# Chapter 7
# Radical Chain Polymerization

The polymerization of unsaturated monomers typically involves a chain reaction. In a chain polymerization, one act of initiation may lead to the polymerization of thousands of monomer molecules. Table 7.1 lists the characteristics of chain polymerization as compared with step polymerization. The chain polymerization starts with an active center responsible for the growth of the chain which is associated with a single polymer molecule through the addition of many monomer units. Thus polymeric molecules are formed from the beginning, and almost no intermediate species between monomer and high molecular weight polymer are found.

Chain polymerization is initiated by a reactive species $R^*$ produced from an *initiator I*:

$$I \rightarrow R^* \tag{7.1}$$

The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the $\pi$-bond to form a new radical, cation, or anion center. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center as the following:



$$\tag{7.2}$$
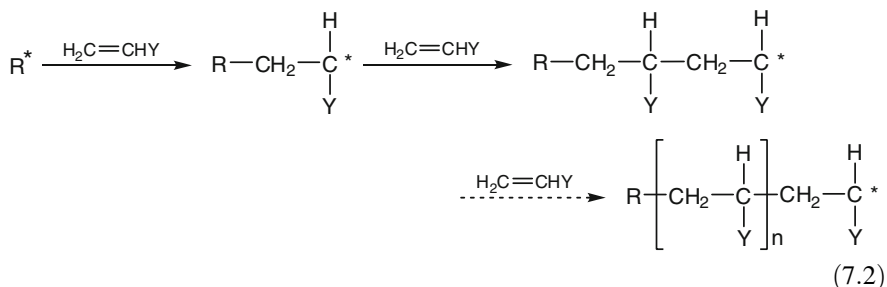
*R\**: Radical, cationic, anionic.

Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.
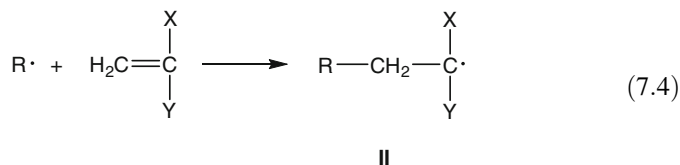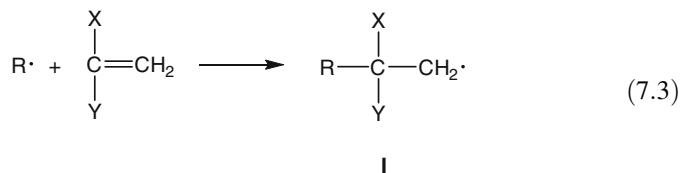
**Table 7.1** Comparison of chain polymerization and step polymerization

| Situation | Chain polymerization | Step polymerization |
|---|---|---|
| Molecular weight | High molecular weight formed immediately, doesn't change with time | High molecular weight molecule formed at the end of reaction, change with time |
| Monomer concentration | Change throughout the course of the reaction | Only available in the beginning of the reaction, then form dimer, trimer, etc |
| Any time of the reaction | Contain monomer, high polymer, and growing chain | Beginning—monomer Middle—growing chain End—high polymer |
| Polymerization step | Only monomer and propagation species can react | Any two molecules can react |
| Reaction time | Short | Long |
| Reaction temperature | Low | High |

In this chapter, we only discuss free radical chain polymerization. The ionic chain polymerization will be discussed in Chap. 8. Table 7.2 lists some common free radical chain-growth polymers and their uses. The chain-growth polymers count more than 80 % total usage of polymers in our daily life.

## 7.1 Effect of Chemical Structure of Monomer on the Structural Arrangement of Polymer

There are two possible points of attachment on monosubstituted ($X = H$) or 1,1-disubstituted monomers for a propagating radical, either on carbon 1 to form I or on carbon 2 to form II as the following:
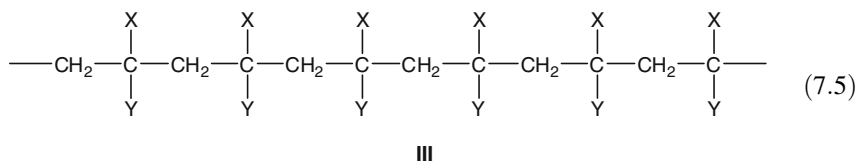
$$R\cdot \; + \; \underset{Y}{\overset{X}{C}}{=}CH_2 \; \longrightarrow \; R{-}\underset{Y}{\overset{X}{C}}{-}CH_2\cdot \qquad (7.3)$$

$$\mathbf{I}$$

$$R\cdot \; + \; H_2C{=}\underset{Y}{\overset{X}{C}} \; \longrightarrow \; R{-}CH_2{-}\underset{Y}{\overset{X}{C}}\cdot \qquad (7.4)$$

$$\mathbf{II}$$

If each successive addition of monomer molecules to the propagating radical occurs in the same manner as Eqs. 7.3 or 7.4, the final polymer product will have
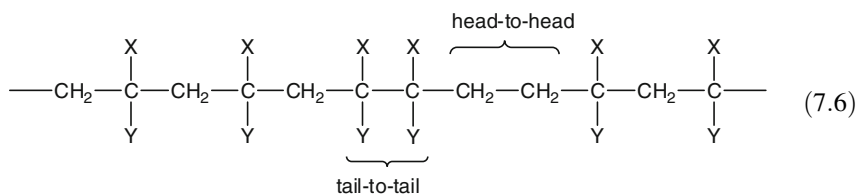
Table 7.2 Some commercial chain-growth (vinyl) polymers prepared by free radical polymerization [1, 2]

| Monomer name | Formula | Polymer | Uses |
|---|---|---|---|
| Ethylene (ethene) | $H_2C{=}CH_2$ | Polyethylene | Sheets, films, bottles, toys and house wares, wire and cable, coverings, shipping containers, insulation |
| Propylene (propene) | $H_2C{=}CHCH_3$ | Polpropylene | Carpeting, car and truck parts, packaging, toys, house wares, pipes, insulation |
| Styrene | $H_2C{=}CH-$ (phenyl) | Polystyrene | Packaging and containers (Styrofoam), toys, appliance parts, disposable food containers and utensils, insulation |
| Acrylonitrile (propenenitrile) | $H_2C{=}CHCN$ | Polyacrylonitrile (Orion, Acrilan) | Sweaters, clothing, fiber |
| Vinyl acetate (ethenyl ethanoate) | $H_2C{=}CH-O\overset{O}{\overset{\|}{C}}CH_3$ | Poly(vinyl acetate) | Adhesives, latex paints |
| Methyl methacrylate (methyl 2-methylpropenoate) | $H_2C{=}CCH_3-\overset{O}{\overset{\|}{C}}OCH_3$ | Poly(methyl methacrylate) (Plexiglas, Lucite) | Lens, windows, coatings |
| Vinyl chloride (chloroethene) | $H_2C{=}CHCl$ | Poly(vinyl chloride)(PVC) | Plastic pipe and pipe fittings, films and sheets, floor tile, records, coatings, building materials, insulation |
| Tetrafluoroethylene (tetrafluoroethene) | $F_2C{=}CF_2$ | Poly(tetrafluoro ethylene) (Teflon) | Coatings for utensils, electric insulators, battery, solar cell |

an arrangement of monomer units in which the substituents are on alternate carbon atoms as shown in Eq. 7.5:

$$\begin{array}{ccccccccccc}
& X & & X & & X & & X & & X & & X \\
& | & & | & & | & & | & & | & & | \\
-CH_2- & C & -CH_2- & C & -CH_2- & C & -CH_2- & C & -CH_2- & C & -CH_2- & C- \\
& | & & | & & | & & | & & | & & | \\
& Y & & Y & & Y & & Y & & Y & & Y \\
\end{array} \qquad (7.5)$$

**III**

This type of arrangement III is usually referred to as a *head-to-tail* (H–T) or 1,3-*placement* of monomer units. An inversion of this mode of addition, by the polymer chain propagating alternately via Eqs. 7.3 and 7.4, would lead to a polymer structure with a 1,2-placement of substituents at one or more places in the final polymer chain. The 1,2-placement is usually referred to as *head-to-head* (H–H) placement as shown in Eq. 7.6.

head-to-head

$$\begin{array}{ccccccccccc}
& X & & X & & X & X & & & X & & X \\
& | & & | & & | & | & & & | & & | \\
-CH_2- & C & -CH_2- & C & -CH_2- & C & C & -CH_2- & CH_2- & C & -CH_2- & C- \\
& | & & | & & | & | & & & | & & | \\
& Y & & Y & & Y & Y & & & Y & & Y \\
\end{array} \qquad (7.6)$$

tail-to-tail

The head-to-tail placement is predominant, since successive propagations by Eq. 7.4 are favored on both steric and resonance grounds. The propagating radical (radical II) formed by attachment of a radical at carbon 2 is the more stable one. The radical II can be stabilized by the resonance effects of the X and Y substituents. The substituents cannot stabilize radical I, since they are not attached to the carbon bearing the unpaired electron. Furthermore, the attachment of a propagating radical at the unsubstituted carbon 2 of a monomer molecule is much less sterically hindered compared with the attachment at the substituted carbon 1. A propagation proceeding with predominantly H–T placement is a *regioselective* process, that is, one orientation (H–T) is favored over another (H–H). The term *isoregic* has been used to indicate a polymer structure with exclusive head-to-tail placements. The terms *syndioregic* and *aregic* are used for polymer structures with alternating and random arrangements, respectively, of H–T and H–H placements.

These theoretical predictions have been experimentally verified for a number of polymers. The presence of no more than 1–2 % head-to-head placement in various polymers of vinyl esters such as poly (vinyl acetate) has been determined by hydrolysis of the polymer to poly(vinyl alcohol) and the periodate oxidation of the 1,2-glycol units (see Sect. 5.2.1). Other polymers with head-to-head arrangement have been determined by $^{19}F$, $^{13}C$, and $^{1}HNMR$ analysis.

The H–T propagation is indeed the predominant (>98–99 %) mode of propagation in chain polymerization. For instance, the synthesis of styrene, there is no

**Table 7.3** The extent of H–H replacement in fluoro polymers [3]

| Reaction | % Head–Head |
|---|---|
| C=CF → (–C–CF–)$_n$ | 10 |
| C=CF$_2$ → (–C–CF$_2$–)$_n$ | 5 |
| CF=CF$_2$ → (–CF–CF$_2$–)$_n$ | 12 |
| CFCl=CF$_2$ → (–CFCl–CF$_2$–)$_n$ | 2 |

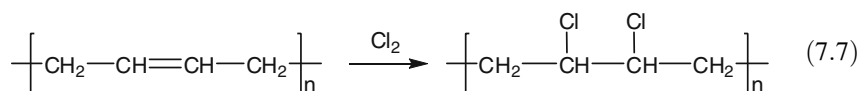**Table 7.4** Reaction temperature effect on the extent of H–H replacement of polymer [3]

| Polymer | Temperature (°C) | % Head–Head |
|---|---|---|
| Poly(vinyl acetate) | 40 | 1 |
| | 100 | 2 |
| Poly(trifluoro ethylene) | −80 | 10 |
| | 80 | 14 |

detectable H–H placement of polystyrene. The only exceptions occur when the substituents on the double bond are small (and do not offer appreciable steric hindrance to the approaching radical) and do not have a significant resonance stabilizing effect, specifically when fluorine is the substituent. Table 7.3 shows the extent of H–H placements of fluoro polymers.

By increasing the polymerization temperature, the extent of H–H placement is increased, but the effect is small. Table 7.4 shows the compositions of polymers with the effects from reaction temperature.

Some polymers consisting entirely of head-to-head (H–H) placements have been deliberately synthesized to determine if significant property differences exist compared to the head-to-tail polymers. The synthetic approach involves an appropriate choice of monomer for the particular H–H polymer. For example, H–H poly (vinyl chloride) was obtained by chlorination of 1,4-poly-1,3-butadiene (Eq. 7.7).

$$\left[CH_2-CH=CH-CH_2\right]_n \xrightarrow{Cl_2} \left[CH_2-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_2\right]_n \quad (7.7)$$

H–H polystyrene was obtained by hydrogenation of 1,4-poly-2,3-diphenylbutadiene (Eq. 7.8).

$$\left[CH_2-C=C-CH_2\right]_n \xrightarrow{H_2} \left[CH_2-CH-CH-CH_2\right]_n \quad (7.8)$$
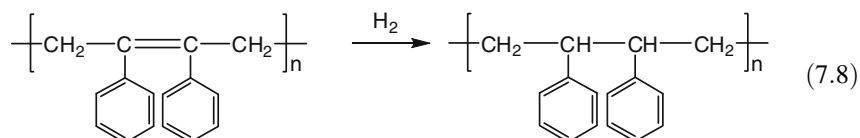
## 7.2  Initiators of Radical Chain Polymerization

Ideally, the initiators should be relatively stable at room temperature but should decompose rapidly enough at polymer processing condition to ensure a practical reaction rate. A large number of free radical initiators are available [2–4]; they may be classified into three major types: (1) *thermal initiators* including peroxides and azo compounds, (2) *redox initiators*, and (3) *photoinitiators*, certain compounds that form radicals under influence of light. Electrons can be used as initiating agent to generate radical ions for chain polymerization.

### *7.2.1  Thermal Initiators*

The most commonly used peroxide is benzoyl peroxide **1**, which undergoes thermal homolysis to form benzoyloxy radicals (Eq. 7.9). The benzoyloxy radicals may undergo a variety of reactions besides adding to monomer, including recombination (reverse of Eq. 7.9), decomposition to phenyl radicals and carbon dioxide (Eq. 7.10), and radical combination (Eqs. 7.11 and 7.12). These secondary reactions occur because of the confining effect of solvent molecules (cage effect), and as a result, the concentration of initiator radicals is depleted. Another "wastage" of initiator reaction is induced decomposition (Eq. 7.13).



$$(7.9)$$

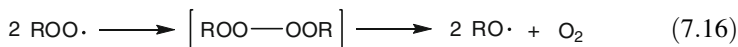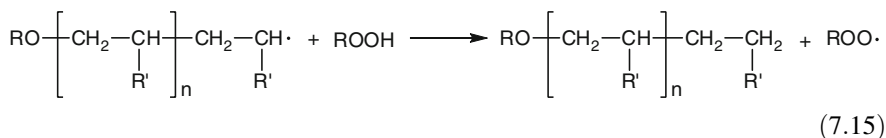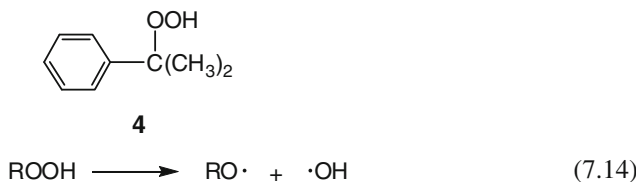**1**



$$(7.10)$$



$$(7.11)$$



$$(7.12)$$

$$(7.13)$$
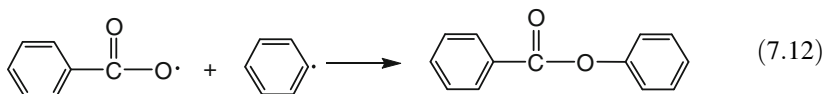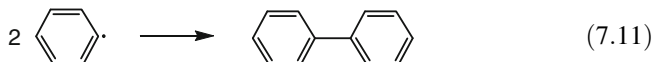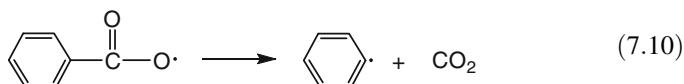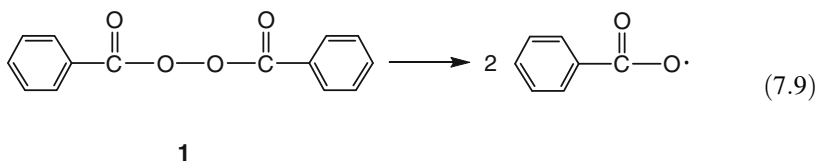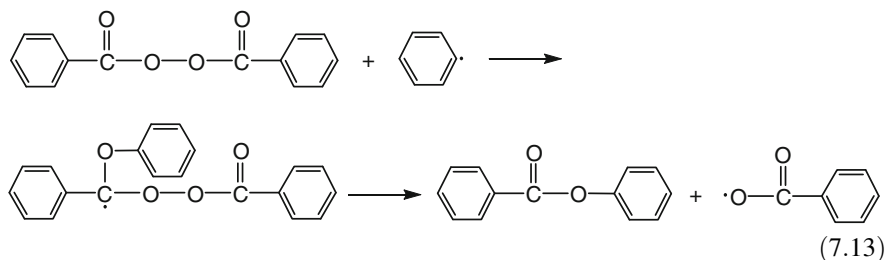
Two other common peroxide initiators are diacetyl peroxide **2** and di-t-butyl peroxide **3**.
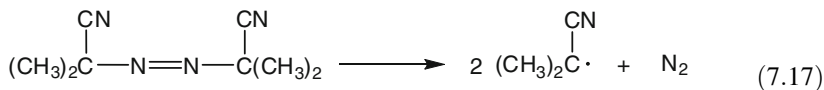


**2**        **3**
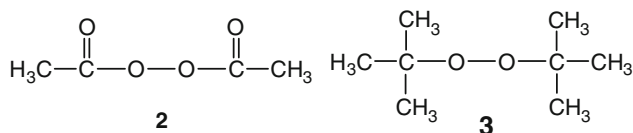
Hydroperoxides such as cumyl hydroperoxide **4** decompose to form alkoxy and hydroxyl radicals (Eq. 7.14). Because hydroperoxides contain an active hydrogen atom, induced decomposition occurs readily, for example, by a chain-end radical (Eq. 7.15). Peroxy radicals may also combine with subsequent formation of oxygen (Eq. 7.16).



**4**

$$ROOH \longrightarrow RO\cdot \ + \ \cdot OH \qquad\qquad (7.14)$$



$$(7.15)$$

$$2\ ROO\cdot \longrightarrow \left[ ROO\!-\!OOR \right] \longrightarrow 2\ RO\cdot \ + \ O_2 \qquad (7.16)$$

The extent of side reactions depends on the structure of peroxide, the stability of the initially formed radicals, and the reactivity of the monomers.

$\alpha, \alpha'$-Azobis(isobutyronitrile) **5**, is the most widely used azo compound which decomposes at relatively low temperatures. The driving force for decomposition is the formation of nitrogen and the resonance-stabilized cyanopropyl radical (Eq. 7.17). The initially formed radicals can also combine in the solvent cage to deplete initiator concentration as with the peroxide decomposition. The combination

of the radicals leads to both tetramethylsuccinonitrile **6** (Eq. 7.18) and the ketenimine **7** (Eq. 7.19).

$$
\underset{\textbf{5}}{(CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}\!-\!N\!=\!N\!-\!\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2} \quad\longrightarrow\quad 2\ (CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}\!\cdot \ +\ N_2 \tag{7.17}
$$

(7.18)

$$
2\ (CH_3)_2\overset{\overset{\displaystyle CN}{|}}{C}\!\cdot \quad
\begin{cases}
\nearrow & (H_3C)_2\overset{\overset{\displaystyle CN}{|}}{C}\!-\!\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2 \qquad \textbf{6} \\[2ex]
\searrow & (CH_3)_2C\!=\!C\!=\!N\!-\!\overset{\overset{\displaystyle CN}{|}}{C}(CH_3)_2 \qquad (7.19)
\end{cases}
$$

**7**
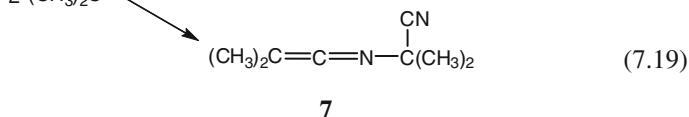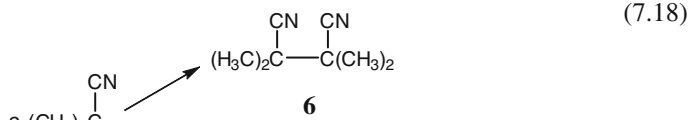
The stability of thermal initiator is expressed by their half-life at different temperature as discussed below.

## *7.2.2 Decomposition Temperature and Half-Life of Thermal Initiators*

The *thermal, homolytic dissociation* of initiators is the most widely used mode of generating radicals to initiate polymerization for both commercial polymerization and theoretical studies. Polymerizations initiated in this manner are often referred to as *thermal initiated* or *thermal catalyzed* polymerizations. Thermal initiators are usually having dissociation energies in the range 100–170 kJ mol$^{-1}$. Compounds with higher or lower dissociation energies will dissociate too slowly or too rapidly. Only a few classes of compounds—including those with O–O, S–S, or N=N bonds—possess the desired range of dissociation energies. The peroxides are most extensively used as radical sources. Several common peroxy compounds are tabulated in Table 7.5.

The differences in the decomposition rates of various initiators are conveniently expressed in terms of the *initiator half-life* ($t_{1/2}$) defined as the time for the concentration of *I* to decrease to one half its original value. The rate of initiator disappearance is

$$
\frac{-d[I]}{dt} = k_d[I] \tag{7.20}
$$

**Table 7.5** Peroxides and their decomposition temperature [3]

| Peroxide | Decomposition temperature (°C) |
|---|---|
|  Acyl peroxide | 70–90 |
|  Benzoyl peroxide | 80–95 |
|  Cumyl peroxide | 120–140 |
|  Di-t-butyl peroxide | 120–140 |

with integration yields

$$[I] = [I]_0 e^{-k_d t} \qquad (7.21a)$$

or

$$\ln \frac{[I]_0}{[I]} = k_d t \qquad (7.21b)$$

where $[I]_0$ is the initiator concentration at the start of polymerization. $t_{1/2}$ is obtained by setting $[I] = [I]_0/2$, then

$$t_{1/2} = \frac{0.693}{k_d} \qquad (7.22)$$

Table 7.6 lists the initiator half-life for several common initiators at various temperatures. The peroxides are rather unstable. They should store in the refrigerator to prolong their shelf life. Azobis (isobutyronitrile), benzoyl peroxide, and acetyl peroxide are decomposed at relatively low temperature, so they usually add into monomer right before the polymerization to avoid any premature decomposition and polymerization. *t*-Butyl peroxide and t-butyl hydroperoxide are

**Table 7.6** Half-life of initiators [3]

| Initiator | Half-Life at | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
|  | 50°C | 60°C | 70°C | 85°C | 100°C | 115°C | 130°C | 145°C | 155°C | 175°C |
| Azobis (isobutyronitrile) | 74 h | | 4.8 h | | 7.2 min | | | | | |
| Benzoyl peroxide | | | 7.3 h | 1.4 h | 19.8 min | | | | | |
| Acetyl peroxide | 158 h | | 8.1 h | 1.1 h | | | | | | |
| Lauryl peroxide | 47.7 h | 12.8 h | 3.5 h | 31 min | | | | | | |
| t-Butyl peracetate | | | | 88 h | 12.5 h | 1.9 h | 18 min | | | |
| Cumyl peroxide | | | | | | 13 h | 1.7 h | 16.8 min | | |
| t-Butyl peroxide | | | | | 218 h | 34 h | 6.4 h | 1.38 h | | |
| t-Butyl hydroperoxide | | | | | 338 h | | | | 44.9 h | 4.81 h |

decomposed at high temperature. They can be mixed with monomer and stored in room temperature without premature reaction for more than 3 months.

### 7.2.3  Initiation Promoters

Decomposition of peroxides can be induced at lower temperatures by the addition of *promoters*. For example, addition of *N, N*-dimethylaniline to benzoyl peroxide causes the latter to decompose rapidly at room temperature. Kinetics studies indicate that the decomposition involves formation of an unstable ionic intermediate (Eq. 7.23) that reacts further to give benzoyloxy radical and a radical cation (Eq. 7.24).



$$(7.23)$$



$$(7.24)$$
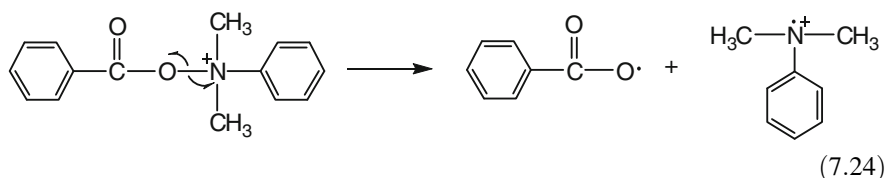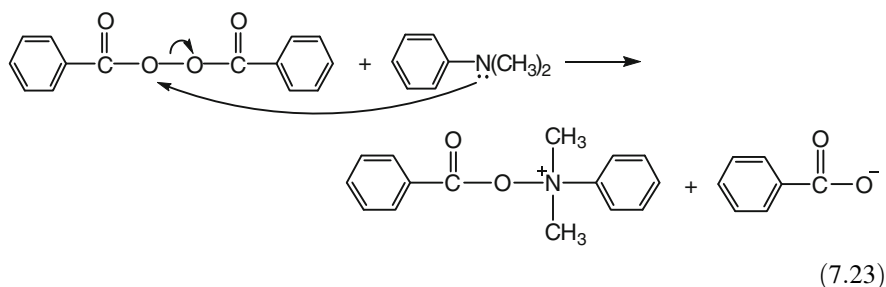
### 7.2.4  Redox Initiators

The redox initiators are useful in initiation of low temperature polymerization and emulsion polymerization. Reaction rates are easy to control by varying the concentration of metal ion or peroxide. For nonaqueous polymerization, metal ions: $Co^{2+}$, $Mn^{2+}$, $Cu^{2+}$, and $Fe^{2+}$ are generally introduced as the naphthenates shown in below. Cobalt naphthenate is commonly used as unsaturated polyester (Alkyd resin) drying agents for the autoxidative crosslinking of the double bond.
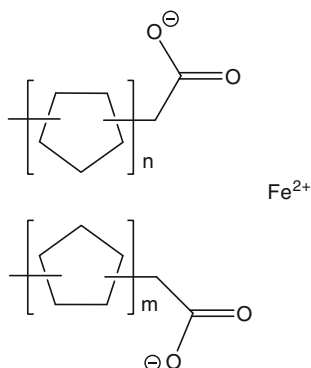
Iron Naphthenate

Some typical examples of redox initiators are given in Eqs. 7.25–7.27. They have been used in the emulsion copolymerization of styrene and butadiene to form styrene—butadiene rubber in low temperature. Hydrogen peroxide or persulfate systems, Eqs. 7.26 and 7.27, are used in the emulsion polymerization. They can produce radicals in an aqueous phase.



$$HOOH \ + \ Fe^{2+} \longrightarrow \ HO\cdot \ + \ OH^- \ + \ Fe^{3+} \qquad (7.26)$$

$$^-O_3SOOSO_3^- \ + \ S_2O_3^{2-} \longrightarrow \ SO_4^-\cdot \ + \ SO_4^{2-} \ + \ \cdot S_2O_3^- \qquad (7.27)$$
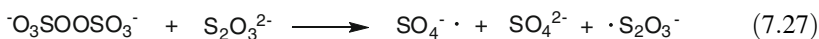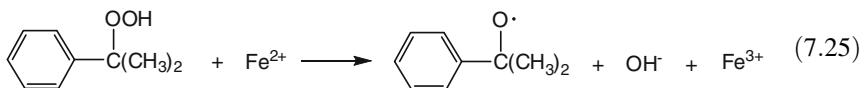
### 7.2.5 Photoinitiators

Peroxides and azo compounds dissociate photolytically as well as thermally. The major advantage of photoinitiation is that the reaction is essentially independent of temperature. Furthermore, better control of the polymerization reaction is generally possible because narrow wavelength bands may be used to initiate decomposition (less side reactions), and the reaction can be stopped simply by removing the light source. The reaction is fast (s vs. min) as compared to the thermal initiation. A wide variety of photolabile compounds are available, including disulfides (Eq. 7.28), benzoin **8** (Eq. 7.29), and benzyl **9** (Eq. 7.30). Table 7.7 lists some commercial available photoinitiators and their decomposition wavelength. It is interesting to note that most of the initiators contain benzoyl group which can form stable benzoyl radical through the resonance stabilization of phenyl ring.

**Table 7.7** Commercial photoinitiators and their initiated wavelength [5]

| Chemicals | $\lambda_{max}(nm)$ |
|---|---|
| 1-hydroxy-cyclohexyl-phenyl-ketone | 245 |
| 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone | 307 |
| 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone | 324 |

$$RSSR \xrightarrow{\;h\nu\;} 2\ RS\cdot \tag{7.28}$$



(7.29)



(7.30)
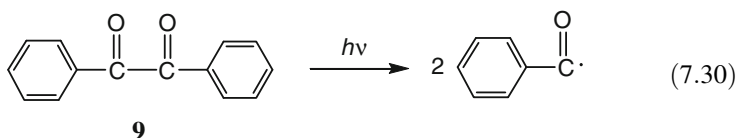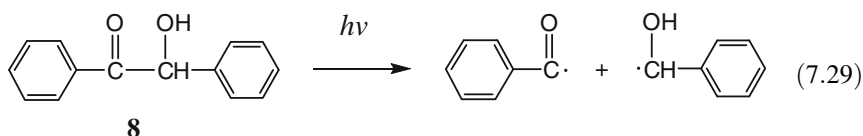
## 7.2.6 Electrochemical Initiation

Electrolysis of a solution containing both monomer and electrolyte can be used to initiate polymerization. At the cathode an electron may be transferred to a monomer molecule to form a radical anion (Eq. 7.31), and at the anode a monomer molecule may give up an electron to form a radical cation (Eq. 7.32). The radical ions in turn initiate free radical or ionic polymerization or both, depending on electrolysis conditions.

$$RHC{=}CH_2 + e^- \longrightarrow RH\ddot{\overset{..}{C}}{-}\dot{C}H_2 \tag{7.31}$$

$$RHC{=}CH_2 \longrightarrow RH\overset{+}{C}{-}\dot{C}H_2 + e^- \tag{7.32}$$
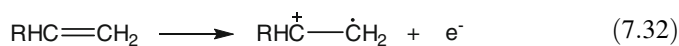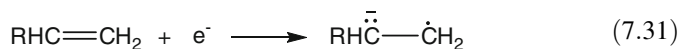
## 7.3  Techniques of Free Radical Chain Polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Ionic and other nonradical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as outlined in Table 7.8.

### 7.3.1  Bulk Polymerization

The bulk polymerization is the simplest polymerization reaction without contamination of solvent and other impurities or using especial equipment. However, it is usually difficult to control due to the exothermic polymerization reaction. When polymer is insoluble in monomer, polymer precipitates and the viscosity of the medium does not change appreciably. The polymer droplet may contain free radicals that can lead to *autoacceleration*—a rapid increase in the polymerization rate. The bulk polymerization is usually used in the casting large sheet of PMMA plastics or in the low molecular weight polymers synthesis for applications in adhesives, plasticizers, tackifiers, etc.

### 7.3.2  Suspension Polymerization

The suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water. Then, the resultant monomer droplets are polymerized by use of a monomer soluble initiator. Monomer is kept in suspension

**Table 7.8**  Free radical polymerization techniques

| Method | Advantages | Disadvantages |
|---|---|---|
| Bulk | Simple; no contaminants added | Reaction exotherm difficult to control; high viscosity |
| Suspension | Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly | Washing and/or drying required; agglomeration may occur; contamination by stabilizer |
| Solution | Heat readily dispersed; low viscosity; may be used directly as solution | Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution |
| Emulsion | Heat readily dispersed; low viscosity; high molecular weight obtainable; may be used directly as emulsion; works on tacky polymers | Contamination by emulsifier and other ingredients; chain transfer agents often needed to control degree of polymerization; washing and drying necessary for bulk polymer |

by continuous agitation and the use of *stabilizers* such as polyvinyl alcohol or methyl cellulose (ether). Granular beads are obtained which are easy to handle and can be isolated by filtration, etc. Polystyrene, poly(vinyl chloride), and poly(methyl methacrylate) have been prepared by this method.

### 7.3.3  Solution Polymerization

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully to avoid chain transfer reactions that may limit the growth of molecular weight of polymer. Apart from the environmental concerns associated with organic solvents, a major problem in solution polymerization is that it is often difficult to remove solvent. As a result, supercritical carbon dioxide has been used to do the polymerization as a solvent. However, it is only suitable for polar monomers such as acrylates; there is need for more development work for other monomers.

### 7.3.4  Emulsion Polymerization

Emulsion polymerization and suspension polymerization are two water-based heterogeneous polymerizations that are used extensively to control the thermal, viscosity, and environmental problems of polymer industry. However, they are quite different in the components and behaviors in the polymerization. The comparison between the two polymerization processes is summarized in Table 7.9. The major difference between the two polymerizations is the reaction site, micelle for emulsion polymerization, and monomer for suspension polymerization.

When the concentration of a surfactant exceeds its *critical micelle concentration* (CMC), the excess surfactant molecules aggregate together to form small colloidal

Table 7.9   Comparison between suspension polymerization and emulsion polymerization [3]

| Component/Characteristic | Emulsion | Suspension |
|---|---|---|
| Particle size | 1–10 μm monomer 2–10 nm micelle | 5–500 μm monomer droplets |
| Monomer/water ratio | 30/70 to 60/40 | 25/75 to 50/50 |
| Surfactant | 0.2–3 % in micelle form | 0.1 % |
| Initiator | Water soluble | Oil soluble |
| Water-soluble stabilizer | None | >1 % |
| Product particle size | 0.05–0.2 μm | 0.5–10 μm |
| Phase | One | Two |
| Polymerization site | Micelle | Monomer |

clusters called *micelles*. Typical micelles have dimensions of 2–10 nm, with each micelle containing 50–150 surfactant molecules. The largest portion of the monomer (>95 %) is dispersed as *monomer droplets* whose size depends on the stirring rate. Monomer droplets have diameters in the range 1–100 μm. Thus, in a typical emulsion polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is $10^{19}$–$10^{21}$ L$^{-1}$, the concentration of monomer droplets is at most $10^{12}$–$10^{14}$ L$^{-1}$. A further difference between micelles and monomer droplets is that the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude.

Polymerization takes place exclusively in micelle. Monomer droplets do not compete effectively with micelles in capturing radicals produced in solution because of the much smaller total surface area of the droplets. The micelles act as a meeting place for the organic (oil soluble) monomer and the water-soluble initiator. The micelles are favored as the reaction site because of their high monomer concentration compared to the monomer in solution. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by dissolution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 7.1. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization are occurring. The latter are no longer considered as micelles but are referred to as *polymer particles*. An emulsifier molecule is shown as ○— to indicate one end (○) is polar or ionic and the other end (—) is nonpolar.



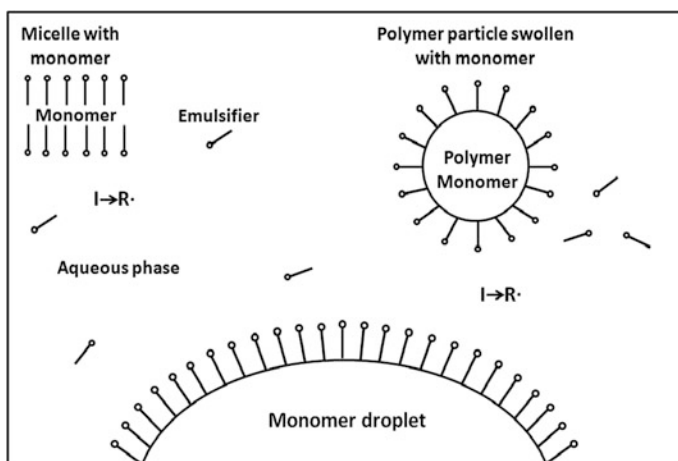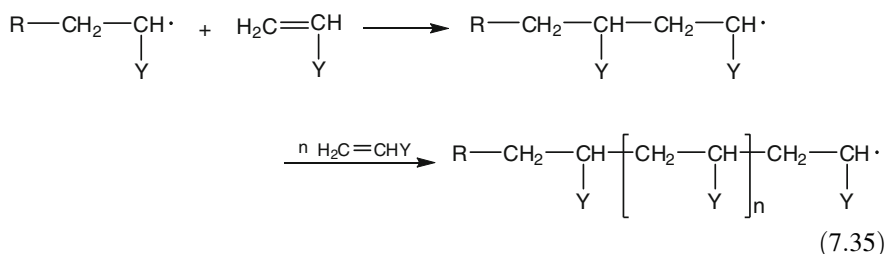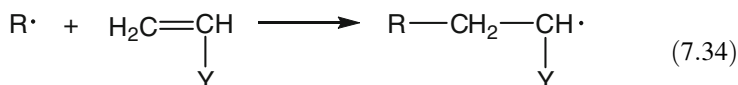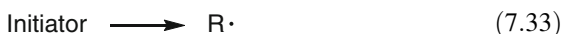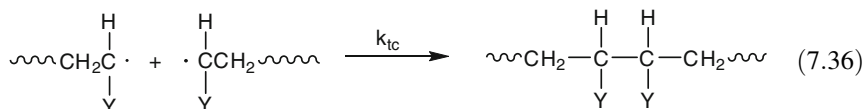**Fig. 7.1** Simplified representation of an emulsion polymerization system [3]

## 7.4  Reaction Mechanism of Free Radical Chain Polymerization

Two reactions are involved in the initiation of free radical chain polymerization: formation of the initiator radical (Eq. 7.33), and addition of the initiator radical to monomer (Eq. 7.34). The end group analysis of propagating chain shows the initiator radicals are incorporated into the polymer. The propagation reactions comprise addition of monomer radical to another monomer molecule, followed by successive additions of oligomer and polymer radicals to available monomer (Eq. 7.35).

$$\text{Initiator} \longrightarrow R\cdot \tag{7.33}$$

$$R\cdot \ + \ H_2C{=}CH\ \big|\ Y \longrightarrow R{-}CH_2{-}CH\cdot\ \big|\ Y \tag{7.34}$$

$$R{-}CH_2{-}CH\cdot\ \big|\ Y \ + \ H_2C{=}CH\ \big|\ Y \longrightarrow R{-}CH_2{-}CH{-}CH_2{-}CH\cdot\ \big|\ Y \quad \big|\ Y$$

$$\xrightarrow{n\ H_2C=CHY} R{-}CH_2{-}CH{-}\!\!\left[CH_2{-}CH\right]_n\!\!{-}CH_2{-}CH\cdot \tag{7.35}$$

Propagation continues until some reaction occurs to terminate it. Two radicals are easily be terminated by a *combination (coupling)* reaction as shown in Eq. 7.36.

$$\text{∿}CH_2\overset{H}{\underset{Y}{C}}\cdot \ + \ \cdot\overset{H}{\underset{Y}{C}}CH_2\text{∿} \xrightarrow{k_{tc}} \text{∿}CH_2{-}\overset{H}{\underset{Y}{C}}{-}\overset{H}{\underset{Y}{C}}{-}CH_2\text{∿} \tag{7.36}$$

On the other hand, more rarely, they can be terminated by a *disproportionation* reaction, in which a hydrogen radical that is *beta* to one radical center is transferred to another radical center. This results in the formation of two polymer molecules—one saturated and one unsaturated as shown in Eq. 7.37:

$$\text{∿}CH_2\overset{H}{\underset{Y}{C}}\cdot \ + \ \cdot\overset{H}{\underset{Y}{C}}CH_2\text{∿} \xrightarrow{k_{td}} \text{∿}CH{=}\underset{Y}{CH} \ + \ \underset{Y}{CH_2}CH_2\text{∿} \tag{7.37}$$
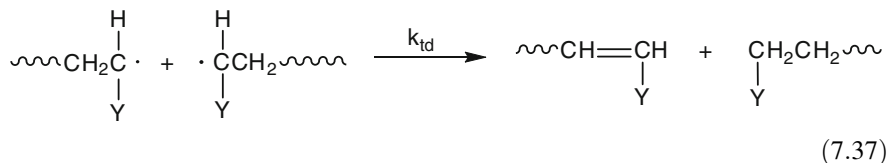
The two different modes of termination can be represented in general term by

$$M_n \cdot + M_m \cdot \xrightarrow{k_{tc}} M_{n+m} \tag{7.38}$$

$$M_n \cdot + M_m \cdot \xrightarrow{k_{td}} M_n + M_m \tag{7.39}$$
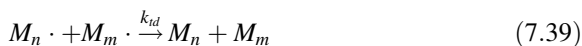
where $k_{tc}$ and $k_{td}$ are the rate constants for termination by coupling and dispro-portionation, respectively. One can also express the termination step by

$$M_n \cdot + M_m \cdot \rightarrow \text{dead polymer} \tag{7.40}$$

where the particular mode of termination is not specified and

$$k_t = \alpha k_{tc} + (1 - \alpha)k_{td} \tag{7.41}$$

where $\alpha$ and $(1 - \alpha)$ are the fractions of termination by coupling and dispropor-tionation, respectively.

Typical termination rate constants are in the range of $10^6$–$10^8$ dL mol$^{-1}$ s$^{-1}$ or orders of magnitude greater than the propagation rate constants. The much greater value of $k_t$ (whether $k_{tc}$ or $k_{td}$) compared to $k_p$ does not prevent propagation because the radical species are present in very low concentrations and the poly-merization rate is only dependent on the one half power of $k_t$. Thus, whether termination occurs by coupling or by disproportionation depends on monomer structure or, more exactly, on the structure of the chain-end radical, e.g., steric repulsion, electrostatic repulsion (raise the activation energy for coupling), and availability of alpha hydrogen. Polystyryl radicals undergo coupling (Eq. 7.42) almost exclusively at low temperatures, whereas poly(methyl methacrylate) radi-cals undergo mainly disproportionation (Eq. 7.43). The polystyryl radical is more reactive than methacrylate radical due to the resonance stabilization, so it will undergo coupling instead of disproportionation.



$$\tag{7.42}$$

$$(7.43)$$
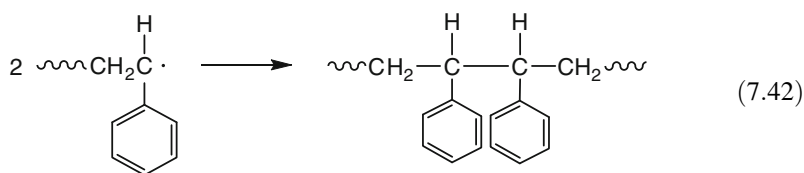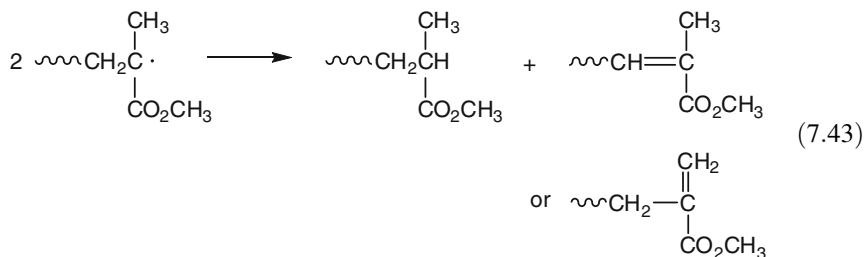
Another possible termination reaction involves combination of initiator radicals with chain end radicals (Eq. 7.44) called *primary radical termination.* This process occurs at high initiator concentration or high viscosity that limits the diffusion of polymer radicals.



$$(7.44)$$
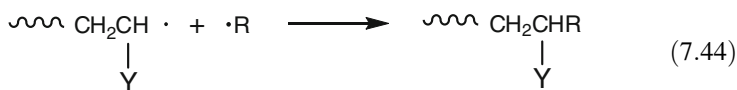
## 7.5 Kinetics of Free Radical Chain Polymerization

Radical chain polymerization is a chain reaction consisting of a sequence of three steps—*initiation*, *propagation*, and, *termination*. The initiation step involves two reactions (Eqs. 7.45 and 7.46). The first is the production of free radicals by homolytic dissociation of an initiator species I to yield a pair of radicals $R\cdot$

$$I \xrightarrow{k_d} 2R\cdot \tag{7.45}$$

where $k_d$ is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce radical $M_1\cdot$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \tag{7.46}$$

Propagation consists of the growth of $M_n\cdot$ by the successive additions of large numbers (hundreds and perhaps thousands) of monomer molecules. Each addition creates a new radical that has the same identity as the one previously, except that it is larger by one monomer unit. The successive additions may be represented by

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \tag{7.47}$$

Monomer disappears by the initiation reaction (Eq. 7.45) as well as by the propagation (Eq. 7.46). The *rate of monomer disappearance*, also called the *rate of polymerization*, is given by

$$-\frac{d[M]}{dt} = R_i + R_p \tag{7.48}$$

where $R_i$ and $R_p$ are the rates of initiation and propagation, respectively. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. Thus, the rate of initiation can be neglected and the polymerization rate is given simply by the rate of propagation. The rate of propagation, and therefore the rate of polymerization, is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate by

$$-\frac{d[M]}{dt} = R_p = k_p[M\cdot][M] \tag{7.49}$$

where $[M]$ is the monomer concentration and $[M\cdot]$ is the total concentration of all chain radicals, that is, all radicals of size $M_1\cdot$ and larger.

   The polymerization rate (Eq. 7.49) is not directly usable because it contains a term of radical concentration. Radical concentrations are difficult to measure quantitatively, since they are very low ($\sim 10^{-8}M$), and it is therefore desirable to eliminate $[M\cdot]$ from Eq. 7.49. In order to do this, one can use *steady-state* assumption: the concentration of radicals increases initially, but almost instantaneously reaches a constant, steady-state value. That means the rate of change of the concentration of radicals is zero during the course of the polymerization. Therefore, the rates of initiation $R_i$ and termination $R_t$ of radicals are equal

$$R_t = R_i = 2k_t[M\cdot]^2 \tag{7.50}$$

Rearrange Eq. 7.50 to obtain

$$[M\cdot] = \left(\frac{R_i}{2k_t}\right)^{1/2} \tag{7.51}$$

and substitute Eq. 7.51 into Eq. 7.49 that yields the rate of polymerization equation.

$$R_p = k_p[M](R_i/2k_t)^{1/2} \tag{7.52}$$

### 7.5.1  Rate of Polymerization

The rate of polymerization equation can be modified to include the initiator efficiency (*f*) as shown in Eq. 7.53. The equation indicates the polymerization rate is proportional to the square root of initiator concentration and to the first power of monomer concentration. Thus, doubling the initiator concentration causes the rate

**Table 7.10**  Representative propagation and termination rate constants, $k_p$ and $k_t$ [2]

| Monomer | Temperature (°C) | $k_p$ (L/mol-s) | $k_t \times 10^{-6}$ (L/mol-s) |
|---|---|---|---|
| Acrylonitrile | 60 | 1,960 | 782 |
| Ethylene | 83 | 240 | 540 |
| Methyl acrylate | 60 | 2,090 | 9.5 |
| Methyl methacrylate | 60 | 515 | 25.5 |
| Styrene | 60 | 176 | 72 |
| Vinyl acetate | 50 | 2,640 | 116.8 |
| Vinyl chloride | 50 | 11,000 | 2,100 |
| Tetrafluoroethylene | 40 | 7,400 | $7.4 \times 10^{-5}$ |

to increase by a factor of about 1.4. This relationship has been confirmed experimentally for a variety of free radical polymerizations. Propagation and termination rate constants, for several commercially important monomers are given in Table 7.10. The tetrafluoroethylene has an extremely low $k_t$ which results in higher molecular weight polymer as compared with the polymerization of ethylene.

$$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}} \qquad (7.53)$$

### 7.5.2 Average Kinetic Chain Length $\bar{v}$

Another important parameter related to polymerization rate is the *average kinetic chain length*, $\bar{v}$, which is defined as the average number of monomer units polymerized per chain initiated, which is equal to the rate of polymerization per rate of initiation. Since $R_i = R_t$ under steady-state conditions,

$$\bar{v} = \frac{R_p}{R_i} = \frac{R_p}{R_t} \qquad (7.54)$$

Substituting for $R_p$ and $R_t$ into Eq. 7.54:

$$\bar{v} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]} \qquad (7.55)$$

Substituting the expression for $[M\cdot]$ from Eq. 7.51,

$$\bar{v} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}} \qquad (7.56)$$

Kinetic chain length is related to a variety of rate and concentration parameters. It will decrease as both of initiator concentration and initiator efficiency increase.

This is reasonable because increasing the number of growing chains increases the probability of termination. Thus, varying initiator concentration can control molecular weight. In the absence of any side reactions, kinetic chain length is related directly to degree of polymerization depending on the mode of termination. If termination occurs exclusively by disproportionation, $\overline{DP} = \overline{v}$; if it occurs by coupling, $\overline{DP} = 2\overline{v}$.

Autoacceleration, a marked increase in polymerization rate, can occur at very viscous medium even though the chain mobility is reduced and the termination is reduced. The small monomer molecules can still diffuse to the active chain ends to be polymerized. Autoacceleration may cause processing difficulties, particularly in bulk polymerizations, because the increase in rate is usually accompanied by an increase in reaction exotherm and gelation of polymer.

## 7.5.3 Chain Transfer Reactions

Chain transfer reactions are the process transferring the growing polymer chain to another species which terminates the chain, but at the same time generates a new radical. The chain transfer reactions result in low molecular weight polymer and broad molecular weight distributions. Chain transfer can occur among polymer, monomer, initiator, solvent in the reaction mixture. Equations 7.57 and 7.58 show the polymer inter- and intrachain transfer reactions, respectively. A chain-end radical may abstract a hydrogen atom from a chain, leading to a reactive site for chain branching (Eq. 7.57).



$$(7.57)$$
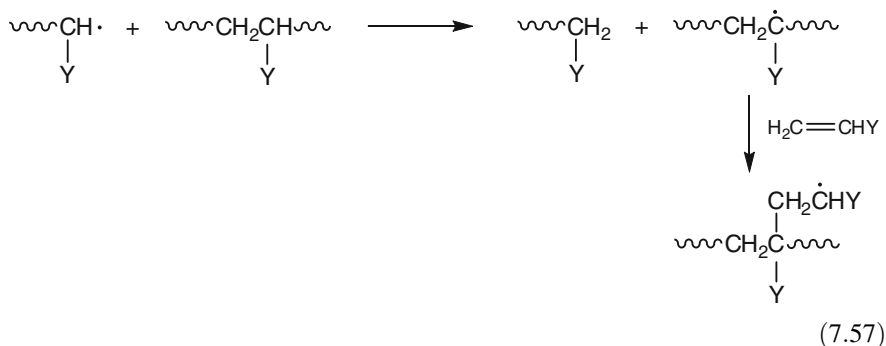
Hydrogen abstraction may also occur intramolecularly, a process referred to as *backbiting*. Polyethylene, produced by high-pressure free radical polymerization of ethylene, is highly branched through backbiting involving five- or six-membered cyclic transition states (Eq. 7.58). The properties of branched polymers are expected to differ remarkably from those of the corresponding linear polymers as we discussed in Chaps. 3 and 4.

$$\text{(7.58)}$$
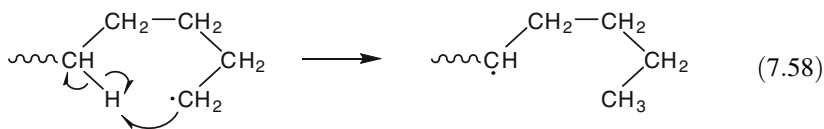
Chain transfer may also occur with initiator (Eq. 7.59) or monomer (Eq. 7.60), or it may take place with solvent. Polystyrene prepared in carbon tetrachloride, for example, contains chlorine at the chain end of polymer due to chlorine transfer (Eq. 7.61) and initiation by the resultant $\cdot CCl_3$ radicals (Eq. 7.62). Transfer to monomer is particularly important with monomers containing allylic hydrogen, such as propylene, because the formation of resonance-stabilized allylic radicals (Eq. 7.63) is highly favorable. Thus, high-molecular-weight polypropylene cannot be prepared using conventional free radical polymerization described here. The coordination polymerization is used to obtain high molecular weight polypropylene (detailed in Chap. 9).

$$\text{(7.59)}$$

$$\text{(7.60)}$$

$$\text{(7.61)}$$

$$\text{(7.62)}$$

$$\text{(7.63)}$$
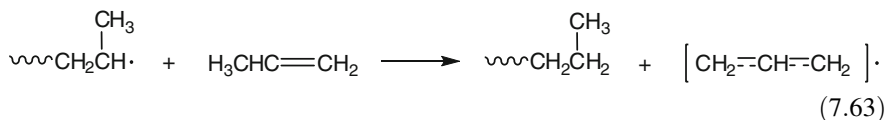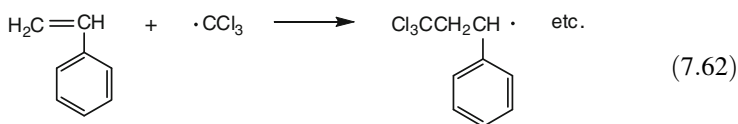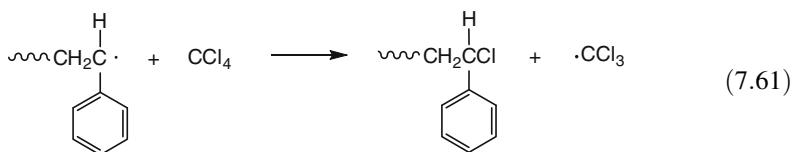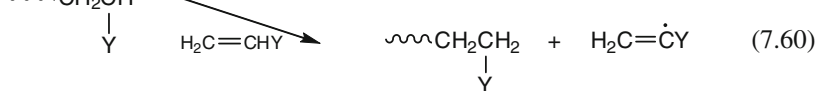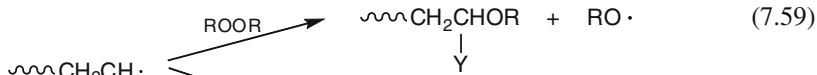
From the molecular weight control point of view, the chain transfer agent plays the most effective way. For instance, a thiol compound has been used widely as chain transfer agent due to its high affinity for hydrogen transfer as

$$\text{\wwn CH}_2\text{CH} \cdot \ + \ \text{RSH} \ \longrightarrow \ \text{\wwn CH}_2\text{CH}_2 \ + \ \text{RS} \cdot \qquad\qquad (7.64)$$
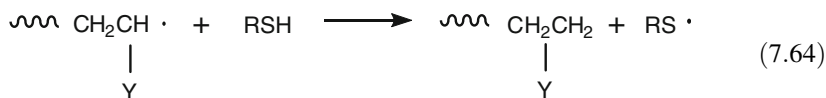
When a chain transfer agent is used in polymerization, it is necessary to redefine the kinetic chain length as being the ratio of propagation rate to the combined rates of termination and transfer, as

$$\bar{v}_{tr} = \frac{R_p}{R_i + R_{tr}} \qquad\qquad (7.65)$$

Since transfer reactions are second order, with

$$R_{tr} = k_{tr}[M\cdot][T] \qquad\qquad (7.66)$$

where $T$ is the transfer agent, one can rewrite the expression for $\bar{v}_{tr}$, taking into account all possible transfer reactions, as

$$\bar{v}_{tr} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2 + \sum k_{tr}[M\cdot][T]} = \frac{k_p[M]}{2k_t[M\cdot] + \sum k_{tr}[T]} \qquad\qquad (7.67)$$

It is known that

$$\bar{v} = \frac{k_p[M]}{2k_t[M\cdot]}$$

One can write the reciprocal of Eq. 7.67 for $\bar{v}_{tr}$ as

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + \frac{\sum k_{tr}[T]}{k_p[M]} \qquad\qquad (7.68)$$

The ratio of the transfer rate constant to that of propagation is commonly defined as the chain transfer constant, $C_T$, for a particular monomer:

$$\frac{k_{tr}}{k_p} = C_T \qquad\qquad (7.69)$$

Substituting Eq. 7.69 into Eq. 7.68, one obtains

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + \frac{\sum C_T[T]}{[M]} \qquad\qquad (7.70)$$

As the rate of transfer and concentration of the transfer agent increase, the kinetic chain length becomes progressively smaller. Chain transfer constants for a number of compounds and monomers are available in the polymer literature, several of which are given in Table 7.11.

**Table 7.11** Representative chain transfer constants $C_T$, propagation rate constants $k_p$, and termination rate constants $k_t$, for styrene and methyl methacrylate (reaction temperature 60°C) [3]

| Transfer Agent | $C_T \times 10^4$ | |
|---|---|---|
| | Styrene | Methyl Methacrylate |
| Benzene | 0.023 | 0.04 |
| Toluene | 0.125 | 0.20 |
| Chloroform | 0.5 | 1.77 |
| Carbon tetrachloride | 90 | 2.40 |
| Carbon tetrabromide | 22,000 | 2,700 |
| 1-Butanethiol | 210,000 | 6,600 |
| $k_p$ (L/mol-s) | 176 | 515 |
| $k_t \times 10^{-6}$ (L/mol-s) | 73 | 25.5 |

When the concentration of transfer agent is high and $k_{tr}$ is much greater than $k_p$, very low molecular weight polymers called telomers are obtained. The process is called *telomerization*. Chain transfer reactions can also be used to prevent free radical polymerizations. One type of compound, added as a stabilizer to vinyl monomers, is an alkylated phenol **10**, which can transfer its phenolic hydrogen to form a new radical (Eq. 7.71) that undergoes coupling reaction (Eq. 7.72) rather than initiating polymerization. Such compounds, called *inhibitors*, are commonly added to monomers to prevent premature polymerization during shipment or storage.



$$(7.71)$$



$$(7.72)$$
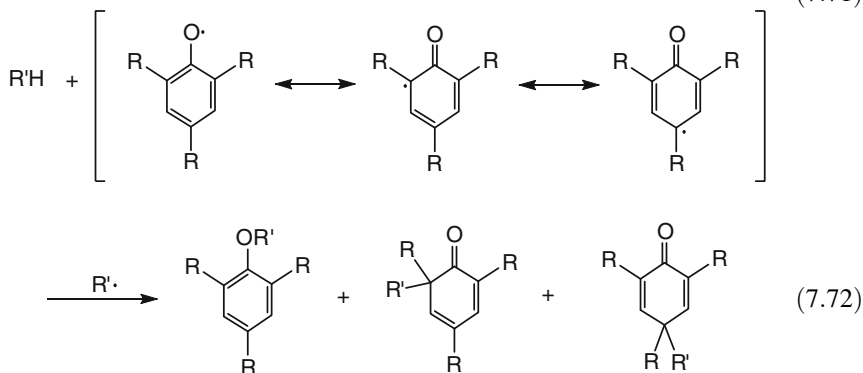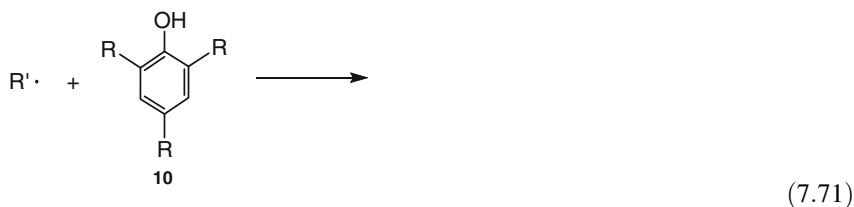
## 7.6 Living Polymerization

When the termination reaction is not present in the polymerization of monomers, we call the polymerization is living polymerization. An important consequence of living polymerization is that the average degree of polymerization is simply equal to the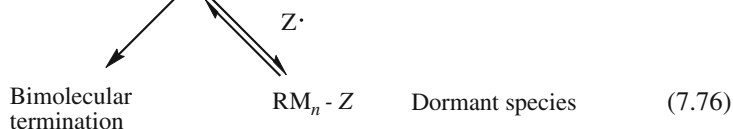 ratio of the initial monomer concentration to the initiator concentration as shown in Eq. 7.73. There are different approaches to achieve living radical polymerizations which are discussed below.

$$\overline{DP} = \frac{[M]_0}{[I]_0} \tag{7.73}$$

### 7.6.1 Living Radical Polymerization

The living radical polymerization is also called controlled radical polymerization. The formal IUPAC name of this type of polymerization is called reversible deactivation radical polymerization (RDRP) [6]. The lifetime in the conventional radical polymerization is very short (in second) because of the presence of bimolecular termination. The living radical polymerization can be achieved by minimizing normal bimolecular termination and prolonging the lifetime of living polymers. Special mode of reaction for the propagating radicals by either reversible termination or reversible transfer has been developed [3]. Living radical polymerization (LRP) with reversible termination generally proceeds as follows:

$$R\text{-}Z \; \rightleftharpoons \; R\cdot \;\; + \;\; Z\cdot \tag{7.74}$$

R· Reactive radical    Z· Stable radical

$$\downarrow M$$

$$RM_n\cdot \qquad \text{Propagating radical} \tag{7.75}$$

Bimolecular termination        $RM_n\text{-}Z$    Dormant species    (7.76)

Z·
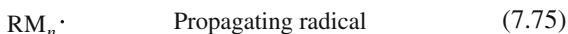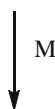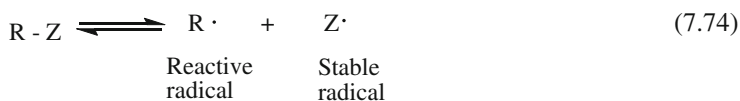
The initiator RZ undergoes homolytic bond breakage to produce one reactive and one stable free radical (Eq. 7.74). The reactive radicals quickly initiate polymerization (Eq. 7.75), but the stable radicals are too stable to initiate poly-merization. However, the stable radicals preserve the propagation chain being

living without any termination (Eq. 7.76). For living polymerization, it is important to have all the initiator decomposes at once so that all propagating radicals grow almost at the same time. Fast initiation is important, but it is the fast equilibrium between the propagating radical and dormant species with an appropriate equilibrium constant that determines the living characteristics of polymerization. The equilibrium constant must be low but not too low; that is, 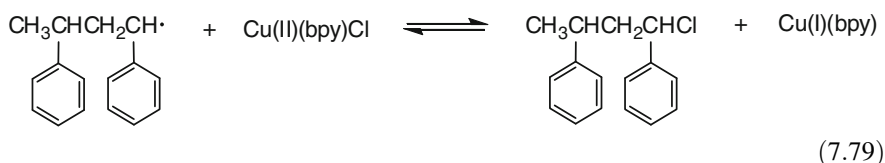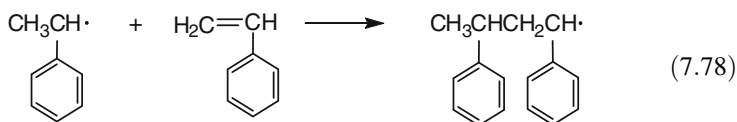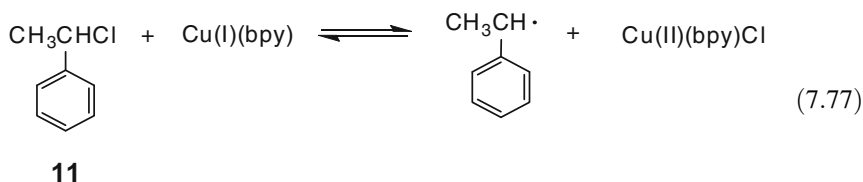the concentration of propagating radical must be sufficient to achieve a reasonable propagation rate but not so high that normal bimolecular termination becomes important.

At the beginning of the reaction, the concentrations of propagating and stable radicals are equal, but they change rapidly with the progress of reactions. The concentrations of stable radicals are increasing while the concentrations of propagating radicals are decreasing because the reactions are shifted toward more stable species as shown in Eqs. 7.74 and 7.76. Overall, the concentration of stable radicals is about four orders higher than that of propagating radicals. The concentration of propagating radicals is about the same or lower than the conventional radical polymerization. The stable radicals function as controlling agent to form reversible dormant species with propagating radicals. The equilibrium favors the dormant species by several orders of magnitude as compared with the propagating radicals. Thus, the concentration of dormant species is about six orders higher than that of propagating radical. In short summary, the introduction of the dormant species in the radical polymerization suppresses the bimolecular termination reaction to have a living polymer. The average life time of the living polymer has been increased by at least four orders of magnitude. Thus, the living free radical polymerization becomes possible due to the formation of stable radicals and reversible dormant species. By sequential living polymerization of one kind of monomer to another kind of monomer, well-defined block copolymers can be obtained through living polymerization. The second type of monomers usually has to add quickly after the first kind monomers are consumed to avoid any bimolecular reactions among propagating radicals. Currently, reversible termination reactions and reversible chain transfer reactions are employed in the living free radical polymerizations. They are discussed below.

## 7.6.2 Atom Transfer Radical Polymerization

The reactions of atom transfer radical polymerization (ATRP), involves an atom transfer, usually a halogen atom, to form propagating radicals and dormant species from the complex of atom transfer agent and copper (I) catalyst [6]. For instance, the polymerization of styrene using 1-chloro-1-phenylethane (**11**, or the bromo analog) as initiator in the presence of a copper (I) bipyridyl (bpy) complex. Initiation occurs when a halogen atom is transferred from **11** to the complex (Eq. 7.77). The resultant 1-phenylethyl radical in turn adds to a styrene molecule (Eq. 7.78). The halogen atom is then reversibly transferred to the styryl radical (Eq. 7.79), thus preventing radical termination reactions from occurring while

allowing the propagation reaction to proceed.

$$CH_3CHCl \; + \; Cu(I)(bpy) \; \rightleftharpoons \; CH_3CH\cdot \; + \; Cu(II)(bpy)Cl \quad (7.77)$$

**11**

$$CH_3CH\cdot \; + \; H_2C{=}CH \; \longrightarrow \; CH_3CHCH_2CH\cdot \quad (7.78)$$

$$CH_3CHCH_2CH\cdot \; + \; Cu(II)(bpy)Cl \; \rightleftharpoons \; CH_3CHCH_2CHCl \; + \; Cu(I)(bpy) \quad (7.79)$$

### 7.6.3 Nitroxide-Mediated Polymerization (NMP)

Stable nitroxide radical such as TEMPO **12** can mediate polymerization as shown in Eq. 7.80. The TEMPO is too stable to initiate polymerization, but it does promote decomposition of benzoyl peroxide to benzoyloxy radicals which initiate chain growth. Then TEMPO combines reversibly with the growing polymer chain ends which protect the chain end radicals from termination. Dissociation in turn frees the chain end radical to add to other styrene molecules.

$$\sim\sim CH_2CH\cdot \; + \; \cdot O{-}N \; \rightleftharpoons \; \sim\sim CH_2CH{-}O{-}N \quad (7.80)$$

**12**
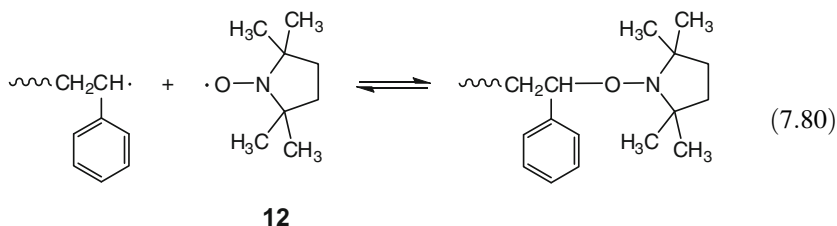
### 7.6.4 Radical Addition-Fragmentation Transfer (RAFT)

ATRP and NMP control chain growth by reversible termination. RAFT living polymerizations control chain growth through reversible chain transfer. A chain-

transfer agent R'CSSR, such as cumyl dithiobenzoate **13** reversibly transfer a labile end group (a dithioester end group) to a propagating chain (Eq. 7.81). The polymerization is carried out with a conventional initiator such as a peroxide or AIBN in the presence of the chain-transfer agent. The key that makes RAFT a living polymerization is the choice of the RAFT transfer agent. Living polymerization occurs with dithioesters because the transferred end group in the polymeric dithioester is as labile as the dithioester group in R'CSSR. This results in an equilibrium between dormant polymer chains and propagating radicals (Eq. 7.82 with $K = 1$), which controls the living polymerization.



**13**

$$M_n\cdot \; + \quad \underset{S \qquad SR}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \quad \rightleftharpoons \quad \underset{M_nS \quad \overset{\cdot}{} \quad SR}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \quad \rightleftharpoons \quad \underset{M_nS \qquad S}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \; + \; R\cdot \quad (7.81)$$

$$M_m\cdot \; + \quad \underset{S \qquad SM_n}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \quad \rightleftharpoons \quad \underset{M_mS \quad \overset{\cdot}{} \quad SM_n}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \quad \rightleftharpoons \quad \underset{M_mS \qquad S}{\overset{R'}{\diagup\!\!\!\!\diagdown}} \; + \; M_n\cdot \quad (7.82)$$
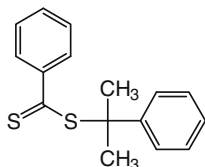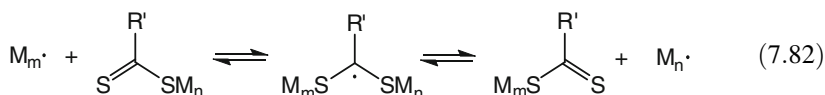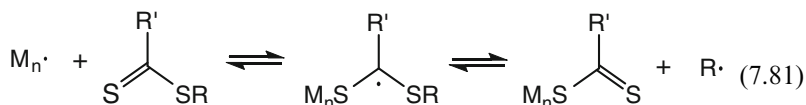
RAFT works with a wider range of monomers than TEMPO and ATRP. RAFT does not produce polymers with metal catalysts but produce polymers with dithioester group with odors and colors. The design and synthesis of RAFT agent has been thoroughly reviewed and outlined. The methods are extended to functional RAFT agent and macro-RAFT agent [7].

The limitations of living radical polymerization are that irreversible bimolecular termination of propagating radicals will occur at high monomer conversion, polyfunctional initiators, high initiator concentration, and high target molecular weight (>100,000).

## 7.7 Polymerization of Dienes

Polymerization of isolated dienes leads to crosslinked polymers when the double bonds react independently of each other. In certain cases, the addition reactions can occur within the double bonds of molecule and lead to cyclic polymers. Polymerization of divinylformal **14** illustrates this process as shown in Eq. 7.83.

$$(7.83)$$
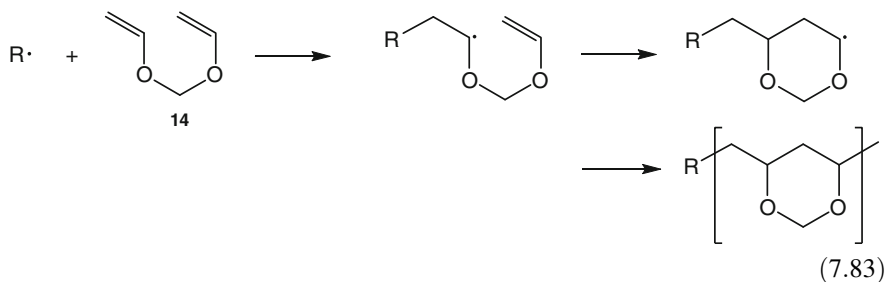
The normal (head-to-tail) mode of addition yields the six-membered ring, whereas abnormal (head-to-head) addition (Eq. 7.84) gives the five-membered ring. The former is preferred, but both are formed in significant amounts.



$$(7.84)$$
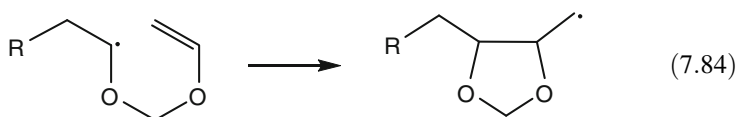
Several diallyl monomers such as **15** and **16** are used commercially to prepare highly cross-linked thermosetting *allyl resins* or for crosslinking other polymers. Diallyl phthalate **15** is used widely in the manufacturing of printed wiring boards, electrical insulations, fiber reinforced composites, etc. Diethylene glycol bis (allyl carbonate) **16** is used to make optical clear polymers for the applications in eye-wares, lenses, camera filters, panel covers, and the like.
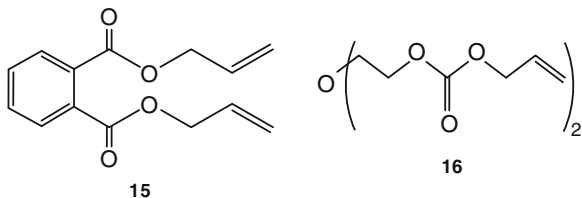


Conjugated dienes such as 1,3-butadiene **17** undergo both 1,2- and 1,4-addition to obtain polymers through the delocalized radical intermediate **18** (Eq. 7.85). Thus 1,2-addition gives polymer **19** with pendant vinyl groups, while 1,4-addition leads to polymer with unsaturation in the chain. In the latter case, both *cis* **20** and *trans* **21** configurations are possible.

$$CH_2=CH-CH=CH_2 \xrightarrow{R\cdot} \left[R-CH_2-CH\text{----}CH\text{----}CH_2\right]\cdot \tag{7.85}$$

**17**      **18**

**19**      **20**      **21**
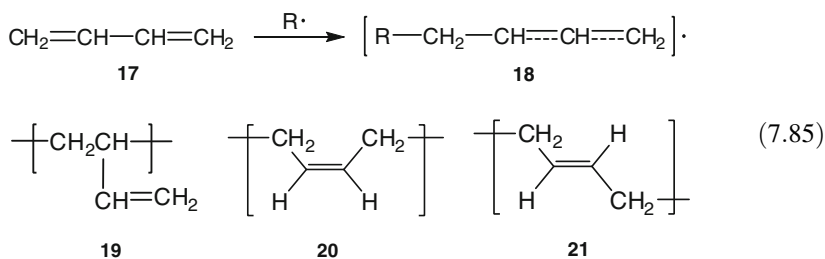
With substituted dienes like isoprene (2-methyl-1,3-butadiene) the situation is more complicated; 1,2 and 3,4 structures (**22** and **23**, respectively) as well as *cis*- and *trans*-1,4 (**24** and **25**), are possible. All are formed in free radical polymerization but as expected the head-to-tail*trans*-1,4 **25** predominates. Natural *Hevea* rubber contains the head-to-tail of 1,4-polyisoprene units with *cis* structure **24**.

**22**      **23**

**24**      **25**
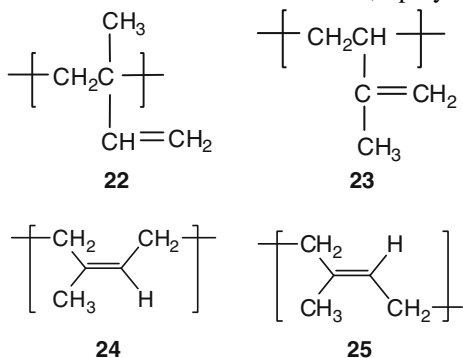
Table 7.12 lists the percentages of each structural unit at different polymerization temperatures for the three most important diene monomers—butadiene, isoprene, and chloroprene (2-chloro-1,3-butadiene). It is interesting to note that, for isoprene, the amount of *cis*-1,4 structure increases with increasing temperature up to about 100 °C, then it decreases. The total amount of 1,2 and 3,4 polymer (approximately 10 %) does not change appreciably with temperature; however, the 3,4 structure is favored at higher temperatures. With chloroprene, the *trans*-1,4 structure also decreases with increasing temperature, but the amount of *trans*-1,4 is slightly higher than that of isoprene over the temperature range measured. The results may be from the larger size of Cl group than that of $CH_3$ group, a steric hinderance dominated factor.

**Table 7.12**  Compositions of free radical-initiated diene polymers [2]

| Monomer | Polymerization temperature(°C) | Percent | | | |
|---|---|---|---|---|---|
| | | cis-1,4 | trans-1,4 | 1,2 | 3,4 |
| Butadiene | −20 | 6 | 77 | 17 | – |
| | 20 | 22 | 58 | 20 | – |
| | 100 | 28 | 51 | 21 | – |
| | 233 | 43 | 39 | 18 | – |
| Isoprene | −20 | 1 | 90 | 5 | 4 |
| | −5 | 7 | 82 | 5 | 5 |
| | 50 | 18 | 72 | 5 | 5 |
| | 100 | 23 | 66 | 5 | 6 |
| | 257 | 12 | 77 | 2 | 9 |
| Chloroprene | −46 | 5 | 94 | 1 | 0.3 |
| | 46 | 10 | 81–86 | 2 | 1 |
| | 100 | 13 | 71 | 2.4 | 2.4 |

## 7.8  Temperature Effect of the Free Radical Polymerization

By varying the polymerization temperature, there is big effect on the rate and degree of polymerization [3]. When the temperature increases, the rate of polymerization increases, but the degree of polymerization decreases as shown in Fig. 7.2. The quantitative effect of temperature is complicated and is discussed in the following sections.



**Fig. 7.2** Dependence of the polymerization rate (○) and polymer molecular weight (□) on the temperature for the thermal self-initiated polymerization of styrene [3]
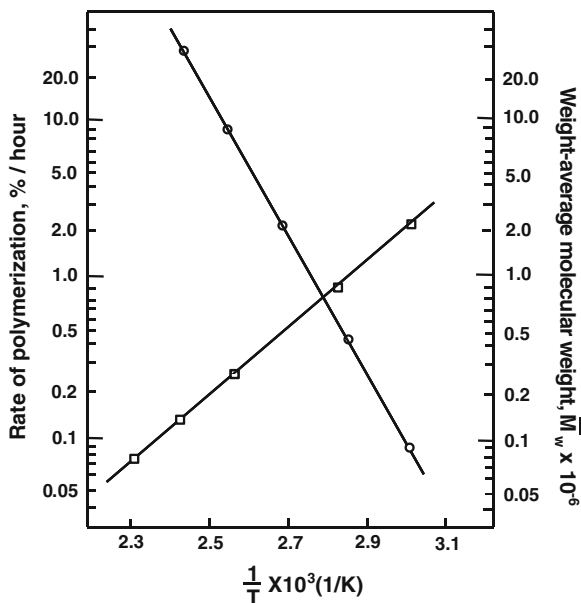
## 7.8.1 Activation Energy and Frequency Factor

The quantitative effect of temperature on rate of polymerization ($R_p$) and degree of polymerization ($\overline{X}_n$) is very complex since they depend on a combination of three rate constants of initiation ($k_d$), propagation ($k_p$) and termination ($k_t$). Each of the rate constants can be expressed by an Arrhenius equation

$$k = Ae^{-E/RT} \tag{7.86}$$

or

$$\ln k = \ln A - \frac{E}{RT} \tag{7.87}$$

where $A$ is the collision frequency factor, $E$ the Arrhenius activation energy, and $T$ the kelvin temperature. A plot of $\ln k$ versus $1/T$ allows the determination of both $E$ and $A$ from the slope and intercept, respectively. Table 7.13 shows the values of the frequency factor and activation energy of propagation ($E_p$) and termination ($E_t$) of several monomers.

The variations in the values of the frequency factor of propagation ($A_p$) are greater than those in $E_p$ which indicates that steric effects are probably the more important factor to determine the absolute value of $k_p$. Thus, the more hindered monomers such as methyl methacrylate have lower $k_p$ and $A_p$ values than the less hindered ones such as methyl acrylate. The $A_p$ values in general are lower than the usual value ($10^{11}$–$10^{13}$) of the frequency factor of a bimolecular reaction. The result is probably due to a large decrease in entropy on polymerization. The variations in the values of the frequency factor of termination ($A_t$), generally follow the trend of $A_p$ values, but with larger values.

**Table 7.13** Kinetic parameters in radical chain polymerization[a] [3]

| Monomer | $E_p$ | $A_p \times 10^{-7}$ | $E_t$ | $A_t \times 10^{-9}$ |
|---|---|---|---|---|
| 1,3-Butadiene | 24.3 | 12 | – | – |
| 2-Vinylpyridine | 33 | – | 21 | – |
| Acrylonitrile | 16.2 | – | 15.5 | – |
| Ethylene | 18.4 | – | 1.3 | – |
| Methyl acrylate | 29.7 | 10 | 22.2 | 15 |
| Methyl methacrylate | 26.4 | 0.087 | 11.9 | 0.11 |
| Styrene | 26 | 0.45 | 8.0 | 0.058 |
| Vinyl acetate | 18 | 3.2 | 21.9 | 3.7 |
| Vinyl chloride (50°C) | 16 | 0.33 | 17.6 | 600 |
| Tetrafluoroethylene(83°C) | 17.4 | – | – | – |

[a] $E_p$ values are in kJ/mole of polymerizing monomer; $E_t$ values are in kJ/mole of propagating radicals; $A_p$ and $A_t$ values are in liters/mole-second. The data are obtained at 60°C unless otherwise noted

## 7.8.2 Rate of Polymerization

For a polymerization initiated by the thermal decomposition of an initiator, the polymerization rate depends on the ratio of three rate constants $k_p(k_d/k_t)^{1/2}$ according to Eq. 7.53. The temperature dependence of this ratio can be obtained by combining three separate Arrhenius equations as below

$$\ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{[E_p + (\frac{E_d}{2}) - (\frac{E_t}{2})]}{RT} \qquad (7.88)$$

The overall activation energy of rate of polymerization $E_R$ is equal to $E_p + (E_d/2) - (E_t/2)$. From Eq. 7.53, one can rewrite the above equation as

$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[(f[I])^{\frac{1}{2}}[M]\right] - \frac{E_R}{RT} \qquad (7.89)$$

By plotting $\ln R_p$ versus $1/T$, one can obtain $E_R$ and $A_p(A_d/A_t)^{1/2}$ from the slope and intercept, respectively.

Table 7.14 shows the thermal properties of commonly used initiators. The activation energy of initiator decomposition is in the range of 120–150 kJ mole$^{-1}$ in general. The $E_p$ and $E_t$ value of most monomers are in the ranges of 20–40 kJ mole$^{-1}$ and 8–20 kJ mole$^{-1}$ respectively (Table 7.13). Thus the $E_R$ of most polymerization initiated by thermal initiator decomposition is about 80–90 kJ mole$^{-1}$. This corresponds to a two to three time rate increase for every 10°C temperature increase. The situation is different for other mode of initiation. The redox initiation (e.g., Fe$^{2+}$ with thiosulfate or cumene hydroperoxide) usually takes place at lower temperature as compared to the thermal polymerizations because the former has lower activation energy. The $E_d$ value of redox initiation is only about 40–60 kJ mole$^{-1}$ or about 80 kJ mole$^{-1}$ less than that of thermal initiation. This leads to an $E_R$ redox polymerization about 40 kJ mole$^{-1}$ or about half of the nonredox initiators.

The initiation step of photo polymerization is temperature independent ($E_d = 0$), because the decomposition of initiator is induced by light rather than by

**Table 7.14** Properties of common thermal initiators[a,b] [3]

| Initiator | $k_d \times 10^5$ | $T$ (°C) | $E_d$ |
|---|---|---|---|
| 2,2′-Azobisisobutyronitrile | 0.845 | 60 | 123.4 |
| Acetyl peroxide | 2.39 | 70 | 136.0 |
| Benzoyl peroxide | 5.50 | 85 | 124.3 |
| Cumyl peroxide | 1.56 | 115 | 170.3 |
| t-Butyl peroxide | 3.00 | 130 | 146.9 |
| t-Butyl hydroperoxide | 0.429 | 155 | 170.7 |

[a] All data are for decompositions in benzene solution
[b] The units of $k_d$ are s$^{-1}$; the units of $E_d$ are kJ/mole

heat. The overall activation energy of photo polymerization is then only about 20 kJ mole$^{-1}$ which indicates this polymerization is relatively insensitive to temperature. However, most photo initiators can also be decomposed thermally; the initiators may undergo appreciable thermal decomposition in addition to photo decomposition at higher temperatures. In such cases, one must take into account both the thermal and photo initiations. The initiation and overall activation energies for a purely thermal self-initiated polymerization are approximately the same as for initiation by the thermal decomposition of an initiator. For the thermal, self-initiated polymerization of styrene, its $E_d$ is 121 kJ mole$^{-1}$ and $E_R$ is 86 kJ mole$^{-1}$. However, pure thermal polymerization proceeds at very slow rates because of very low frequency factor ($10^4$–$10^6$) resulting in very low probability of initiation process.

### 7.8.3  Degree of Polymerization

The effect of temperature on the molecular weight of the polymer produced by thermally initiated polymerization will be determined by the ratio of $k_p/(k_d/k_t)^{1/2}$ according to Eq. 7.56 of the degree of polymerization, if transfer reactions are negligible. The variation of the ratio with temperature can be expressed by

$$\ln\left[\frac{k_p}{(k_d k_t)^{1/2}}\right] = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] - \frac{\left[E_p - \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right]}{RT} \tag{7.90}$$

The overall activation energy of degree of polymerization ($E_{\overline{X}_n}$) is equal to $\left[E_p - (E_d/2) - (E_t/2)\right]$. Then the temperature effect on the degree of polymerization can be expressed by

$$\ln\overline{X}_n = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] + \ln\left[\frac{[M]}{(f[I])^{1/2}}\right] - \frac{E_{\overline{X}_n}}{RT} \tag{7.91}$$

$E_{\overline{X}_n}$ has a value of about $-60$ kJ mole$^{-1}$ and $\overline{X}_n$ decreases rapidly with increasing temperature. $E_{\overline{X}_n}$ is about the same for a purely thermal, self-initiated polymerization (Fig. 7.2). For a pure photo polymerization, $E_{\overline{X}_n}$ is positive by approximately 20 kJ mole$^{-1}$, since $E_d$ is zero, and $\overline{X}_n$ increases moderately with temperature. For all other cases, $\overline{X}_n$ decreases with temperature.

When chain transfer occurs in the polymerization, the temperature effect on the $\overline{X}_n$ depends on the relative importance of the chain transfer reaction. For the case where chain transfer to chain transfer agent $T$, one can obtain the following equation according to Eq. 7.70.

**Table 7.15** Activation parameters for chain transfer in styrene polymerization (60°C) [3]

| Transfer agent | $-(E_p - E_{tr,S})$ | $\log(A_{tr,S}/A_p)$ |
|---|---|---|
| Benzene | 62.0 | 3.9 |
| Carbon tetrachloride | 20.9 | 1 |
| Cyclohexane | 56.1 | 3.1 |
| Ethyl benzene | 23.0 | −0.55 |
| Isopropyl benzene | 23.0 | −0.47 |
| $n$-Butyl bromide | 46.1 | 2 |
| $n$-Butyl chloride | 58.6 | 4 |
| $n$-Butyl iodide | 29.3 | 1 |
| $t$-Butyl benzene | 57.4 | 3.8 |
| Toluene | 42.3 | 1.7 |

$$-\ln\left[\frac{[M]}{[T]}\left(\frac{1}{\overline{X}_n} - \frac{1}{(\overline{X}_n)_0}\right)\right] = \ln\frac{k_p}{k_{tr}} = \ln\frac{A_p}{A_{tr}} - \frac{(E_p - E_{tr})}{RT} \qquad (7.92)$$

Now, $E_{\overline{X}_n}$ is equal to $(E_p - E_{tr})$ and can be obtained by plotting the left side of equation versus $1/T$. The $(E_p - E_{tr})$ is usually in the range of −20 to −65 kJ more$^{-1}$ and the molecular weight decreases with increasing temperature. Table 7.15 shows the activation parameters for chain transfer in styrene polymerization using different chain transfer agents. The frequency factors for transfer reactions are usually greater than those of propagations.

## 7.9 Thermodynamics of Free Radical Polymerization

The thermodynamics of free radical polymerization [3] can be expressed by $\Delta G_p = \Delta H_p - T\Delta S_p$. The $\Delta G_p$, $\Delta H_p$, and $\Delta S_p$ for a polymerization are the difference in *free energy*, *enthalpy*, and *entropy*, respectively, between 1 mol of monomer and 1 mol of repeating units in the polymer product. The thermodynamic properties of a polymerization relate only to the propagation step, since polymerization consists of single acts of initiation and termination and a large number of propagation steps.

Chain polymerizations of alkene are exothermic ($\Delta H_p$ is "negative") and exoentropic ($\Delta S_p$ is "negative"). The exothermic nature of polymerization arises because the process involves the exothermic conversion of $\pi$-bonds (less stable) in monomer molecules into $\sigma$-bond (more stable) in the polymer. The negative $\Delta S_p$ for polymerization arises from the decreased degrees of freedom for the polymer relative to the monomer. Thus, polymerization is favorable from the enthalpy viewpoint, but unfavorable from the entropy viewpoint. Table 7.16 shows the wide range of $\Delta H_p$ values for various monomers and also shows the general thermodynamic feasibility for any carbon–carbon double bond ($\Delta G_p$ is negative). However, thermodynamic feasibility does not indicate the experimental conditions of

**Table 7.16** Enthalpy and entropy of polymerization at 25 °C[3]

| Monomer | $-\triangle H$ | $-\triangle S$ |
|---|---|---|
| Ethylene | 93 | 155 |
| Propene | 84 | 116 |
| 1-Butene | 83.5 | 113 |
| Isobutylene | 48 | 121 |
| 1,3-Butadiene | 73 | 89 |
| Isoprene | 75 | 101 |
| Styrene | 73 | 104 |
| α-Methylstyrene | 35 | 110 |
| Vinyl chloride | 72 | – |
| Vinylidene chloride | 73 | 89 |
| Tetrafluoro ethylene | 163 | 112 |
| Acrylic acid | 67 | – |
| Acrylonitrile | 76.5 | 109 |
| Maleic anhydride | 59 | – |
| Vinyl acetate | 88 | 110 |
| Methyl acrylate | 78 | – |
| Methyl methacrylate | 56 | 117 |

$\triangle H$ refer to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer. $\triangle S$ refers to the conversion of monomer (at a concentration of 1 M) to amorphous or slightly crystalline polymer. The subscripts lc are often used with $\triangle H$ and $\triangle S$ to show the initial and final states (that is, $\triangle H_{lc}$ and $\triangle S_{lc}$). The units of $\triangle H$ are kJ/mole of polymerized monomer; the units of $\triangle S$ are J/K-mole

polymerization. The $\Delta S_p$ values fall in a narrower range of values. $\Delta S_p$ is in a small range $\sim 100$ to $\sim 150$ J/K-mol and $\Delta G_p$ is "negative" due to $-T\Delta S_p$ over weight $\Delta H_p$. Thus, polymerization is a favored reaction from thermodynamic point of view.
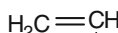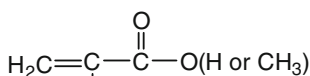
## 7.9.1 Monomer Reactivity

Although the polymerization reaction is thermodynamically favored, the kinetic feasibility of polymerization varies considerably from one monomer to another depending on the stability of monomer radical and polymer radical [3].

As shown in Table 7.16, the $\Delta H$ values for ethylene, propene, and 1-butene are very close to the difference (82–90 kJ/mole) between the bond energies of the $\pi$-bond in an alkene and the $\sigma$-bond in an alkane. The $\Delta H$ values for the other monomers vary considerably. The variations in $\Delta H$ for differently substituted ethylenes arise from any of the following effects: (1) differences in the resonance stabilization of monomer and polymer due to differences in conjugation or hyperconjugation, (2) steric strain differences in the monomer and polymer arising

from bond angle deformation, bond stretching, or interactions between nonbonded atoms, and (3) differences in hydrogen bonding or dipole interactions in the monomer and polymer. The following monomers (I) can be stabilized through resonance that decreases $\Delta H$ of polymerization. However, the monomer (II) is poorly conjugated and its $\Delta H$ is similar to that of ethylene.

**Type I Monomer**

$H_2C$=$CH$

$CH_3$
$H_2C$=$C$

$CH_2$=$CH$—$CH$=$CH_2$

$H_2C$=$C$—$CH_3$
$\qquad\quad |$
$\qquad\quad CH_3$

$\qquad\qquad O$
$\qquad\qquad \|$
$H_2C$=$C$—$C$—$O(H \text{ or } CH_3)$
$\qquad |$
$\qquad CH_3$

$H_2C$=$CH$
$\qquad\quad |$
$\qquad\quad CN$

**Type II Monomer**

$\qquad\qquad\qquad O$
$\qquad\qquad\qquad \|$
$CH_2$=$CH$—$O$—$C$—$CH_3$
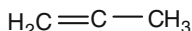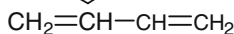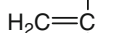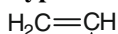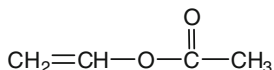
Many substituents stabilize the monomer but have no appreciable effect on polymer stability, since resonance is only possible with the former. The net effect is to decrease the exothermicity of the polymerization. Thus, hyperconjugation of alkyl groups with the C=C lowers $\Delta H$ for propylene and 1-butene polymerizations. Conjugation of the C=C with substituents such as the benzene ring (styrene and $\alpha$-methylstyrene), and alkene double bond (butadiene and isoprene), the carbonyl linkage (acrylic acid, methyl acrylate, methyl methacrylate), and the nitrile group (acrylonitrile) similarly leads to stabilization of the monomer and decreases enthalpies of polymerization. When the substituent is poorly conjugating as in vinyl acetate, the $\Delta H$ is close to the value for ethylene.

The effect of 1,1-disubstitution manifests itself by decreased $\Delta H$ values [3]. This is a consequence of steric strain in the polymer due to interactions between substituents on alternating carbon atoms of the polymer chain. In **25**, the polymer chain is drawn in the plane of the text with the H and Y substituents placed above

and below the plane of the text. The dotted and triangular lines indicate substituents below and above this plane, respectively. Such interactions are referred to as 1,3-interactions and are responsible for the decreased $\Delta H$ values in monomers such as isobutylene, $\alpha$-methyl styrene, methyl methacrylate, and vinyl chloride. The effect in $\alpha$-methyl styrene is especially significant. The $\Delta H$ value of $-35$ kJ/mole is the smallest heat of polymerization of any monomer. To summarize, the stability of the polymer radical is more important than the stability of the monomer toward addition of a free radical in the propagation reactions.
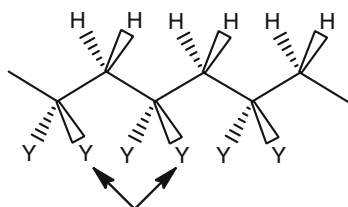


1,3-Interaction in polymer

**25**

## 7.9.2  Ceiling Temperature

The reversibility of vinyl polymerization reactions has been observed which depends on the monomer reactivity and the stability of polymer radical as shown in the following:

$$M_x \cdot + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{(x+1)} \cdot \qquad (7.93)$$

where $k_{dp}$ is the depropagation rate constant. Just as radical stability retards propagation, it enhances depropagation. As the polymerization temperature is raised, the depropagation rate increases until a point is reached where the forward and back reactions are equal. The temperature at which this occurs is called the *ceiling temperature* ($T_c$), and at that temperature $\Delta G$ of polymerization is zero, or

**Table 7.17** Representative ceiling temperatures, $T_c$, of pure liquid monomers [3]

| Monomer | $T_c$ (°C) |
|---|---|
| 1,3-Butadiene | 585 |
| Ethylene | 610 |
| Isobutylene | 175 |
| Isoprene | 466 |
| Methyl methacrylate | 198 |
| α-Methyl styrene | 66 |
| Styrene | 395 |
| Tetrafluoro ethylene | 1,100 |

$$T_c = \frac{\Delta H}{\Delta S} \tag{7.94}$$

It follows that whatever affects $\Delta H$ or $\Delta S$ for a given monomer (e.g., monomer concentration, pressure) will also affect $T_c$. Table 7.17 lists ceiling temperatures for several pure liquid monomers.

### 7.9.3 Characteristics of ΔS Values of Free Radical Polymerization

While the $\Delta H$ values vary over a wide range for different monomers, the $\Delta S$ values are less sensitive to monomer structure, being relatively constant within the range of $\sim 100$–120 J/K-mole. The $T\Delta S$ contribution to the $\Delta G$ of polymerization will be small and will vary only within a narrow range. Thus, the variation in the $T\Delta S$ term at 50°C for all monomers is in the narrow range of 30–40 kJ/mole. The $\Delta S$ of polymerization arises primarily from the loss of the translation entropy of the monomer. Losses in the rotational and vibration entropies of the monomers are essentially balanced by gains in the rotation and vibration entropies of the polymer. Thus, $\Delta S$ for polymerization is essentially the translational entropy of the monomer, which is relatively insensitive to the structure of the monomer.

## 7.10 Molecular Weight Distribution at Low Conversion

The molecular weight of radical chain polymerization is complicated because several possible terminations–disproportions, coupling, and various transfer reactions are involved. Molecular weight changes with % conversion, due to the changes in the concentrations of monomer and catalyst, and the rate constant of propagation and termination.

At low conversion where all of the kinetic parameters ($[M], [I], k_d, k_p, k_t$) are approximately constant. Under these conditions, the polymer molecular weight does not change with conversion. The molecular weight distributions can be derived as did in the step polymerization and are shown in Eqs. 7.95, 7.96, 7.97, 7.98, 7.99, and 7.100 as the number-fraction, number-, and weight-fraction distributions, the number- and weight-average degrees of polymerization, and the breadth of the distribution, respectively.

$$\underline{N}_x = p^{x-1}(1-p) \tag{7.95}$$

$$N_x = N_0(1-p)^2 p^{x-1} \tag{7.96}$$

$$W_x = x(1-p)^2 p^{x-1} \tag{7.97}$$

$$\overline{X}_n = \frac{1}{(1-p)} \tag{7.98}$$

$$\overline{X}_w = \frac{(1+p)}{(1-p)} \tag{7.99}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + p \tag{7.100}$$

Disproportional or chain transfer or a combination of two: one polymer molecule is produced from each kinetic chain. When $p$ is used as the probability to continue propagation, the molecular weight distribution can be shown in the following.

$$p = R_p/(R_p + R_t + R_{tr}) \tag{7.101}$$

where $R_p$, $R_t$, and $R_{tr}$ are the rates of propagation, termination by disproportionation, and chain transfer, respectively. The breadth of the size distribution $\overline{X}_w/\overline{X}_n$ is equal to 2 as $p$ approaches unity. For termination by coupling ($R_{tr} = 0$ and $R_t$ is the rate of coupling), a polymer arises from the combination of two kinetic chains, the size distribution is narrow.

Consider the probability $\underline{N}_{Y+Z}$ of formation of an $x$-sized polymer by the coupling of $y$- and $z$-sized propagating radicals. $\underline{N}_{Y+Z}$ is the product of the probabilities, $\underline{N}_Y$ and $\underline{N}_Z$, of forming the $y$- and $z$-sized propagating radicals.

According to Eq. 7.95, $\underline{N}_Y$ and $\underline{N}_Z$ are given in the following:

$$\underline{N}_Y = (1-p)p^{y-1} \tag{7.102}$$

$$\underline{N}_Z = (1-p)p^{z-1} \tag{7.103}$$

$$\because y + z = x$$

$$\therefore \underline{N}_Z = (1-p)p^{x-y-1} \tag{7.104}$$

$$\text{Then} \qquad \underline{N}_{y+z} = (1-p)^2 p^{x-2} \tag{7.105}$$

Equation 7.105 gives the probability of forming an x-sized polymer molecule by only one of many equally probable pathways. There are $(x-1)$ possible pathways of producing an x-sized polymer molecule when $x$ is an even number. Each of the pathways has the same probability. Therefore, the total probability $\underline{N}_x$ of forming an x-sized polymer molecule is given by

$$\underline{N}_x = (x-1)(1-p)^2 p^{x-2} \tag{7.106}$$

where $\underline{N}_x$ is mole or number-fraction distribution.

When $x$ is an odd number there are $x$ pathways

$$\underline{N}_x = x(1 - p)^2 p^{x-2} \tag{7.107}$$

For polymerization yielding in high polymer, the difference between $x$ and $(x + 1)$ is negligible and can be ignored. Then, we can have the following relationship:

$$W_x = \frac{1}{2}x(1 - p)^3(x - 1)p^{x-2} \tag{7.108}$$

$$\overline{X}_n = 2/(1 - p) \tag{7.109}$$

$$\overline{X}_w = (2 + p)/(1 - p) \tag{7.110}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = (2 + p)/2 \tag{7.111}$$

At high conversion, the size distributions become much broader than those described above for low concentration case. Kinetic chain length $\overline{v}$ is defined below:

$$\overline{v} = k_p[M]/2(fk_d k_t[I])^{1/2} \tag{7.56}$$

then,

$$\overline{v} \propto [M]/[I]^{\frac{1}{2}} \tag{7.112}$$

The molecular weight   is increased according to Eq. 7.56. Because $[I]$ is decreased faster than $[M]$, then the molecular weight of polymer is increased with % conversion. For polymer having practical usage, we want its PDI as narrow as possible. Sometimes, it is necessary to have multiple addition of initiator, monomer during the polymerization to minimize the molecular weight broadening. For auto-acceleration, the PDI is even larger with a value of 5–10. For chain transfer branch polymer, is also large with a PDI of 20–50, because chain transfer to polymer increases as the polymer size increases.

## 7.11  Synthesis of Commercial Polymers

The synthesis of some common polymers in the industrial scale is discussed below.

### 7.11.1  Polyethylene

Radical chain polymerization of ethylene to polyethylene is carried out at high pressures of 120–300 MPa and at temperature above the $T_m$ of polyethylene. Batch

processes are not useful since the long residence time gives relatively poor control of product properties. Long-chain branching due to intermolecular chain transfer becomes excessive with deleterious effects on the physical properties. Continuous processes allow better control of the polymerization.

The polyethylene produced by radical polymerization is referred to as *low-density polyethylene* (LDPE) or *high-pressure polyethylene* to distinguish it from the polyethylene synthesized using coordination catalysts. The latter polyethylene is referred to as *high-density polyethylene* (HDPE) or *low-pressure polyethylene*. Low-density polyethylene is more highly branched (both short and long branches) than high-density polyethylene and is therefore lower in crystallinity (40–60 % vs. 70–90 %) and density (0.91–0.93 g cm$^{-3}$ vs. 0.94–0.96 g cm$^{-3}$).

Low-density polyethylene (LDPE) has a wide range and combination of desirable properties. Its very low $T_g$ of about $-120°C$ and moderately crystallinity and $T_m$ of 105–110°C, give it flexibility and utility over a wide temperature range. Commercial low-density polyethylenes have number-average molecular weights in the range of 20,000–100,000, with $\overline{X}_w/\overline{X}_n$ in the range of 3–20.

Film application accounts for over 60 % of polyethylene consumption. Injection molding of toys, housewares, paint-can lids, and containers accounts for another 10–15 %. About 5 % of the LDPE produced is used as electrical wire and cable insulation. Extrusion coating of paper to produce milk, juice, and other food cartons and multiwall bags accounts for another 10 %. Trade names for polyethylene include *marlex*, *nipolon,* etc.

### 7.11.2 *Polystyrene*

Continuous solution polymerization is the most important method for the commercial production of polystyrene although suspension polymerization is also used. Emulsion polymerization is important for the synthesis of copolymer of acrylonitrile butadiene styrene(ABS). Commercial polystyrene (PS) has number-average molecular weights in the range of 50,000–150,000 with $\overline{X}_w/\overline{X}_n$ values of 2–4. Although completely amorphous ($T_g = 85\ °C$), its bulky rigid chains (due to phenyl–phenyl interactions) impart good strength with high-dimensional stability (only 1–3 % elongation); PS is a typical rigid plastic. Expandable polystyrene, either crystal polystyrene or styrene copolymers impregnated with a blowing agent, e.g., pentane, is used to produce various foam products such as disposable drinking cap, egg cartons, etc.

### 7.11.3 Polyvinyl Chloride

Most poly(vinyl chloride) (PVC) is commercially produced by suspension poly-merization. A typical polymerization includes 180 parts water, and 100 parts vinyl chloride monomer, chain transfer agent (trichloro ethylene). The reactants are then heated in the closed system to about 50°C, and the pressure rises to about 0.5 MPa. Typical number-average molecular weights for commercial PVC are in the range of 30,000–80,000. Tough and rigid PVC became flexible by using plasticizers (e.g., di-i-octylphthalate, tritolyl phosphate, epoxidized oils). Rigid pipe is used for home and construction, vinyl siding, window frames, rain-gutter, packaging, and gloves.

### 7.11.4 Polyvinyl Acetate

Polyvinyl acetate (PVAC) $[–CH_2–C(H)(O–CO–CH_3)–]_n$ is synthesized from vinyl acetate monomer via emulsion or solution polymerization. The $T_g$ of PVAC is about 28°C which is not very useful, but widely used in water based paints, adhesives for papers, textiles, and wood. PVAC is also used for producing poly-vinylalcohol (PVA) by hydrolysis that is used as thickening agents, coatings, and adhesives.

### 7.11.5 Polyvinylidene Chloride

Polyvinylidene chloride $(–CH_2–CCl_2–)_n$ and its copolymer with vinyl chloride, acrylonitrile, and acrylates, usually prepared by suspension or emulsion poly-merization. They are useful as oil, fat, oxygen and moisture-resistant packaging films (Saran wrap), container, coatings, tank liners, and monofilaments in drapery fabrics and industrial filter cloths.

### 7.11.6 Acryl Polymer

Poly(methyl methacrylate) (PMMA) can be polymerized by bulk, solution, sus-pension, and emulsion processes. PMMA is completely amorphous but has high strength and excellent dimensional stability due to the rigid polymer chains ($T_g = 105°C$). Polyacrylates differ considerably from the polymethacrylates. They are softer since the polymer chains are not nearly as rigid [e.g., poly(ethyl acrylate) (PEA), $T_g = -24°C$], due to the absence of the methyl groups on alternating carbons of the polymer chains.

Various rigid PMMA products, such as sheet, rod, and tube, are produced by bulk polymerization in a *casting* process. Polymerization is carried out in stages to allow easier dissipation of heat and control of product dimensions since there is a very large (21 %) volume contraction on polymerization. Partially polymerized monomer like syrup (about 20 % conversion) is produced by heating for about 10 min at 90°C with a peroxide. The syrup is cooled to ambient temperature and poured into a mold, and then the assembly is heated in a water or air bath to progressively higher temperatures. The maximum temperature used is 90 °C, since higher temperatures can lead to bubble formation in the product as the boiling point of methyl methacrylate is 100.5°C. Trade name for acrylate and methacrylate polymer products includes *Acrylite*, *Plexiglas*, *Lucite*, etc.

In commercial production, polyacrylonitrile ($[-C-C(CN)-]_n$) (PAN) is synthesized by either solution or suspension polymerization. Polyacrylonitrile contains polar group to have high secondary force, so it exhibits good fiber property. PAN is a source of carbon fiber which is produced by cyclization of polymer at 2,000 °C or above.

From the viewpoint of sales volume, all other members of the acrylic family constitute a small fraction of the total. However, many of them are useful specialty products. Polyacrylamide, poly(acrylic acid), and poly(methacrylic acid) and some of their copolymers are used in various applications that take advantage of their solubility in water. Poly(acrylic acid) and poly(methacrylic acid) are used as thickening agents, adhesives, dispersants for inorganic pigments in paints, flocculants, and crosslinked ion-exchange resins.

## *7.11.7  Fluoropolymers*

The fluoropolymers are obtained mainly by suspension polymerization; emulsion polymerization is also practiced. The most important members of this family are poly(tetrafluoro ethylene) (PTFE), poly(chloro trifluoro ethylene) (PCTFE), poly (vinyl fluoride) (PVF), and poly(vinylidene fluoride) (PVDF). High molecular weight PTFE is usually obtained due to lack of chain-transfer reactions and precipitation of growing radicals (leading to greatly decreased termination). Fluoropolymers can withstand a wide variety of chemical environments and are useful at temperatures as low as −200°C and as high as 260°C. The various copolymers of tetrafluoro ethylene and the other fluoropolymers, possessing lower $T_m$ and crystallinity, were developed to overcome the lack of melt processability of PTFE. A true melt processable PTFE has been developed by blending two different molecular weight polymers [8]. They are DuPont Zonyl MP 1000 and Zonyl MP 1,500 J at a specific mixing window of weight ratio of 40/60 and 20/80, respectively. The PVDF exhibits novel piezoelectric properties which are useful for the applications of actuators, artificial arms/legs, and so on.

## 7.11.8  Cost of Common Polymers

The cost of common polymers depends on the ease of synthesis and raw material cost. Fluoropolymer is usually a high cost polymer compared to other polymers. The cost comparison is in the increasing order of $PE \sim PS <$ phenolic alkyds $< PMMA < Nylon < PTFE$. The raw materials used for polymer synthesis are derived from petroleum, with the increase in petroleum price and possible depletion someday. Raw materials obtained from renewable source such as plants or biomolecules are currently under intensive development. For instance, poly-lactic acid can be obtained from bacterial fermentation of corn starch. It is bio-degradable and has been used in disposable cups and plates.

## 7.12  Problems

1. Polymers can be synthesized via free radical polymerization among monomers of ethylene, monosubstituted ethylene, 1,1-disubstituted ethylene. However, polymers are difficult to obtain from 1,2-disubstitute ethylene by free radical polymerization. Please explain.

2. Please show how degree of polymerization depends on temperature in (a) polymerization initiated by thermal decomposition of an initiator, (b) photo-polymerization (i.e., without initiator), and (c) without transfer reactions to control molecular weight.

3. Please derive kinetic equations for radical chain polymerization in the presence of an inhibitor such that, essentially, all the chains are terminated by reaction with the inhibitor. Show how the rate of polymerization depends on the concentrations of monomer, initiator, and inhibitor at the steady state.

4. Please write the possible reaction products of two thermal initiators: diacetyl peroxide, di-t-butyl peroxide, respectively.

5. In normal free radical processes with added initiator, the polymerization rate and $\overline{DP}$ are proportional to the first power of monomer concentration. What would be the effect of monomer concentration on $\overline{DP}$ in the thermal polymerization of styrene? Derive a kinetics expression to support your conclusion. (*Reminder*: Initiation involves two monomer molecules.)

6. If equal concentrations of acrylonitrile ($k_p = 1{,}960$ L/mol-s, $k_t = 782 \times 10^{-6}$ L/mol-s) and methyl methacrylate ($k_p = 515$ L/mol-s, $k_t = 25.5 \times 10^{-6}$ L/mol-s) were each polymerized at 60°C with equal concentrations of the same initiators, which polymer would have the higher $\overline{DP}$ and by how much? Assume polyacrylonitrile undergoes termination only by radical combination and PMMA by disproportionation. Which polymer would have the higher $\bar{M}_n$, and by how much?

7. A certain monomer is polymerized by benzoyl peroxide labeled in the benzene ring with carbon-14. (a) Analysis by carbon counting shows that the polymer

contains an average of 1.27 labeled phenyl groups per molecule. Assuming no chain transfer occurred, what does this indicate about the mechanism of termination? (b) Vigorous basic hydrolysis removed 60 % of the carbon-14. What does this indicate about the mechanism of initiation?

8. Predict the order of polymer molecular weight obtainable (highest to lowest) by the free radical solution polymerization of styrene in benzene, toluene, ethyl benzene, t-butyl benzene, and isopropyl benzene.

9. Poly(vinyl acetate) of number-average molecular weight 100,000 is hydrolyzed to poly(vinyl alcohol). Oxidation of the latter with periodic acid to cleave 1,2-diol linkages yield a poly(vinyl alcohol) with degree of polymerization of 200. Calculate the percentages of head-to-tail and head-to-head linkages in the poly(vinyl acetate).

10. The living character of living radical polymerization is limited under certain conditions, such as high monomer conversion, high initiator concentration, and high targeted molecular weight(>100,000). Please explain why these conditions result in broadening of PDI and some difficulties in producing block copolymers with well-defined block lengths of the different monomers.

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