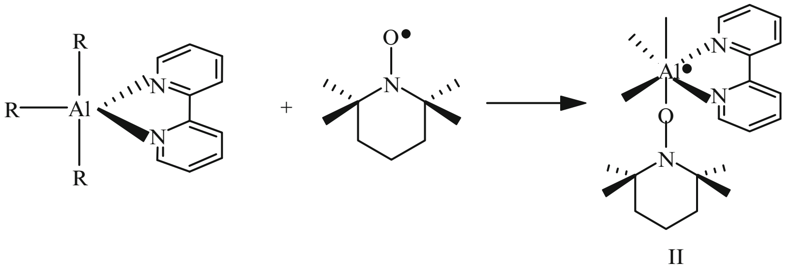
A low-temperature method for the preparation of unimolecular initiators was reported [268]. In this method, oxidation is used to generate carbon radicals in the presence of nitroxide traps such as TEMPO.

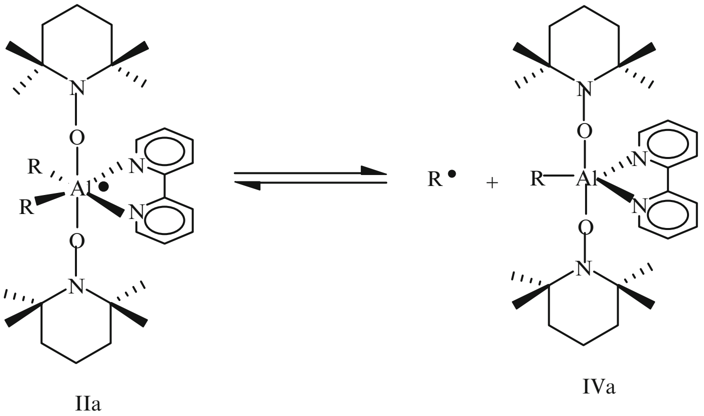


A variation in controlled/"living" polymerization of vinyl acetate by the use of a bidentate ligand, 2,2′-bipyridyl and TEMPO composition in 2:1.2 ratio that was reported by Mardare and Matyjaszewski [267]. The following mechanism was proposed.

(1) Pentacoordinated complexes (I) are formed at a molar ratio of 1.1



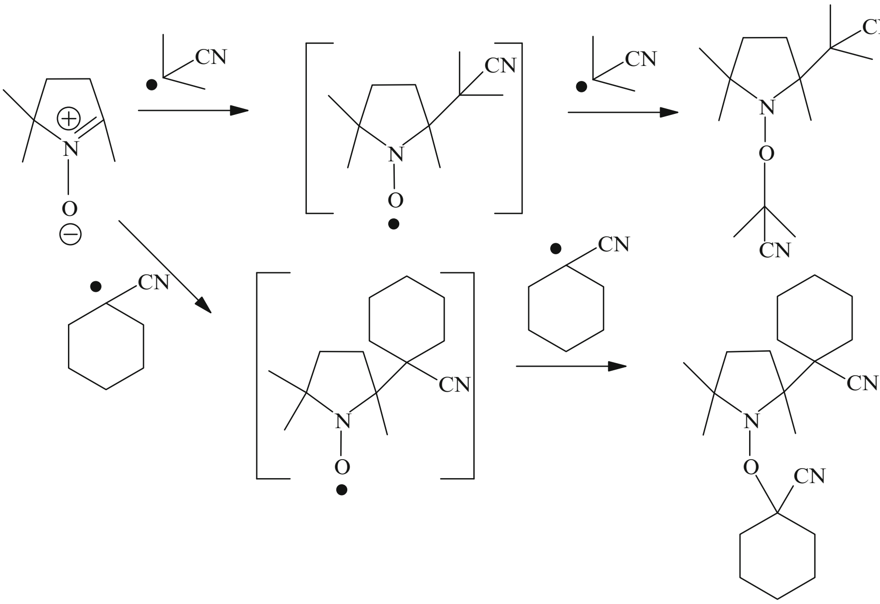




(2) The irreversible attacks by TEMPO on the pentacoordinated complexes, $(\mathrm{Al}(i\mathrm{Bu})_3)$:BPy (I), lead to relatively stable and delocalized radicals(II). TEMPO also reacts with some short-lived radicals present at stage (1) to form alkoxyamines and pentacoordinated complexes of type IV. The radicals II could be in equilibrium with tiny amounts of very reactive radicals R• capable of initiations and subsequent propagations.

Aldabbagh and coworkers [269] reported that carrying out the nitroxide-mediated polymerization in supercritical carbon dioxide allows improved control of the reaction.

Nesvadba and coworkers [270] used nitrones in controlled radical polymerization of vinyl monomers. This was the beginning of the in situ **NMP** concept. The alkoxyamines were prepared by reaction of free radicals obtained from decomposition of azo-initiators, such as azobisisobutyronitrile or l,1′-azobis(cyclohexanecarbonitrile) with selected nitrones:



The alkoxyamines were utilized in radical polymerization of acrylates and styrene in bulk or in solution between 100 and 145°C. Low molecular weight polymers, 3,000–14,000 g/mol formed rapidly with polydispersity, M_w/M_n between 1.2 and 3.4. High styrene conversion was observed together with a low polydispersity.

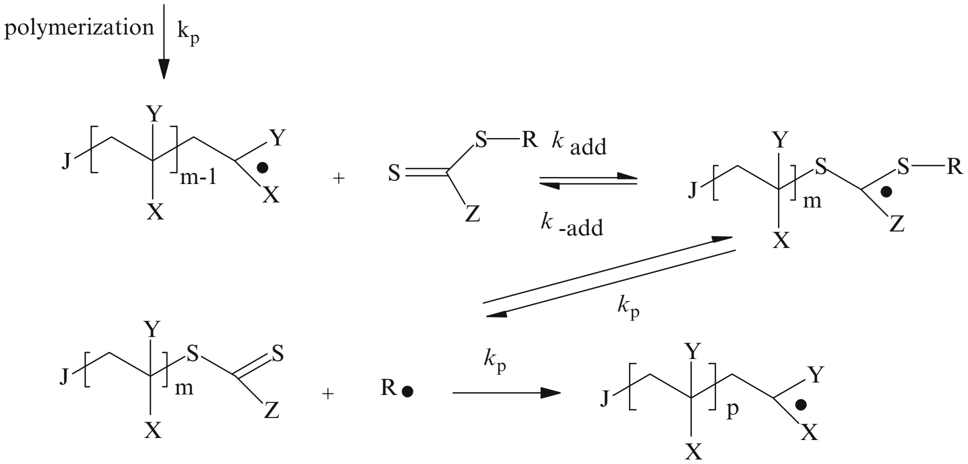
Subsequently, nitroxides and parent alkoxyamines were formed directly in the polymerization medium (in situ **NMP**) by reaction of the nitrone with the free radical initiators [270]. Two types of reactions were carried out. One was a reaction before monomer addition and the other one after the addition. In either case, a prereaction was systematically carried out at temperatures ranging from 60 to 80°C. This was followed by polymerizations at 130°C. The in situ-formed nitroxides and alkoxyamines controlled the radical polymerizations of *n*-butyl acrylate yielding, however, low molecular weight polymers, of $M_n < 10{,}000$ and M_w/M_n equal to 1.65–2.0.

A patent was issued to Wertmer and coworkers [271] for controlled radical (co)polymerization of vinyl monomers mediated by nitrones substituted by longer alkyl groups that contained as much as 18 carbon atoms. The nitrone was simply heated in the presence of peroxide and a monomer, such as styrene at 130°C for 24 h. High-molecular-weight polystyrene, $M_n = 98{,}000–146{,}000$ was formed. The ratio of M_w/M_n, however, was not disclosed

Recently, Grubbs and coworkers [272] have synthesized an active alkoxyamine by reaction of 2-methyl-2-nitrosopropane with 1-bromoethylbenzene, catalyzed by ligated CuBr in the presence of metallic copper. A purified alkoxyamine was used to initiate the radical polymerization of styrene and isoprene. Well-defined low polydispersity polymers formed with $M_w/M_n = 1.14$ for polystyrene and 1.28 for polyisoprene. Subsequently, Grubbs and coworkers [273] used this alkoxyamine and successfully controlled the radical polymerization of *n*-butyl acylate at 125°C. Lower ratio of M_w/M_n was observed when the alkoxyamine was preheated at temperatures up to 125 for 30 mm prior to adding the monomer. This prereaction was needed for an excess of free nitroxide to be formed in situ and for polymerization to be controlled.

3.14.4 Reversible Addition-Fragmentation Chain Transfer Polymerization

Another type of "living"/controlled radical polymerization involves ***reversible addition-fragmentation chain transfer***. It was named, therefore, ***RAFT polymerization***. Great versatility and effectiveness was shown for the process [274]. The process is said to be compatible with a very wide range of monomers including functional monomers containing such functional groups as acids, acid salts, and hydroxyl or tertiary amine groups. The conditions of polymerization are those used in conventional free-radical polymerizations. They can be carried out in bulk, solution, emulsion and suspension (see Sect. 3.16). The usual azo or peroxide initiators are employed [274]. The reaction was originally illustrated as follows [274]:

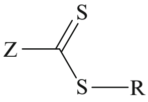


The RAFT process depends upon rapid addition—fragmentation equilibrium reaction between propagating (P_n•) as well as intermediate radicals, and chain activity and dormancy, as shown below in the reaction scheme. The concentrations of each of the species within the equilibrium is dependent on the relative rate coefficients for addition of a propagating radical to the RAFT agent (K_{add}) and fragmentation of the formed intermediate radical (K_{frag}). This equilibrium applies correctly only for polymeric chains that are present in significant concentrations after an initialization period. During the initiation period there are mainly shorter chains present. The important part of this equilibrium is the relatively stable radical intermediates.

It was reported that RAFT-mediated polymerization reactions typically contain anomalies, such as an "inhibition" period and rate retardation. The rate retardations or reductions in the polymerization rates apparently occur in the presence of RAFT agents, and are not observed when RAFT agents are absent. Examples are dithiobenzoate-mediated polymerization reactions [275].

Tonge and coworkers [276] investigated the reactions of short-chain species during the initial period of cumyl dithiobenzoate mediated polymerization of styrene at 84°C. Using electron spin resonance and hydrogen and carbon NMR spectroscopies they were able to demonstrate that the reactions are very specific during the initial stages. There is a strong preference to add single monomer species. This is followed by fragmentation and release of shorter radicals prior to formation of longer chains.

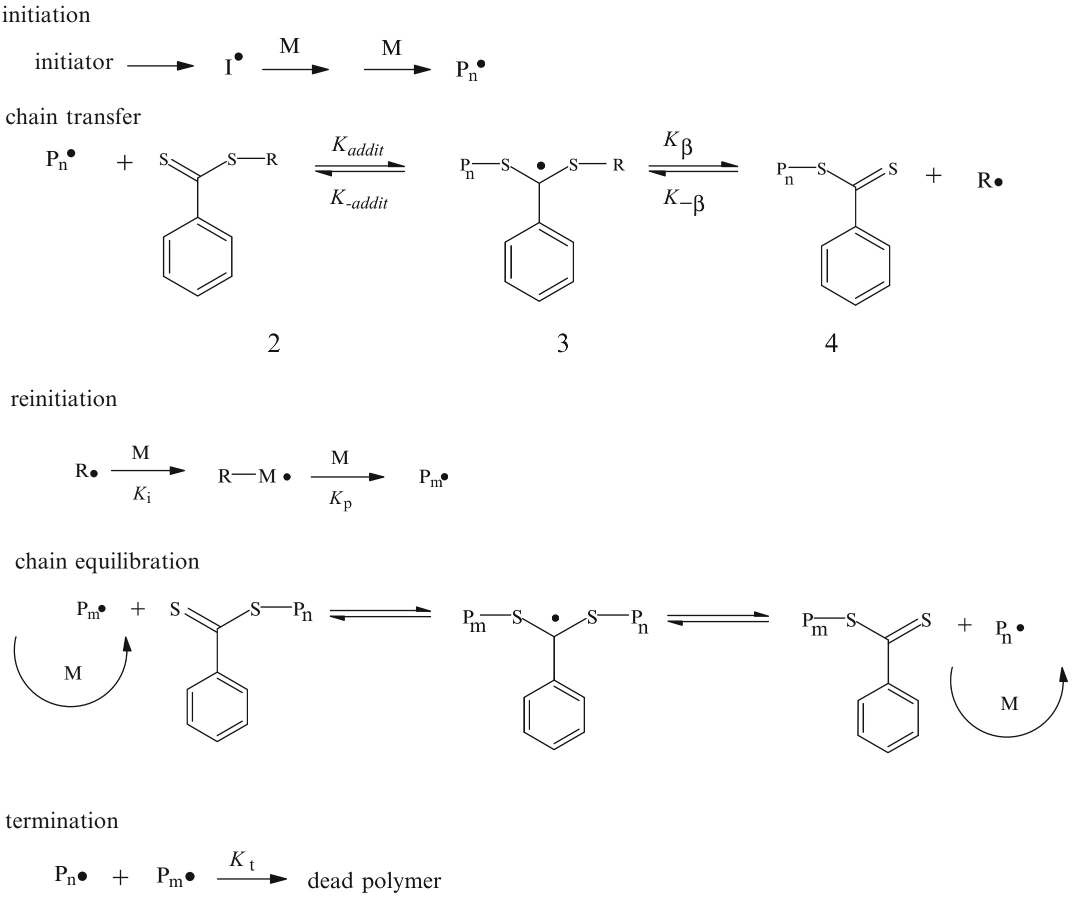
The effectiveness RAFT agents were investigated by Moad and coworkers [277]. These RAFT agents, such as thiocarbonylthio compounds, depend in effectiveness on the nature of the group, Z and R (shown below) that modify the reactivity of the thiocarbonyl group toward free radical addition. R is the free radical leaving group [277]:



These RAFT agents are based on the structure [S=C(Ph)S–R] [277] They found that the effectiveness of these agents also depends upon the nature of the monomer and on the polymerization conditions. For the polymerization of styrene, methyl methacrylate, butyl acrylate, and methyl acrylate at 60°C, the effectiveness of R decreases in the following order [277]:

$$\mathrm{R = C(alkyl)_2CN \sim C(CH_3)_2Ar > C(CH_3)_2C(=O)O(alkyl) > C(CH_3)_2C(=O)NH(alkyl) > C(CH_3)_2CH_2C(CH_3)_3 \geqslant C(CH_3)HPh > C(CH_3)_3 \sim CH_2Ph}$$

In addition, among the above compounds, only when R=$C(CH_3)_2CN$ or $C(CH_3)_2Ph$ did these thiocarbonylthio compounds yield polymers with narrower polydispersities in batch polymerizations. Also, only these compounds allowed molecular weight control that may be expected from a living polymerization. The reaction mechanism was proposed by Moad and coworkers as follows [277]:



Moad and coworkers concluded [277] that a major factor that determines the transfer coefficient of dithiobenzoate derivatives is the way the intermediate 3 (see the above in equation) partitions between starting materials and products. This in turn is determined by the relative ability of the leaving group R• and by the propagating radical. Steric factors and radical stability of R• are also important. They conclude that more stable, more electrophilic, and bulkier radicals are better leaving groups. The partitioning of R• between the monomers (to reinitiate) or by adding to polymeric RAFT can also have a significant effect on the rate of consumption of RAFT agent [277].

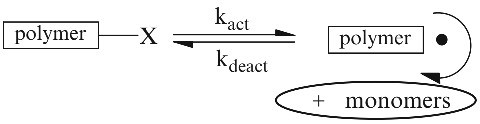
Vana and coworkers [278] studied conversion vs. time and molecular weight distributions in conjunction with the kinetic scheme for the RAPT process. In particular, conditions leading to inhibition and rate retardation were examined to act as a guide to optimizing the reaction. They demonstrated that there is an inhibition period of considerable length. It is induced by either slow fragmentation of the intermediate RAFT radicals appearing in the preequilibrium or is due to slow reinitiation of the leaving group radicals from the initial RAFT agent. The absolute values of the rate coefficients governing the core equilibrium of the RAFT process (at a fixed value of the equilibrium constant) are found to be crucial in controlling the polydispersity of the resulting M_w/M_n values. Higher interchange frequency effects narrower distributions. They also demonstrated that the size of the rate coefficient controlling the addition reaction of propagating radicals to polymer-RAFT agent, K_β, is mainly responsible for optimizing the control of the polymerization. The fragmentation rate coefficient, $K_{-\beta}$, of the macro RAFT intermediate radical, on the other hand, may be varied over orders of magnitude without affecting the amount of control exerted over the polymerization. Based on the basic RAFT mechanism, shown above, its value mainly governs the extent of rate retardation in RAFT polymerizations [278].

Calitz, Tonge, and Sanderson reported the results of a study of RAFT polymerization by means of electron spin resonance spectroscopy [276]. They observed intermediate radical signals that were not consistent with current RAFT theory [276].

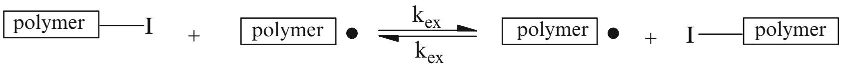
Sawamoto and coworkers reported obtaining simultaneous control of molecular weight and steric structure in RAFT polymerization of *N*-isopropylacrylamide by addition of rare earth metal, Y(*O*-tetrafluoromethanesulfonate)$_3$, Lewis acid. The M_w/M_n ratio of the products ranged between 1.4–1.9 and the isotactic content was 80–84% [277].

Goto et al. [279] developed a process that they describe as **reversible living chain transfer radical polymerization** [278], where they us Ge, Sn, P, and N compounds iodides in the iodide mediated polymerizations.^{ref} In this process, a compound such as GeI_4 is a chain transferring agent and the polymer-iodide is catalytically activated via a RFT process. They proposed that the new reversible activation process be referred to as RTCP [279]. The process can be illustrated by them as follows [279]:

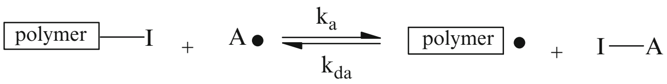
1. reversible activation:



2. exchange or degenerative chain transfer with X=1



3. RT or reversible chain transfer with X=1

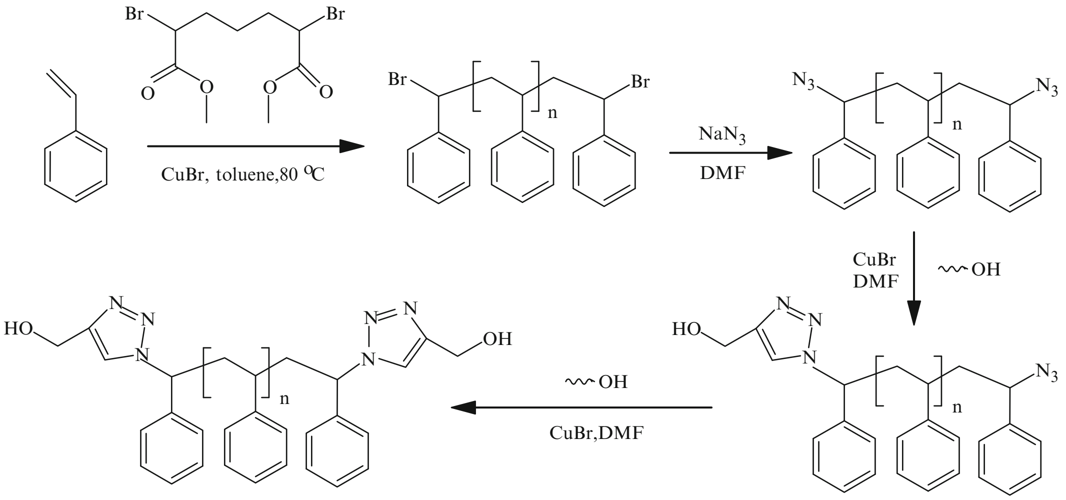


where, I—A is GeI_4; SnI_4; PI_3; NIS; etc.

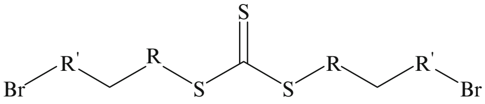
3.14.4.1 Combinations of Click Chemistry and ATP as Well as ATP and RAFT Polymerizations

In the last few years, "click reactions," as termed by Sharpless et al. [280] received attention due to their high specificity, quantitative yields, and good fidelity in the presence of most functional groups. The "click chemistry" reaction includes a copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyne leading to 1,2,3-triazole. Recent publications on this "click reaction" indicate that it is a useful method for preparation of functional polymers [281].

Matyjaszewski and Gao synthesized functional polymers by combining ATRP and the "click reactions." They also prepared telechelic polymers, star polymers and brush polymers [282]. Formation of telechelic polymers was illustrated as follows:



Also, a synthesis of an iniferter that consists of a trithiocarbonate moiety and two bromine chains ends was reported [282]. This iniferter was used to conduct either independently or concurrently both ATRP and reversible addition-fragmentation chain transfer polymerizations. The iniferter was illustrated as follows:

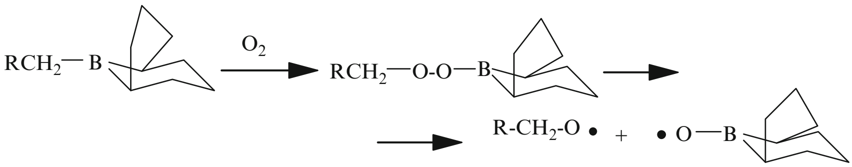


RAFT polymerizations with this iniferter of *N*-butyl acrylate and styrene yielded polymers with M_w/M_n equal to 1.15 and 1.16 respectively. Polymerization of methyl methacrylate, however, yielded a polymer with a broad M_w/M_n ratio. On the other hand, polymerization in the presence of CuBr/TMPA by ATRP exclusively through the bromine chain ends yielded a polymer with narrow M_w/M_n ratio [282].

3.14.5 Special Types of Controlled/"Living" Polymerizations

It was reported that it is possible to employ persistent phosphorus-based radicals in controlled/living free-radical polymerization [283, 284]. Also, in cases of low stability of the hyper coordinated radicals, the ligand exchanges become facile and some organoaluminum, organoboron, and other compounds have been used successfully as transfer agents in polymerization of styrene, acrylics, and vinyl acetate [283, 284].

Chung and coworkers [286] described a "living" radical initiator that is based on oxidation adducts of alkyl-9-borabicyclononanes, such as hexyl-9-borabicyclononane. The "living" radical polymerizations take place at room temperature. The initiators form in situ by reactions with oxygen:



The alkoxy radicals are very reactive and initiate radical polymerizations readily On the other hand, the borinate radicals are stabilized by the empty p-orbitals of boron through back-donating electron density and are too stable to initiate polymerizations. During the polymerization, the borinate radicals may form weak and reversible bonds with the growing chains.

Boroxyl mediated living radical polymerizations were subsequently described by Chung [287] in a review article. The chemistry is centered on the living radical initiator, i.e., alkylperoxydialkylborane (C—O—O—BR) species, similar to the one shown above, that are formed by mono oxidation of an asymmetric trialkylborane with oxygen. In the presence of polar monomers (including acrylates and methacrylates), the C—O—O—BR., undergoes a spontaneous hemolytic cleavage at ambient temperature to form an active alkoxy radical and a stable boroxyl radical The alkoxyl radical is active in initiating the polymerization of vinyl monomers, and the stable boroxyl radical forms a reversible bond with the propagating radical site to prevent undesirable termination reactions. The living polymerizations were characterized by predictable polymer molecular weight, narrow molecular weight distributions, and by formation of telechelic polymers and block copolymers through sequential monomer addition. Furthermore, this living radical initiator system benefits from two unique features of trialkylborane. These are (a) easy incorporation into polymer chains (chain ends or side chains) and (b) in situ auto-transformation to living radical initiators.

Lacroix and coworkers reported a reverse iodine transfer polymerization (RITP), where elemental iodine is used as a control agent in living radical polymerization [288]. Styrene, butyl acrylate, methyl acrylate, and butyl α-fluoroacrylate were homopolymerized, using a radical catalyst and I_2 as a chain transfer agent. Methyl acrylate was also copolymerized with vinylidene chloride using this process.

3.14.6 Kinetics of Controlled/Living Free-Radical Polymerizations

Several papers were published to describe the kinetics of controlled free radical polymerization. Goto and Fukuda [289] postulate two activation processes for nitroxy/styrene polymerization systems:

$$\text{process I:}\ \ \mathrm{P{-\!\!-}X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \mathrm{P\bullet} + \mathrm{X\bullet}$$

$$\text{process II:}\ \ \mathrm{P{-\!\!-}X} + \mathrm{P'\bullet} \underset{k_{ex}}{\rightleftharpoons} \mathrm{P\bullet} + \mathrm{P'} - X$$

The equilibrium constant, $K = K_d/K_c$. Stationary-state concentrations of P• and X• are

$$[\mathrm{P\bullet}] = (R_i/k_i)^{1/2}$$

$$[\mathrm{X\bullet}] = k[\mathrm{P}-\mathrm{X}]/[\mathrm{P\bullet}]$$

The stationary concentration of P• and X• are determined by different mechanisms. [P•] is determined by the balance of the initiation rate R_I and the termination rate k_t [P•] [2]. This is the same as in conventional free radical polymerization systems. [X•] is determined, however, from the equilibrium equation shown for process I. It depends, therefore upon the equilibrium constant K and on the concentration of the adduct [P–X] and [P•] [289]. The rate of polymerization during the stationary state is

$$R_p = k_p[\mathrm{P\bullet}][\mathrm{M}] = (k_p/k_t)^{1/2}R_i^{1/2}[\mathrm{M}]$$

The polymer-nitroxyl adduct P–X reversibly dissociates thermally, in process I into the polymer radical P• and the nitroxyl radical X•. The rate constants of dissociation and combination are k_d and k_c, respectively. The, so-called, "degenerative transfer" takes place in process II. The second-order rate constant for active species in either direction is k_{ex}. Here all the rate constants are assumed to be independent of chain length. Since the frequency of cleavage of the P–X bond is proportional to [P–X] in process I and to [P•1[P′–X]] in process II, the overall frequency, f_a per unit time and per unit volume, of the bond-cleaving or activation reactions, may be expressed by [277]:

$$f_a = k_a[\mathrm{P-X}]$$

with $k_a = k_d + k_d[\mathrm{P}\bullet]$
where k_a is the overall activation rate constant, viewed as a first-order reaction. Goto and Fukuda concluded that it may be more convenient to represent the above equation in the form [289]:

$$k_a = k_d + (k_{ex}/k_p)(R_p/[\mathrm{M}])$$

and show the general expression of the time-averaged k_a for a batch system:

$$k_a = k_d + (k_{ex}/k_pT)\ln([\mathrm{M}_0]/[\mathrm{M}])$$

Matyjaszewski et al. wrote the kinetic equation for atom transfer polymreization [290, 291]. It is based on the ATP reaction mechanism that was described above. By assuming fast initiations, insignificant termination reactions and steady concentrations of the propagating radicals, the following relationship was derived [290, 291]:

$$R_p = k_pk_{eq}[\mathrm{M}][\mathrm{RX}]_0\frac{[\mathrm{Mt}^{Z}\mathrm{L}_m]}{[\mathrm{XMt}^{z+1}\mathrm{L}_m]} = k_{app}[\mathrm{M}]$$

3.15 Thermodynamics of the Free-Radical Polymerization Reaction

3.15.1 Effects of Monomer Structure on the Thermodynamics of the Polymerization

There is a close relationship between monomer structure and changes in free energy, in enthalpy and in entropy. Thus, for instance, knowledge of changes in enthalpy will allow appropriate thermal control of the reaction and yield proper rate of propagation and molecular weight distribution. The quantities of ΔF, ΔH, and ΔS relate only to the rate of propagation because initiation and termination are single steps, while propagation consists of multiple steps.

Free radical polymerization is generally exothermic because it involves conversion of π bonds to σ bonds. Thus, the change in enthalpy ΔH is negative. Also, because there is a decrease in randomness in conversion of monomers to polymer, the change in entropy ΔS is also negative. The overall change in free energy of the free radical polymerization process is,

$$\Delta F = \Delta H - T\Delta S$$

The free energy is generally negative for the free-radical polymerization process. Variations in monomer structures have a significant effect on the values of ΔH for the following reasons. These are differences in resonance stabilizations due to differences in conjugation and hyperconjugation. Also, due to steric strains that arise from bond angle deformation and bond stretching, as well as variations in secondary bond forces, such as hydrogen bonding and dipole interactions.

3.15.2 Thermodynamics of the Constrains of the Free-Radical Polymerization Reaction

Free-radical polymerization reactions are equilibrium reactions. The equilibrium between the monomer and the growing polymer is subject to thermodynamic conditions. At equilibrium, therefore, the change in free energy is zero:

$$\Delta F = 0$$

The change in free energy for the reaction can, therefore, be written;

$$\Delta F = \Delta F^0 + RT\ \ln K = \Delta H^0 - T\Delta S^0 + RT\ \ln K = 0$$

In the above equation, ΔF^0, ΔH^0, and ΔS^0 represent statistical variations in the changes in free energy, enthalpy, and entropy, representing the transition that the monomer undergoes by being placed into the polymeric chain.

The equilibrium constant can then be written as:

$$K = [\mathrm{PM}^*_{\mathrm{n+1}}]/\{[\mathrm{PM}^*_{\mathrm{n}}][\mathrm{M}]\}$$

where, $\mathrm{PM}^*_{\mathrm{n+1}}$ and $\mathrm{PM}^*_{\mathrm{n}}$ are concentrations of species. Assuming that they are practically equal, one can write:

$$K = 1/\mathrm{M}$$

it would then mean that:

$$RT \ln \mathrm{M} = \Delta H^0 - T\Delta S^0$$

$$RT\ \ln \mathrm{M} = (\Delta \boldsymbol{H}^{\mathbf{0}}/T) - \Delta \boldsymbol{S}^{\mathbf{0}}$$

The ceiling temperature can then be written as

$$T_{\mathrm{c}} = \ \Delta H^0/\{\ \Delta S^0 + R \ln[\mathrm{M}]_{\mathrm{equ}}\}$$

3.16 Polymer Preparation Techniques

Four general techniques are used for preparation of polymers by free-radical mechanism: polymerization in ***bulk***, in ***solution***, in ***suspension*** and in ***emulsion***. The ***bulk*** or ***mass*** polymerization is probably the simplest of the four methods. Only the monomer and the initiator are present in the reaction mixture. It makes the reaction simple to carry out, though the exotherm of the reaction might be hard to control, particularly if it is done on a large scale. Also there is a chance that local hot spots might develop. Once bulk polymerization of vinyl monomers is initiated, there can be two types of results, depending upon the solubility of the polymer. If it is soluble in the monomer, the reaction may go to completions with the polymer remaining soluble throughout all stages of conversion. As the polymerization progresses, the viscosity of the reaction mixture increases markedly. The propagation proceeds in a medium of associated polymeric chains dissolved in or swollen by the monomer until all the monomer is consumed.

If the polymer is insoluble, it precipitates out without any noticeable increase in solution viscosity. Examples of this type of a reaction can be polymerizations of acrylonitrile or vinylidene chloride. The activation energy is still similar to most of the polymerizations of soluble polymers and the initial rates are proportional to the square root of initiator concentration. Also, the molecular weights of the polymerization products are inversely proportional to the polymerization temperatures and to initiator concentrations. Furthermore, the molecular weights of the resultant polymers far exceed the solubility limits of the polymers in the monomers. The limit of acrylonitrile solubility in the monomer is at a molecular weight of 10,000. Yet, polymers with molecular weights as high as 1,000,000 are obtained by this process. This means that the polymerizations must proceed in the precipitated polymer particles, swollen and surrounded by monomer molecules.

The kinetic picture of free-radical polymerization applies best to bulk polymerizations at low points of conversion. As the conversion progresses, however, the reaction becomes complicated by chain transferring to the polymer and by gel effect. The amount of chain transferring varies, of course, with the reactivity of the polymer radical.

Bulk polymerization is employed when some special properties are required, such as high molecular weight or maximum clarity, or convenience in handling. Industrially, bulk polymerization in special equipment can have economic advantages, as with bulk polymerization of styrene. This is discussed in Chap. 6.

Solution polymerization differs from bulk polymerization because a solvent is present in the reaction mixture. The monomer may be fully or only partially soluble in the solvent. This, the polymer may be (1) completely soluble in the solvent, (2) only partially soluble in the solvent, and (3) insoluble in the solvent.

When the monomer and the polymer are both soluble in the solvent, initiation and propagation occur in a homogeneous environment of the solvent. The rate of the polymerization is lower, however, than in bulk. In addition, the higher the dilution of the reactants the lower is the rate and the lower is the molecular weight of the product. This is due to chain transferring to the solvent. In addition, any solvent that can react to form telomers will also combine with the growing chains.

If the monomer is soluble in the solvent, but the polymer is only partially soluble or insoluble, the initiation still takes place in a homogeneous medium. As the chains grow, there is some increase in viscosity that is followed by precipitation. The polymer precipitates in a swollen state and remains swollen by the diffused and adsorbed monomer. Further propagation takes place in these swollen particles.

Because propagation continues in the precipitated swollen polymer, the precipitation does not exert a strong effect on the molecular weight of the product. This was demonstrated on polymerization of styrene in benzene (where the polymer is soluble) and in ethyl alcohol (where the polymer is insoluble). The average molecular weight obtained in benzene at 100°C was 53,000 while in ethyl alcohol at the same temperature it was 51,000 [280]. When the monomers are only partially soluble and the polymers are insoluble in the solvents the products might still be close in molecular weights to those obtained with soluble monomers and polymers. Polymerization of acrylonitrile in water can serve as an example. The monomer is only soluble to the extent of 5–7% and the polymer is effectively insoluble. When aqueous saturated solutions of acrylonitrile are polymerized with water-soluble initiators, the systems behave initially as typical solution polymerizations. The polymers, however, precipitate out rather quickly as they form. Yet, molecular weights over 50,000 are readily obtainable under these conditions.

There are different techniques for carrying out solution polymerization reactions. Some can be as simple as combining the monomer and the initiator in a solvent and then applying agitation, heat and an inert atmosphere [292]. Others may consist of feeding into a stirred and heated solvent the monomer or the initiator, or both continuously, or at given intervals. It can be done throughout the course of the reaction or through part of it [293]. Such a set up can be applied to laboratory preparations or to large-scale commercial preparations. It allows a somewhat better control of the exotherm during the reaction.

In both techniques the initiator concentration changes only a few percent during the early stages of the reaction, if the reaction temperature is not too high. The polymerization may, therefore, approach a steady state character during these early stages. After the initial stages, however, and at higher temperatures, the square root dependence of rates upon the initiator concentration no longer holds. This is a result of the initiator being depleted rapidly. The second technique, where the initiator, or the monomer and the initiator are added continuously was investigated at various temperatures and rates of addition [294–299]. If the initiator and monomer are replenished at such a rates that their ratios remains constant, steady state conditions might be extended beyond the early stages of the reactions. How long they can be maintained, however, is uncertain.

Suspension polymerization [298] can be considered as a form of mass polymerization. It is carried out in small droplets of liquid monomer dispersed in water or some other media and caused to polymerize to solid spherical particles. The process generally involves dispersing the monomer in a non solvent liquid into small droplets. The agitated stabilized medium usually consists of nonsolvent (often water) containing small amounts of some suspending or dispersing agent. The initiator is dissolved in the monomer if it is a liquid or it is included in the reaction medium, if the monomer is a gas.

To form a dispersion, the monomer must be quite insoluble in the suspension system. To decrease the solubility and to sometimes also increase the particle size of the resultant polymer bead, partially polymerized monomers or prepolymers may be used. Optimum results are obtained with initiators that are soluble in the monomer. Often, no differences in rates are observed between polymerization in bulk and suspension. Kinetic studies of styrene suspension polymerization have shown that all the reaction steps, initiation, propagation, and termination, occur inside the particles [299].

The main difficulty in suspension polymerization is in the forming and in the maintaining uniform suspensions. This is because the monomer droplets are slowly converted from thin immiscible liquids to sticky viscous materials that subsequently become rigid granules. The tendency is for the sticky particles to attach to each other and to form one big mass. The suspending agent's sole function is to prevent coalescing of the sticky particles. Such agents are used in small quantities (0.01–0.5% by weight of the monomer). There are many different suspending agents, both organic and inorganic. The organic ones include methylcellulose, ethyl cellulose, poly(acrylic acid), poly(methacrylic acid), salts of these acids, poly(vinyl alcohol), gelatins, starches, gums, alginates, and some proteins, such as casein or zein. Among the inorganic suspending agents can be listed talc, magnesium carbonate, calcium carbonate, calcium phosphate, titanium and aluminum oxides, silicates, clays, such as bentonite, and others. The diameter of the resultant beads varies from 0.1 to 5 mm and often depends upon the rate of agitation. It is usually inversely proportional to the particle size. Suspension polymerization is used in many commercial preparations of polymers.

Zhang, Fu, and Jiang, reported a study of factors influencing the size of polystyrene microspheres in dispersion polymerization [300]. The found that that the size of polystyrene microspheres decreased with an increasing amount of stabilizer and also increased with increasing the amount of monomer and initiator. The amount of stabilizer and monomer concentration were the major factors influencing the size distribution of polystyrene microspheres. The size of the microspheres decreased with an increase of the solvency of reaction media. The size distribution, however, hardly changed. The size of polystyrene microspheres increased with an increase in the reaction temperature. but the size distribution hardly changed.

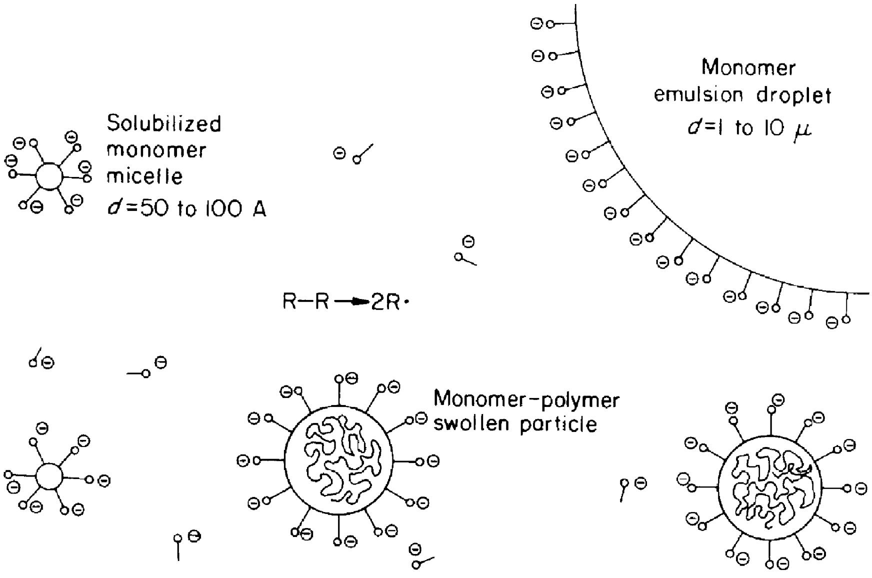


Fig. 3.3 Early stages of emulsion polymerization (from ref. [306])

Emulsion polymerization is used widely in commercial processes [300, 301]. The success of this technique is due in part to the fact that this method yields high-molecular-weight polymers. In addition, the polymerization rates are usually high. Water is the continuous phase and it allows efficient removal of the heat of polymerization. Also, the product from the reaction, the latex, is relatively low in viscosity, in spite of the high molecular weight of the polymer. A disadvantage of the process is that water-soluble emulsifiers are used. These are hard to remove completely from the polymers and may leave some degree of water sensitivity.

The reaction is commonly carried out in water containing the monomer, an emulsifier or a surface-active agent, and a water-soluble initiator. Initiation may be accomplished through thermal decomposition of the initiator or through a redox reaction. The polymer forms as a colloidal dispersion of fine particles and polymer recovery requires breaking up the emulsion.

The full mechanism of emulsion polymerization is still not completely worked out. It is still not clear why a simultaneous increase in the polymerization rate and in the molecular weight of the product is often observed. Also, in emulsion polymerization, at the outset of the reaction the monomer is in a form of finely dispersed droplets. These droplets are about 1 μ in diameter. Yet, during the process of a typical polymerization, they are converted into polymer particles that are submicroscopic, e.g., 1,000 Å in diameter.

At the start of the reaction the emulsifier exists simultaneously in three loci: (a) as a solute in water; (b) as micelles; (c) and as a stabilizing emulsifier at the interface between the monomer droplets and the water. The bulk of the emulsifier, however, is in the micelles. The monomer is also present in three loci: (a) in the monomer droplets that are emulsified and perhaps 1–10 μ in diameter; (b) it is solubilized in the micelles, perhaps 50–100 Å in diameter; (c) and it is present as individual molecules dissolved in the water. The bulk of the monomer is in the droplets. There are on the average 10^{18}/mL of monomer-swollen micelles in the reaction mixture at the outset of the reaction [302]. At the start of the reaction there are also on the average 10^{12}/mL monomer droplets that act as reservoirs. The monomer is supplied from the droplets to radical-containing micelles when the reaction progresses by a process of diffusion through the aqueous phase (Fig. 3.3).

The first hypothesis of the mechanism of emulsion polymerization was formulated by Harkins [305]. According to this hypothesis, the water-soluble initiator decomposes in the aqueous phase.

This results in formation of primary radicals. The primary radicals in turn react with the monomer molecules dissolved in the water (though their number may be quite small). Additional monomer molecules may add to the growing radicals in the water until the growing and propagating chains of free radicals acquire surface-active properties. At that stage, the growing radicals consist of inorganic and organic portions:

These growing radical-ions tend to diffuse into the monomer-water interfaces. The probability that the diffusion takes place into monomer-swollen micelles rather than into monomer droplets is backed by the considerations of the relative surface areas of the two. There are on the average 10^{18} micelles in each milliliter of water. These are approximately 75 Ā in diameter and each swollen micelle contains on the average 30 molecules of the monomer. At the same time, the diameters of the monomer droplets are approximately 1 μ. and it is estimated that there are only approximately 10^{12} such droplets per milliliter of water. Thus, the micelles offer 60 times more surfaces for penetration than do the droplets. The initiating radicals are almost always generated in the water phase. After formation in the water phase, a number of free radicals may be lost due to recombination. Termination is also possible after reaction of free radicals with some of the monomers dissolved in the water.

Several theories tried to explain the entry process. Thus, a "diffusion control" model [307, 308] supposes that diffusion of aqueous-phase radicals into the particle surface is the rate-controlling step for entry. Another theory suggests that displacement of surfactant from the particle surface is the rate-determining step [309]. A third one assumes that the entry can be thought of as a colloidal interaction between a latex particle and primary phase oligomeric aqueous-phase radical. These are the radicals formed through reactions of initiating radicals and monomer molecules dissolved in water [310]. The most accepted entry model appears to be the "control by aqueous-phase growth" model of Maxwells et al. [311]. This theory postulates that free radicals generated in the aqueous phase propagate until they reach a critical degree of polymerization (let us call it *z*), at which point they become surface-active and their only fate is irreversible entry into a latex particle; the rate of entry of *z-mers* into a particle is assumed to be so fast as not to be rate-determining. An efficiency of less than 100% arises if there is significant aqueous-phase termination of the propagating radicals.

The entry model of Maxwells et al. was derived from and/or supported by data on the influence of particle surface characteristics (charge, size) on the entry rate coefficient [312]. It was assumed that the aqueous radicals became surface active when the degree of polymerization reached 2–3. This was based on thermodynamic considerations of the entering species.

Further data on the Maxwell et al. entry model was obtained by Gilbert and coworkers [313] who studied the effects of initiator and particle surface charges. They obtained kinetic data for radical entry in the emulsion polymerization of styrene and concluded that their data further supports the Maxwell et al. entry model and refutes the alternative models mentioned above.

Once the radicals penetrate the micelles, polymerization continues by adding monomers that are inside. The equilibrium is disturbed and the propagation process proceeds at a high rate due to the concentration and crowding of the stabilized monomers. This rapidly transforms the monomer-swollen micelles into polymer particles. The changes result in disruptions of the micelles by growths from within. The amount of emulsifier present in such changing micelles is insufficient to stabilize the polymer particles. In trying to restore the equilibrium, some of the micelles, where there is no polymer growth, disintegrate and supply the growing polymer particles with emulsifier. In the process many micelles disappear per each polymer particle that forms. The final latex usually ends up containing about 10^{15} polymer particles per milliliter of water. By the time conversions reach 10–20% there are no more micelles present in the reaction mixtures. All the emulsifier is now adsorbed on the surface of the polymer particles. This means that no new polymer particles are formed. All further reactions are sustained by diffusion of monomer molecules from the monomer droplets into the growing polymer particles. The amount of monomer diffusing into the particles is always in excess of the amount that is consumed by the polymerization reaction due to osmotic forces [297].

This extra monomer supplied is sufficient for equilibrium swelling of the particles [298]. As a result, the rate of polymerization becomes zero order with respect to time.

When conversion reaches about 70%, all the remaining monomer is absorbed in the polymer particles and there are no more monomer droplets left. At this point the reaction rate becomes first order with respect to time.

The qualitative approach of Harkins was put on a quantitative basis by Smith and Ewart [314–316]. Because 10^{13} radicals are produced per second and can enter between 10^{14} and 10^{15} particles, Smith felt that a free radical can enter a particle once every 10–100 s. It can cause the polymerization to occur for 10–100 s before another free radical would enter and terminate chain growth [317]. A period of inactivity would follow that would last 10–100 s and then the process would repeat itself. Such a "stop and go" mechanism implies that a particle contains a free radical approximately half of the time. It can also be said that the average number of radicals per particle is 0.5. This is predicted on conditions that (a) the rate of chain transfer out of the particle is negligible and (b) the rate of termination is very rapid compared with the rate of radical entry into the particle.

The kinetic relationships derived by Smith and Ewart for the system are as follows:

$$\text{The rate of primary radical entering a particle} = r_{\mathrm{i}} = R_{\mathrm{i}}/N$$

$$\text{Rate of polymerization} = R_{\mathrm{P}} = k_{\mathrm{P}}[\mathrm{M}]N/2$$

$$\text{Average degree of polymerization} = \mathrm{DP} = Nk_{\mathrm{P}}[\mathrm{M}]/R_{\mathrm{i}}$$

where, k_{P} is the constant for propagation, [M] is the concentration of monomer, N is the number of particles containing n radicals (~0.5) and the expression for the number of particles formed:

$$N = K(\rho/\mu)^{0.4}(A_{\mathrm{S}}S)^{0.6}$$

where, μ is the volume increase of the particles, A_{S} is the area occupied by one emulsifier molecule. S is the amount of emulsifier present. K is a constant $= 0.37$ (based on the assumption that the micelles and polymer particles compete for free radicals in proportion to their respective total surface areas). K can also be equal to 0.53 (based on the assumption that the primary radicals enter only micelles, as long as there remain micelles in the reaction mixture). ρ is the rate of entry into the particles. The kinetic chain length can be written as:

$$\overline{\upsilon} = k_{\mathrm{p}}N_{\mathrm{p}}[\mathrm{M}]/2\mathrm{d}[\mathrm{RM}^{*}]/\mathrm{d}t$$

The Smith-Ewart mechanism does not take into account any polymerization in the aqueous phase. This may be true for monomers that are quite insoluble in water, such as styrene, but appears unlikely for more hydrophilic ones such as methyl methacrylate or vinyl acetate. In addition, it was calculated by Flory that there is insufficient time for a typical cation-radical (such as a sulfate ion radical) to add to a dissolved molecule of monomer such as styrene before it becomes captured by a micelle [317]. This was argued against, however, on the ground that Flory's calculations fail to consider the potential energy barrier at the micelle surfaces from the electrical double layer. This barrier would reduce the rate of diffusion of the radical-ions into the micelles [316].

Considerably different mechanisms were proposed by several groups [317, 318]. They are based on a concept that most polymerizations must take place at the surface of the particles or in their outer "shell" and not within the particles. It is claimed that the interiors of the particles are too viscous for free radicals to diffuse inside at a sufficiently fast rate. Two different mechanisms were proposed to explain why polymerization takes place preferentially in the shell layer. One of them suggests that the monomer is distributed nonuniformly in the polymer particles. The outer shell is rich in monomer molecules, while the inside is rich in polymer molecules [319]. The other explanation is that the radical ions that form from the water-soluble initiator are too hydrophilic to be able to penetrate the polymer particles [320].

Surfactant-free emulsion polymerization are carried out in the absence of a surfactant [321]. The technique requires the use of initiators that yields initiating species with surface-active properties and imparts them to the polymer particles. Examples of such initiators are persulfates. The lattices that form are stabilized by chemically bound sulfate groups that are derived from persulfate ions. Because the surface-active groups are chemically bound, the lattices are easier to purify and free the product from unreacted monomer and initiator. Generally, the particle number per milliliter from a surfactant-free emulsion polymerization is smaller than the particle number from typical emulsion polymerization.

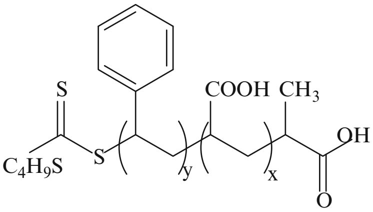
In an ***inverse emulsion polymerization*** an aqueous solution of a hydrophilic monomer is emulsified in an organic solvent and the polymerization is initiated with a solvent soluble initiator. This type of emulsion polymerizations is referred to as ***water in oil*** polymerization. Inverse emulsion polymerization is used in various commercial polymerizations and copolymerization of water-soluble monomers. Often nonionic emulsifiers are utilized. The product emulsions are often less stable than the oil in water emulsions.

A special approach to emulsion polymerization is called ***miniemulsion polymerization*** [322]. These reactions contain both micelles and monomer droplets, but the monomer droplets are smaller than in macrosystems. Usually, a water-soluble surfactant is used for emulsification. An example of such a surfactant can be sodium dodecyl sulfate. In addition, a highly water-insoluble costabilizer is added, such as hexadecanol. Thus, miniemulsions are dispersions of critically stabilized oil droplets with a size between 50 and 500 nm prepared by shearing a system containing oil, water, a surfactant and a hydrophobic material. Polymerizations in such miniemulsions, when carefully prepared, result in latex particles which have about the same size as the initial droplets. An appropriate formulation of a miniemulsion suppresses coalescence of droplets. The polymerization of miniemulsions extends the possibilities of the widely applied emulsion polymerization and provides advantages with respect to copolymerization reactions of monomers with different polarity, incorporation of hydrophobic materials or with respect to the stability of the formed latexes. Although labeled "emulsion," it appears that some may involve a combination of emulsion and suspension polymerizations. It was reported [323] that by using a difunctional alkoxyamine as an initiator for the homopolymerization of butyl acrylate in miniemulsion, to increase the achievable molar mass and to use the polymer as a difunctional macroinitiator for the synthesis of triblock copolymers in aqueous dispersed systems. Well-defined polymers with one alkoxyamine functionality at each end were obtained, providing that monomer conversion was kept below 70%. Beyond this conversion, extensive broadening of the molar mass distribution was evidenced, as the consequence of termination and transfer to polymer.

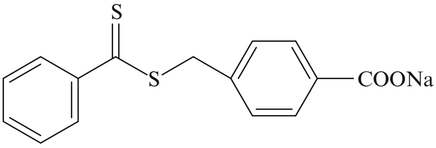
Tsavalas et al. [324] reported that a phenomenon seemingly unique to hybrid miniemulsion polymerization was observed by them, where monomer conversion would either plateau at a limiting value or quickly switch to a dramatically lesser rate. They attributed this phenomenon to a combination of three factors. The first one is the degree to which the monomer and resinous component are compatible. The second is the resultant particle morphology after approximately 80% monomer conversion, which roughly corresponds to the portion of reaction where this morphology is established. The third factor is the degree of interaction between the growing polymer and the resin (a grafting reaction). Of these three, the first two factors were found by them to be much more significant in contributing to the limiting conversion.

RAFT emulsion polymerization is a new development that has attracted considerable attention. It be carried out in a regular emulsion polymerization [325] and in a reverse emulsion polymerization [326].

Also, recently, several reports in the literature have described miniemulsion RAFT polymerizations. In some instances, use is made of water-soluble RAFT agents to control polymer molecular weight [327]. Also, Hawkett and coworkers reported using surface active RAFT agents to emulsify the dispersed phase, stabilize the particles and also control the molecular weight. This yielded polymer latexes that were free from surfactant and costablilizer [328]. One of these special RAFT agents was illustrated as follows:



The other two RAFT agents used by them had similar structures. A surface active iniferter was also reported by Choe and coworkers [330, 331]:



This RAFT agent allowed polymerization of methyl methacrylate initiated by ultraviolet light irradiation in the absence of added surfactant or initiator.

Rieger and coworkers [332] reported a surfactant free RAFT emulsion polymerization of butyl acrylate and styrene using poly(*N*,*N*-dimethylacrylamide) trithiocarbonate macromolecular transfer agent. They observed that the polymerizations were fast and controlled with molar masses that matched well the theoretical values and low polydispersity indexes. Monomer conversions close to 100% were reached and the polymerizations behaved as controlled systems, even at 40% solids contents. The products were poly(*N*,*N*-dimethyl acrylamide)-b-poly(*n*-butyl acrylate) and poly(*N*,*N*-dimethylacrylamide)-b-polystyrene amphiphilic diblock copolymers formed in situ.

Review Questions

Section 3.1

1. What are the three steps in free-radical polymerization? Illustrate each step in free-radical chain polymerization.
2. What is the rate-determining step in free-radical polymerization?
3. Write the kinetic expressions for initiation, propagation, termination, and transfer.
4. What is the steady state assumption? How is it expressed? Why is it necessary?
5. What is the expression for the rate of propagation? Rate of monomer disappearance? The average lifetime of a growing radical under steady state conditions?
6. Why is an initiator efficiency factor needed for the rate equation? What is a kinetic chain length?
7. In polymerization of styrene in benzene at 60°C using 0.1 mol benzoyl peroxide initiator and 1 mol of monomer, k_d is 1.38×10^{-5}, assume steady state and calculate the free-radical concentration during the reaction. If k_p is 176/mol what is the rate of propagation? What is the lifetime of a growing radical if k_t is 7.2×10^{-5}? What is the rate of propagation if the initiator efficiency is 72%?

Section 3.2

1. What sources of initiating free radicals do you know? Illustrate the decomposition reaction of α,α'-azobisisobutyronitrile. Illustrate how free radicals can recombine inside or outside the solvent cage and be lost to the initiation process.
2. Illustrate one or more inorganic and also one or more organic peroxides.
3. How does solvent "cage" affect the initiating free radicals? Explain and illustrate.
4. Explain homolytic and heterolytic cleavage of peroxides.
5. Explain and give chemical equations for *redox* initiations with Fe++, Co++, and Ce++++ ions in the reaction mixture.
6. How are peroxides such as benzoyl peroxide decomposed by aromatic tertiary amines. Show the two postulated mechanisms for the reaction of benzoyl peroxide with dimethyl aniline.

Section 3.3

1. Describe the reaction of the initiating free radical with the monomer. Show this reaction with equations, using a phenyl initiating radical and styrene monomer as an example.
2. Do the same as question 1, but with a redox mechanism, showing a sulfate ion-radical adding to vinyl acetate.

Section 3.4

1. Illustrate the transition state in the propagation reaction.
2. Explain the steric. polar and resonance effects in the propagation reaction.
3. Explain why there is a tendency for a *trans–trans* placement in the propagation reactions when carried out at low temperatures.
4. How does the reaction medium affect the propagation reaction?
5. What is ceiling temperature and what is the kinetic expression for this phenomenon?
6. Explain what is meant by autoacceleration and how does it manifest itself.
7. What is cyclopolymerization? Explain and give several examples.

Section 3.5

1. What are the three termination processes in free-radical polymerization?
2. What is meant by degenerative chain transferring? Illustrate back-biting. The telomerization reaction.
3. What is meant by chain transferring constants?
4. Write the equation for the degree of polymerization including all the chain transferring constants. In a benzoyl peroxide initiated polymerization of 2 moles of styrene in benzene at 85°C ($K_d = 8.94 \times 10^{-5}$ L/mol-s at 85°C). How much benzoyl peroxide will be required in the polymerization solution to attain an average molecular weight of 250,000? Assume that termination occurs only by recombination and no chain-transferring takes place.

5. In the above polymerization, the transferring constant to monomer, $C_M \times 10^{-4} = 3.74$, the transferring constant to solvent, $C_S = 5.6 \times 10^{-4}$ and transferring constant to the initiator, $C_I = 0.75$. Assuming that $f = 0.72$, and k_t is 7.2×10^{-5}, k_p is 176/mol, (k_d is shown above) calculate R_p and the average DP.

Section 3.6

1. Explain what is meant by reactivity ratios and how they are derived.
2. Write the copolymerization equation. In a copolymerization of 1 mol of styrene with 1 mol of butadiene, $r_1 = 0.78$ and $r_2 = 1.39$, what is the expected composition of the copolymer at the early stages of the polymerization?
3. How do substituents on the monomer molecules affect reactivity of the monomers toward attacking radicals?
4. Explain the *Q* and *e* scheme and write the Price–Alfrey equation.
5. How can r_1 and r_2 be derived from the *Q* and *e* values. Show the relationship.
6. From chemical structures alone predict the products from free-radical copolymerizations of pairs of (1) styrene and methyl methacrylate, (2) styrene and vinyl acetate, (3) methyl methacrylate and vinyl chloride. Consult Table 3.8 for reactivity ratios.

Section 3.7

1. How many reactivity ratios are there in a terpolymerization?
2. Write the equation for the terpolymerization reaction.

Section 3.8

1. What is allylic polymerization? If allyl alcohol does not polymerize to a high-molecular-weight polymer by free-radical polymerization, why does triallyl cyanurate form a high-molecular-weight network structure by the same mechanism?

Section 3.9

1. What is inhibition and retardation? Explain.
2. Give an example of a good inhibitor and a good retarder and show by chemical equations the reaction with free radicals.
3. Show the reaction of quinone with free radicals.
4. Write the equation that relates rate data to inhibited polymerizations.
5. Calculate R_p for the polymerization of 1 mol of styrene containing 0.01 mol of hydroquinone inhibitor. with $k_p = 176/\text{mol}$ and $k_t = 7.2 \times 10^{-5}$.

Section 3.10

1. What is thermal polymerization? Show by chemical equations the postulated mechanism of formation of initiating radicals in styrene thermal polymerization.

Section 3.11

1. Show the proposed charge-transfer mechanism for copolymerization of styrene with maleic anhydride and dioxene with maleic anhydride.
2. What determines the stability of charge-transfer complexes? Explain and give examples.

Section 3.12

1. How do some polar monomers complex with Lewis acids? How does that affect polymerization of these monomers? Copolymerization?

Section 3.13

1. How can canal complexes be used for steric control in free-radical polymerization? Give examples.

Section 3.14

1. How do controlled/"living" polymerizations differ from typical living polymerizations?
2. List the different types of controlled/"living" free-radical polymerizations that you can think of. What are the three classes of homogeneous controlled/"living" polymerizations as described by Matyjaszewski? Illustrate.
3. Describe cobalt mediated polymerizations. Illustrate.
4. Describe and illustrate atom transfer polymerizations controlled by copper/bipyridine complex and by carbon tetrachloride, dichloro(triphenyl-phosphine)-ruthenium(II), and methylaluminum bis(2,6-di-*tert*-butyl-phenoxide). Explain what (*ARGENT*)*ATRP* and (SET-*LRP*) mean. Illustrate the proposed Percec mechanism and the Matyjaszewski mechanisms.
5. Describe nitroxyl radical mediated polymerizations. Illustrate TEMPO controlled polymerization of styrene. What is meant by in situ NMP?
6. Explain and illustrate a reversible addition-fragmentation chain transfer polymerization (RAFT).
7. Write the Matyjaszewski proposed kinetic equation of ATP polymerization.

Section 3.15

1. What is meant by bulk or mass polymerization? Explain and discuss.
2. What are some of the techniques for carrying out solution polymerizations?
3. Give a qualitative picture of emulsion polymerization as described by Harkins.
4. How did Smith and Ewart put the Harkins picture of emulsion polymerization on a quantitative basis? What is the equation for the rate of emulsion polymerization?
5. Describe a surfactant-free emulsion polymerization, and inverse emulsion polymerization and a miniemulsion polymerization.

Section 3.16

1. Discuss the effect of monomer structure on the thermodynamics of the free-radical polymerization process.

Recommended Reading

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