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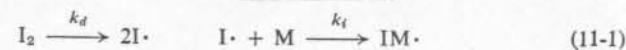
## Free-Radical Polymerization of Olefin Monomers

The free-radical polymerization of olefin monomers was first reported well over 100 years ago, but reproducible, high molecular weight polymers have been synthesized by this route only within the past 30 years or so. Poly(vinylidene chloride) described in 1838 by Regnault<sup>1</sup> may have been the first olefin polymer reported in the literature. Polystyrene was mentioned shortly thereafter in 1839,<sup>2</sup> followed by poly(vinyl chloride) in 1872,<sup>3</sup> polyisoprene in 1879,<sup>4</sup> poly(methacrylic acid)<sup>5</sup> and poly(methyl acrylate)<sup>6</sup> in 1880, polybutadiene in 1911,<sup>7</sup> poly(vinyl acetate) in 1914,<sup>8</sup> and polyethylene in 1933,<sup>9</sup> to mention some of the most important chain-growth polymers which were first prepared by the free-radical polymerization of olefin monomers. The reliable application of this type of polymer synthesis had to await the recognition by Staudinger in 1920<sup>10</sup> of the nature of an olefin polymerization reaction and the elucidation of the mechanism of a free-radical chain reaction by Taylor in 1925,<sup>11</sup> Paneth in 1929,<sup>12</sup> and Haber and Willstätter in 1931.<sup>13</sup>

### 11.1. RADICAL CHAIN-GROWTH POLYMERIZATION

The chain mechanism of the addition of free radicals to double bonds was clearly defined by Kharasch<sup>14</sup> and by Hey and Waters<sup>15</sup> in 1937, and was applied quantitatively to the chain-growth polymerization of olefin monomers by Flory<sup>16</sup> in the same year. Flory showed that a free-radical polymerization reaction, like other radical processes, was a typical chain reaction requiring three distinct steps: initiation, propagation, and termination.

The initiation step is basically the formation (11-1) of a free radical by any of the methods discussed in Section 10.1. As will be discussed in Section 11.1.2, the initiation step (11-1) also includes the reaction in which

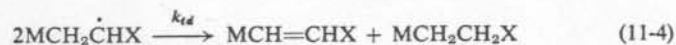
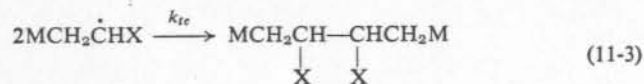


the initiator fragment radical,  $I\cdot$ , is added to the first monomer molecule,  $M$ . This addition reaction proceeds at a different rate than the propagation

reaction. In comparison to the propagation step, which is the addition (11-2) of a free radical to a double bond, and the termination step, which



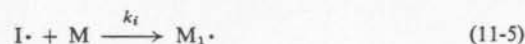
is the coreaction of two radicals by combination (11-3) or disproportionation (11-4), the initiation step is a slow reaction requiring a high activation



energy. For this reason the overall rate of a given radical polymerization reaction is controlled mainly by the rate of dissociation of the initiator, even though the overall rate may involve hundreds or thousands of propagation steps for every initiation step. This relationship is revealed in the kinetic analysis of radical polymerization presented in the next section.

### 11.1.1. Kinetics of Radical Polymerization

The initiation process is a two-step sequence, both steps of which enter into the overall rate equation. The first of the two steps is the dissociation (11-1) of the initiator,  $I_2$ , to generate two radical fragments, and the second step is the addition (11-5) of one of these fragments to a monomer mole-



cule,  $M$ , to start the growth of a polymer chain. The second step may have a much higher rate constant than the first, but it still must be taken into consideration in kinetic treatments because not every free radical formed by dissociation (11-1) of the initiator lives long enough to add (11-5) to a monomer molecule. Some radical fragments from the initiator are lost through recombination within the original solvent cage, as discussed in Section 10.1.1.1, and some are lost by reaction with another initiator radical or a polymer radical after escaping from the cage. The former reaction is termed primary recombination and the latter secondary combination.

The mole fraction of initiator radicals formed which successfully add to monomer molecules to initiate polymer chains is termed the efficiency,  $f$ , which is generally between 0.5 and 1.0. The rate of initiation,  $R_i$ , is then a composite of the dissociation reaction and the initial addition reactions, but a general approximation made in deriving kinetic expressions for chain-growth polymerization is that these two reactions have equal rates (11-6). Equation (11-6) is used for approximating the concentration of free

$$R_i = 2fk_d[I_2] = k_i[I\cdot][M] \quad (11-6)$$

radicals in the derivation of the overall rate equation. This approximation is based on an assumption, termed the steady-state assumption, which implies and requires that the concentration of free radicals is effectively constant throughout the course of a chain-growth polymerization reaction. It is also assumed that the induction period has a negligible effect on the overall rate. For photochemical initiation, the term  $k_d[I_2]$  in Equation (11-6) is replaced with a term for the amount of active radiation absorbed,  $I_{abs}$ , which will generally be a product of the intensity of absorbed light,  $\epsilon I_0$ , and the monomer concentration.

The propagation step involves only one type of reaction, the addition reaction (11-2), but, as shown in Section 10.4, the rate of this reaction may vary considerably at the start of the polymerization reaction with the size of the polymer chain radical. Nevertheless, it is usually assumed that the rate constant for propagation is invariant after the initial addition reaction, so that the kinetic expression (11-7) for the rate of propagation,  $R_p$

$$R_p = k_p[M\cdot][M] \quad (11-7)$$

includes only one rate constant. The termination step can be either a combination (11-3) or disproportionation (11-4) reaction, and both reactions must be included in the kinetic expression for the rate of termination  $R_t$ , (11-8). Normal convention is to include a factor of 2 in this

$$R_t = 2(k_{tc} + k_{td})[M\cdot]^2 \quad (11-8)$$

expression to take into account the disappearance of two radicals and to maintain the identity of the rate constant as a true constant for the radical destruction reaction.

**11.1.1.1. Overall Rate of Polymerization.** The overall rate of polymerization,  $R_o$ , is the rate of disappearance of monomer, which is removed both in the first initiator radical-addition reaction (11-5) and in the propagation step (11-2). The overall rate expression should contain both of these terms (11-9), but because there are hundreds or thousands of propagation steps

$$R_o = k_i[I\cdot][M] + k_p[M\cdot][M] \quad (11-9)$$

for every initiation step in the production of high molecular weight polymer, the former contribution is normally neglected. As a result, the overall rate of polymerization is assumed to be identical to the rate of propagation (11-10).

$$R_o = R_p = k_p[M\cdot][M] \quad (11-10)$$

This rate Equation, (11-10), although adequately representative of the rate of polymerization in most cases, is not very useful because it contains the quantity  $[M\cdot]$ , which is the concentration of free-radical endgroups.

For the preparation of high polymers, this concentration must be maintained below  $10^{-3}M$  to minimize termination, and consequently,  $[M\cdot]$  is very difficult to determine experimentally with any degree of accuracy. At this point in the derivation, to eliminate this difficulty, the steady-state assumption is invoked. In order to achieve a steady state with constancy of radical concentration, the rate of initiation,  $R_i$ , is assumed to be equal to the rate of termination,  $R_t$ , and equating these two expressions (11-11) yields an equation (11-12) for  $[M\cdot]$ . This equation for  $[M\cdot]$ , on substitution in the expression for the overall rate (11-10), yields an equation (11-13)

$$R_i = R_t \quad (11-11)$$

$$2fk_d[I_2] = 2(k_{tc} + k_{td})[M\cdot]^2$$

$$[M\cdot] = [fk_d/(k_{tc} + k_{td})]^{1/2}[I_2]^{1/2} \quad (11-12)$$

$$R_p = k_p[M\cdot][M] = k_p[M][fk_d/(k_{tc} + k_{td})]^{1/2}[I_2]^{1/2} \quad (11-13)$$

containing only quantities which can in principle be determined experimentally. The new Equation (11-13) predicts that the rate of polymerization should be dependent on the first power of the monomer concentration, which is often but not always observed, and on the square root of the initiator concentration, so that doubling the latter will only increase the rate of polymerization by a factor of  $\sqrt{2}$ .

**11.1.1.2. Degree of Polymerization.** These rate expressions can be adapted further to indicate the effect of different reaction variables on the degree of polymerization of the polymeric products. If no side reactions, such as chain transfer, occur during the polymerization reaction, then each polymer chain should contain one or two initiator fragments as endgroups, depending upon whether termination occurs by disproportionation or combination, respectively. If disproportionation occurs exclusively, the degree of polymerization should equal the kinetic chain length,  $\nu$ , while for termination by combination, the degree of polymerization should be twice the kinetic chain length. As discussed in Chapter 9, the kinetic chain length is the number of monomer molecules reacted for a single initiator radical produced, and may be expressed quantitatively as the ratio of the rate of propagation to rate of initiation (11-14) if the previous assumptions hold.

$$\nu = R_p/R_i \quad (11-14)$$

Consequently, the average degree of polymerization,  $\overline{DP}$ , is either equal to or twice this rate ratio for a clean chain-growth polymerization reaction (11-15).

$$\overline{DP} = R_p/R_i \quad \text{For disproportionation} \quad (11-15)$$

$$\overline{DP} = 2R_p/R_i \quad \text{For combination}$$

If the exact rate of initiation is unknown,  $R_i$  may be replaced by its equivalent  $R_t$  (11-16), and this equation on expansion and on substitution

$$\overline{DP} = R_p/R_t \quad (11-16)$$

for  $[M\cdot]$  by the term  $R_p/k_p[M]$  (11-10) yields an expression containing only measurable rate information (11-17). This last relationship (11-17)

$$\overline{DP} = k_p[M\cdot][M]/2(k_{tc} + k_{td})[M\cdot]^2 = k_p^2[M]^2/2(k_{tc} + k_{td})R_p \quad (11-17)$$

reveals that the average degree of polymerization achieved in a polymerization reaction is inversely proportional to the rate of polymerization. However, the inverse relationship is not strictly correct because  $R_p$  can be increased by increasing the monomer concentration which would also increase  $\overline{DP}$ . Instead, this relationship applies only to an increase in  $R_p$  brought on by an increase in the rate of formation of radicals, and consequently by an increase in  $[M\cdot]$ . The important factor is that an increase in  $[M\cdot]$  causes a considerable increase in  $R_t$ , which increases with  $[M\cdot]^2$ , and therefore, a decrease in  $\overline{DP}$  occurs because of the inverse relationship of  $\overline{DP}$  and  $R_t$  (11-16). For this and other reasons mentioned previously, the concentration of initiator and the rate of initiation are both important and controlling variables in a free-radical polymerization reaction of unsaturated compounds.

### 11.1.2. Initiation

The controlling importance of the initiation step to the degree of polymerization and to the overall rate of polymerization can be appreciated from consideration of both Equation (11-17) and Equation (11-13). Rearrangement of Equation (11-13) produces an equation which reveals that a measurement of the rate of polymerization is essentially a measurement of the rate of initiation (11-18). This point is emphasized by a com-

$$R_p = \frac{k_p[M]}{(k_{tc} + k_{td})^{1/2}} (fk_d[I_2])^{1/2} = \text{Constant} \times [M]R_i^{1/2} \quad (11-13)$$

$$\text{Constant} \times \frac{R_p^2}{[M]^2} = R_i \quad (11-18)$$

parison of the overall activation energy for polymerization,  $\Delta E_0$ , with the activation energies for initiation,  $\Delta E_d$ , propagation,  $\Delta E_p$ , and termination,  $\Delta E_t$ , reactions, as indicated by Equation (11-18). Inserting the various rate constants into Equation (11-18) produces a relationship between these constants (11-19) which can readily be converted to a relationship between the various activation energies (11-20).<sup>17</sup>

$$R_p^2 = (k_p^2/k_t)k_d f[I_2][M]^2 \quad (11-19)$$

$$2\Delta E_0 = 2\Delta E_p + \Delta E_d - \Delta E_t$$

$$\Delta E_0 = \Delta E_d/2 + \Delta E_p - \Delta E_t/2 \quad (11-20)$$





Table 11-1

Relative Reactivities of Monomers as Measured by Competition between Monomer Addition (11-24) and Fragmentation (11-23) of Benzoyloxy Radicals<sup>a</sup>

Monomer	$k_a/k_e$ mole liter <sup>-1</sup>	Relative value of $k_a$
2,5-Dimethylstyrene	5.0	2.0
Styrene	2.5	1.0 (Standard)
2,4,6-Trimethylstyrene	1.7	0.67
Vinyl acetate	0.91	0.36
Methyl methacrylate	0.30	0.12
Acrylonitrile	$\leq 0.12$	$\leq 0.05$

<sup>a</sup> For benzoyl peroxide at 60°C.<sup>23</sup>

observed must be determined in part by a polar effect. From the methyl affinity studies discussed in Section 10.2.2, the order of reactivity of these monomers with methyl radicals at 65°C is vinyl acetate < styrene < methyl methacrylate < acrylonitrile, with the difference between the lowest and highest members of the series being almost a factor of 50.

Another pair of competitive reactions has been used to obtain an indication of the relative rates of addition of peroxy radicals or sulfate ion-radicals to monomers. This estimation is based on the competition between oxidation (11-25) of ferrous ion versus addition (11-26) to monomer by a



given radical. The results for the peroxy radicals do not reveal a clear pattern, but the rates do for addition,  $k_a$  (11-26), and oxidation,  $k_o$  (11-25),

Table 11-2

Relative Reactivities of Monomers toward Sulfate Ion-Radicals<sup>a</sup>

Monomer	$k_a/k_o^b$	Relative value of $k_a$
Methyl methacrylate	$7.7 \times 10^{-3}$	1.0 (Standard)
Methyl acrylate	$1.1 \times 10^{-3}$	0.14
Acrylonitrile	$3.9 \times 10^{-4}$	0.051

<sup>a</sup> At 25°C.<sup>25</sup>

<sup>b</sup> Ratio of rate constants for Reactions (11-26) and (11-25).

of the sulfate ion-radical, generated from a persulfate dianion, as indicated in Table 11-2.<sup>25</sup>

**11.1.2.1. Efficiency of Initiation.** Investigations have been made on several monomers and initiators to determine quantitatively the efficiency of initiation, that is the value of  $f$  in Equation (11-6). At least four different methods have been used for this purpose, as follows<sup>26</sup>: (1) comparison of the number of initiator molecules decomposed to the number of polymer molecules formed; (2) comparison of the number of initiator molecules decomposed to the number incorporated into polymer molecules; (3) comparison of the number of initiator molecules decomposed in the presence of a very active radical scavenger with the number of scavenger molecules reacted; and (4) from rate measurements coupled with a knowledge of the kinetic parameters by use of either Equation (11-13) or Equation (11-19). All of the methods except 3 require both a knowledge of the mechanism of termination, meaning an accurate measure of the relative amounts of combination and disproportionation, and a knowledge of the extent of induced decomposition of the initiator.

Method 1 has been used to show that the efficiency of initiation for styrene and methyl methacrylate polymerization by benzoyl peroxide is between 0.6 and 1.0,<sup>27</sup> and that for methyl methacrylate polymerization by azobisisobutyronitrile is slightly greater than 0.5.<sup>28</sup> Method 2 was the procedure used to establish the order of efficiencies for five monomers with azobisisobutyronitrile referred to in the previous section.<sup>24</sup> For bulk polymerization at 60°C, the approximate  $f$  values are 0.5 for methyl methacrylate, 0.7 for styrene, and 0.8 for vinyl acetate. The same procedure with the same initiator in another investigation has yielded efficiencies of 0.5–0.55 for both methyl methacrylate<sup>29</sup> and styrene.<sup>30</sup> Method 3, in contrast, yields an efficiency of 0.70 for azobisisobutyronitrile with acrylonitrile, methacrylonitrile, methyl methacrylate, and methyl acrylate.<sup>31</sup> The scavenger used for the last study was ferric chloride, which has been found to be an extremely reactive and efficient chain transfer agent (11-27).<sup>32</sup> Finally for azobisisobutyronitrile, method 4, based on Equation



(11-19), yields an efficiency of 0.60 for both styrene and methyl methacrylate.

Method 4, based on Equation (11-13), has been applied to the determination of efficiencies of initiation for a series of peroxides with styrene at 70°C. The average  $f$  values for several peroxides are as follows: bis(*p*-chlorobenzoyl) peroxide, 0.67; benzoyl peroxide, 0.90; acetyl peroxide, 0.78; lauroyl peroxide, 0.57; bis(2,4-dichlorobenzoyl) peroxide, 0.35. Of these,

$$R_p = k_p [M] \left[ \frac{5 f k_d / k_t}{k_a / k_e} \right]^{1/2} [I_2]^{1/2}$$

the efficiencies for benzoyl peroxide, lauroyl peroxide, and bis(dichlorobenzoyl) peroxide are markedly concentration dependent, decreasing with increasing concentration of the peroxide. This decrease in efficiency can be attributed to the occurrence of induced decomposition of the peroxide at the higher concentrations. The radical causing the induced decomposition is apparently the polymer radical, Equation (11-28),



because a marked decrease in  $\overline{DP}$  is also observed with increasing initiator concentration, as shown in Figure 11-1 for bis(2,4-dichlorobenzoyl)

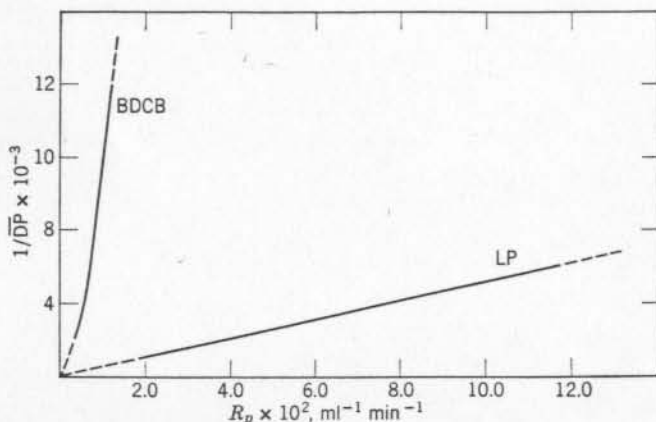


Figure 11-1. Plot of  $1/\overline{DP}$  vs. initial  $R_p$  for bulk polymerization of styrene<sup>34</sup> initiated by either bis(2,4-dichlorobenzoyl) peroxide, BDCB, or lauroyl peroxide, LP, at 60°C.

peroxide, BDCB, at 60°C and lauroyl peroxide, LP, at 84°C.<sup>34</sup>

The same nonlinear behavior of  $\overline{DP}$  vs.  $R_p$ , as shown by BDCB in Figure 11-1, has been observed for *t*-butyl hydroperoxide and cumene hydroperoxide with methyl methacrylate.<sup>35</sup> In contrast, azobisisobutyronitrile and benzoyl peroxide show the expected linear relationship (11-17) with methyl methacrylate. The nonlinear behavior has again been attributed to induced decomposition of the peroxide by polymer radicals. These induced decomposition reactions are nothing more than a type of effective chain transfer and, as such, they can be handled quantitatively by an expression developed by Mayo and co-workers<sup>36,37</sup> to be discussed in the following section.

**11.1.2.2. Chain-Transfer Equation.** Effective chain transfer is the physical termination of a polymer chain without destruction of the kinetic chain.

That is, the new radical formed in the chain-transfer reaction, which terminates the growing polymer chain, is reactive enough to initiate a new polymer chain more or less within the same period of time required for the addition of a monomer molecule to a growing chain endgroup in the normal propagation step. As a result, there is no noticeable decrease in the overall rate of polymerization, only a decrease in the average molecular weight of the polymer produced compared to that from a polymerization reaction in which chain transfer does not occur. Therefore, the equation used to express quantitatively the result of effective chain transfer is one based on  $\overline{DP}$ , namely an extension of Equations (11-16) and (11-17) in which the chain-transfer reaction, being a termination reaction, is included in the  $R_t$  term, Equation (11-29). The chain-transfer reaction is assigned the rate constant  $k_{tr}$  (11-30).

$$\overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M][M\cdot]}{2(k_{tc} + k_{td})[M\cdot]^2 + k_{tr}[M\cdot][I_2]} \quad (11-29)$$



A more convenient form of the chain-transfer equation, (11-29), is its reciprocal, (11-31). In Equation (11-31) the first term on the right hand

$$1/\overline{DP} = 2(k_{tc} + k_{td})[M\cdot]/k_p[M] + k_{tr}[I_2]/k_p[M] \quad (11-31)$$

side is equivalent to the reciprocal of the average degree of polymerization which is obtained under the same conditions but in the absence of chain transfer, that is,  $\overline{DP}_0$ . The second term on the right-hand side is simplified by replacing the ratio of rate constants,  $k_{tr}/k_p$ , by the constant  $C_1$ , which is termed the chain-transfer constant for the initiator and is a measure of the relative ease of transfer compared to monomer addition. The usual chain-transfer equation containing these modifications takes on the form of Equation (11-32). Experimentally,  $C_1$  is readily determined by measuring

$$1/\overline{DP} = 1/\overline{DP}_0 + C_1[I_2]/[M] \quad (11-32)$$

the number-average molecular weight of the polymer in the presence and absence of the chain-transfer agent. In the present case, where the chain-transfer agent is also the initiator, a mixture of two initiators are used, one of which has either a negligible or known value of  $C_1$ . It must be emphasized that this equation is only valid for effective chain transfer where the new radical formed is 100% efficient in initiating a polymerization reaction.

Equation (11-32) explains the curvature observed in Figure 11-1 for initiators, such as bis(2,4-dichlorobenzoyl) peroxide, which are susceptible to a chain-transfer reaction or, in other terms, to an induced decomposition reaction. In the absence of chain transfer,  $1/\overline{DP}$  is proportional to the first



power of  $R_p$ , according to Equation (11-17). With the occurrence of chain transfer,  $1/\overline{DP}$  becomes dependent upon  $[I_2]$ , and the relationship between  $R_p$  and  $[I_2]$  involves the square of  $R_p$  (11-13). Therefore, the relationship between  $1/\overline{DP}$  and  $R_p$  is a quadratic equation in  $R_p$ .

Many initiators have substantial chain transfer constants,  $C_1$ , which would lead to a significant decrease in molecular weight were it not for the fact that the initiator is normally present in the polymerization reaction mixture in a very low concentration. For example, bis(2,4-dichlorobenzoyl) peroxide has a chain-transfer constant of 2.6 in the polymerization of styrene<sup>34</sup> at 70°C, so that the rate of reaction of the polymer radical with this peroxide is almost three times the rate of its addition to styrene, which is normally considered to be a very reactive monomer. It is primarily this high reactivity which is responsible for the anomalous behavior shown in Figure 11-1. Values of  $C_1$  for other initiators relative to styrene are collected in Table 11-3. Two initiators not listed in Table 11-3 which have been shown to have negligible values of  $C_1$  are azobisisobutyronitrile and dicumyl peroxide.<sup>41</sup>

Table 11-3

Chain-Transfer Constants for Various Initiators  
in the Polymerization of Styrene

Initiator	$C_1$	Temperature, °C
Bis( <i>p</i> -chlorobenzoyl) peroxide	0.21	70
<i>n</i> -Propyl peroxide <sup>38</sup>	0.00084	60
Benzoyl peroxide <sup>36, 39</sup>	0.055	60
	0.075	70
<i>t</i> -Butyl hydroperoxide <sup>40</sup>	0.060	70
Cumene hydroperoxide <sup>40</sup>	0.10	70

The application of the chain-transfer equation, (11-32), requires that the generation of radicals from the labile initiator species be the only original source of free radicals for the polymerization reaction. For monomers such as styrene and methyl methacrylate, however, there apparently is an appreciable, spontaneous initiation reaction caused by a coreaction of the monomer molecules alone. This spontaneous initiation is termed thermal initiation and must be taken into account in the term for the rate of propagation in the chain transfer equation. The corrected value of  $R_p$  due to the peroxide alone is given by Equation (11-33), in which  $R_{p,ob}$  is the

$$R_p = (R_{p,ob}^2 - R_{p,th}^2)^{1/2} \quad (11-33)$$

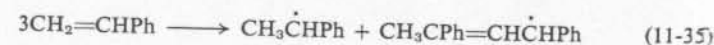
observed rate of polymerization and  $R_{p,th}$  is the rate of polymerization caused by thermal initiation alone.<sup>38</sup> The use of squared terms in the correction is necessary because the rates of initiation,  $R_i$ , are additive and  $R_i$  is proportional to  $R_p^2$ .

**11.1.2.3. Thermal Polymerization.** Elucidation of the mechanism by which the initiation of a controlled free-radical polymerization reaction of certain unsaturated monomers can occur by heat alone in the absence of separate initiator species is an important unsolved problem in polymer chemistry. Initial work in this field led to the proposal that the initiation step was a bimolecular reaction between two monomer molecules (11-34)

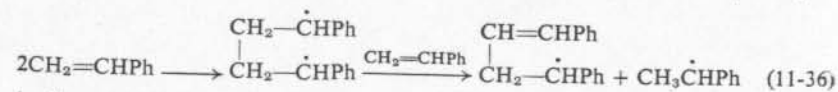


leading to the formation of a diradical which could propagate from both ends.<sup>42</sup> This reaction was calculated to have a heat of reaction of approximately 30 kcal mole<sup>-1</sup> for styrene and was considered, therefore, to be energetically feasible. However, this theory was soon discounted because it was realized that the much higher rate of termination compared to propagation would quickly cause self-combination of the two radical ends before any amount of polymerization could occur.<sup>43</sup> For styrene, for example,  $k_t/k_p$  is approximately  $5 \times 10^4$ .

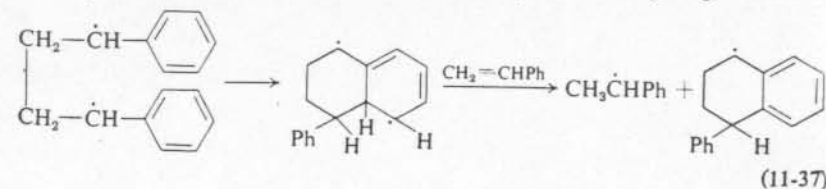
A careful kinetic study of the purely thermal initiation of styrene at 158°C first indicated that the reaction was 5/2 order in monomer concentration, and for this reason, a termolecular reaction (11-35) leading to



the formation of two separate monoradicals was proposed.<sup>44</sup> Subsequent kinetic studies indicated that the initiation was third order in styrene concentration, and a mechanism was proposed which involved an initial bimolecular reaction to form a diradical, which transferred (11-36) a



hydrogen atom to a third molecule of styrene to produce two monoradicals.<sup>45</sup> Another possibility would be the initial formation (11-37) of a tetralin-type diradical, which could conceivably release a hydrogen atom to



styrene monomer. In any case, the initial formation of a diradical is a reasonable suggestion and is consistent with the observation that, in the presence of radical scavengers (initiators), the rate of thermal formation of radicals is much greater than that expected from unmodified thermal polymerization studies.<sup>45</sup> This observation is interpreted to indicate that for styrene many more radicals are generated by purely thermal means than can be used effectively to initiate polymerization reactions, and diradicals would behave in that manner.

Very few monomers exhibit pure thermal initiation. Styrene and methyl methacrylate are the prime examples, and the former is by far the most active known. At 100°C, styrene shows a thermal, self-initiation rate of 14%/hr, while methyl methacrylate has an activity of only about 1% of that of styrene.<sup>46</sup> In contrast, vinyl acetate, methyl acrylate, and vinyl chloride show no measurable polymerization rate at 100°C, and many other monomers undergo only a Diels-Alder reaction at elevated temperatures.<sup>46</sup>

Certain pairs of monomers, such as styrene and maleic anhydride, show an unusually high facility for thermal initiation apparently through cross-initiation.<sup>46</sup> Other monomer pairs, such as styrene and diethyl fumarate,<sup>47</sup> show no tendency for cross-initiation, and some even exhibit a thermal initiation rate considerably below the expected geometric mean of the initiation rates for the two monomers alone. The thermal polymerization of ethylene has been proposed to involve the formation of methylene and methyl radicals, the former by decomposition of excited ethylene molecules, which act as the initiating species.<sup>48</sup>

### 11.1.3. Propagation

In spite of the fact that the activation energy for initiation dominates the apparent activation energy for polymerization, as discussed in Section 11.1.2, still the overall rate of polymerization is generally close to that of the propagation reaction, as assumed in Equation (11-13). Absolute rate constants for propagation can be determined under nonsteady-state conditions, so that the previous statement is not a product of circular reasoning. Some feeling for the magnitude of the quantities involved in the expression for overall rate of polymerization (11-13) can be obtained by assigning approximate, generally observed orders of magnitude to the various rate constants for, in this example, a reaction temperature near 60°C and by assuming normally used concentration ranges, as follows:

Rate constants	Concentrations
$k_p = 10^2 - 10^3 \text{ liter mole}^{-1} \text{ sec}^{-1}$	$[M] = 10^{-1} \text{ to } 10^{-2} \text{ moles liter}^{-1}$
$k_d = 10^{-10} - 10^{-12} \text{ sec}^{-1}$	$[M\cdot] = 10^{-7} \text{ to } 10^{-9} \text{ moles liter}^{-1}$
$k_i = 10^6 - 10^8 \text{ liter mole}^{-1} \text{ sec}^{-1}$	$[I_2] = 10^{-2} \text{ to } 10^{-4} \text{ moles liter}^{-1}$

Using average values for each gives:

$$R_{\text{polym}} = (k_p k_d^{1/2} / k_i^{1/2}) [M] [I_2]^{1/2} \approx 10^{-5} \text{ moles liter}^{-1} \text{ sec}^{-1}$$

$$R_{\text{prop}} = k_p [M] [M\cdot] \approx 10^{-5} \text{ moles liter}^{-1} \text{ sec}^{-1}$$

$$R_i = k_d [I_2] \approx 10^{-9} \text{ moles liter}^{-1} \text{ sec}^{-1}$$

$$R_t = k_i [M\cdot]^2 \approx 10^{-9} \text{ moles liter}^{-1} \text{ sec}^{-1}$$

These estimations are, of course, very rough and seem to be somewhat inconsistent with the steady-state assumption in that  $R_i$  and  $R_t$  are not exactly equal as required. Nevertheless, it does illustrate that the rates of polymerization and propagation are roughly equivalent in most cases.

**11.1.3.1. Dependence on Monomer Concentration.** The rate of polymerization, according to the equation above, should be dependent upon the first power of the monomer concentration when initiation is caused by the thermal decomposition of a separate initiator species. This dependence has been observed in several cases including the homopolymerization reactions of styrene and of methyl methacrylate initiated with benzoyl peroxide, and of methyl methacrylate with azobisisobutyronitrile, all in benzene solution.<sup>50</sup> In other cases, a first-order relationship does not hold, and in some cases the order is not even constant, but varies significantly with monomer concentration. For example, the apparent order of monomer concentration for the polymerization of styrene in toluene initiated with benzoyl peroxide varies from 1.18 at  $[M] = 1.8 \text{ moles liter}^{-1}$  to 1.36 at  $[M] = 0.4$ .<sup>51</sup> For vinyl acetate in benzene, the apparent order of monomer concentration decreases from an unusually high value at high monomer concentrations to a limiting value of about two for dilute solutions.<sup>52</sup>

These exceptions are probably not caused by any abnormality in the growth reaction but have been attributed mainly to one of two causes, either (1) the rate of initiation is not independent of monomer concentration, or (2) premature termination occurs by chain transfer or by reaction with a radical other than that on a polymer chain endgroup. Either one of these occurrences would invalidate the equations used for the kinetic derivations.<sup>53</sup> These two possibilities are also related in that if termination of polymer chains occurred by reaction with initiator radicals, termed primary radicals, to a significant extent, the rate of initiation would become dependent upon  $[M]$  because a decrease in  $[M]$  would tend to reduce the rate of combination of initiator radicals with monomer and increase the rate of termination between polymer radicals and primary radicals. In this case, the order in monomer concentration for  $R_p$  would be greater than 1. For thermal or photochemical initiation, orders of monomer concentration greater than 1 are to be expected because  $[M]$  enters directly into the rate expression for initiation.



**11.1.3.2. Activation Energies and Absolute Rate Constants of Propagation.** For most common monomers the activation energies for the propagation reaction are close to 5 kcal mole<sup>-1</sup>, so that low temperatures may be used for polymerization if an adequate mode of initiation is available. The kinetic parameters for propagation for the more common monomers are collected in Table 11-4.<sup>54</sup> Because of these low activation energies, rates

Table 11-4

Kinetic Parameters for the Propagation Reactions  
in Typical Olefin Polymerizations<sup>54</sup>

Monomer	Log $A_p$ , mole <sup>-1</sup> sec <sup>-1</sup>	$\Delta E_p^\ddagger$ , kcal mole <sup>-1</sup>
Methyl methacrylate	5.9	4.7
Styrene	6.7	7.3
Vinyl acetate	7.5	6.3
Vinyl chloride	6.5	3.7

of propagation show little variation with temperature. The effect of temperature on the overall polymerization rate and on polymer molecular weight is very difficult to predict because temperature changes can affect many variables including the rate of initiation, the efficiency of initiation, the extent of chain transfer, the importance of depropagation (elimination of monomer from the end of an active polymer chain which is the reverse of polymerization), and even the mode of termination.

The activation energies given in Table 11-4 are obtained from absolute rate constants for propagation,  $k_p$ , for each of the monomers listed. Absolute rate constants are best determined by the simultaneous solution of two experimentally obtainable ratios: (1)  $k_p^2/k_t$  obtained from  $R_p$  and Equation (11-13) by knowing  $k_d$ , which can also be obtained experimentally, and (2)  $k_p/k_t$  obtained by two different methods both based upon the variation of radical concentrations in photoinitiated polymerization reactions.<sup>55</sup> In one method for the latter, the decrease in rate of polymerization is measured after the light is turned off, that is, after new free radicals are no longer generated.<sup>56</sup> In such an experimental arrangement, the concentration of free radicals during the dark period,  $[M\cdot]_d$ , would decrease gradually from that during the steady-state period,  $[M\cdot]_s$ , by normal termination reactions according to Equation (11-38). Integration (11-39) followed by substitution of  $R_p/k_p[M]$  for  $[M\cdot]$ , Equation (11-13),

$$-d[M\cdot]/dt = 2k_t[M\cdot]^2 \quad (11-38)$$

$$1/[M\cdot]_d = (1/[M\cdot]_s) - 2k_t t \quad (11-39)$$

yield Equation (11-40) which relates the rate of the polymerization reaction during the initial steady state,  $R_{p,s}$ , and the rate at an instant of time,  $t$ , during the dark period,  $R_{p,d}$ , to the desired rate constant ratio (11-40). A

$$1/R_{p,d} = \frac{1}{R_{p,s}} - 2k_t t/k_p[M] \quad (11-40)$$

plot of  $1/R_{p,d}$  versus  $t$  gives  $k_t/k_p$  from the slope and  $1/R_{p,s}$  as the intercept.

The theory behind the second photochemical method is considerably more complicated. This method, termed the rotating sector method, gives an estimate of the average lifetime,  $\tau_s$ , of a kinetic chain radical under the normal steady-state conditions of constant radical concentration.<sup>55, 57</sup> The desired rate constant ratio can be obtained by relating  $\tau_s$  to the kinetic chain length,  $\nu$ , which is the number of monomer molecules incorporated into one or more polymer molecules (depending on whether or not chain transfer occurs) as the result of propagation reactions caused by one initiator radical. That is,  $\nu$  is the product of  $\tau_s$  and the rate of polymerization per radical (11-41), and this relationship can be converted to measurable quantities (11-42) by use of Equations (11-14) to (11-17).

$$\nu = \tau_s R_p/[M\cdot] \quad (11-41)$$

$$\tau_s = k_p[M]/2k_t R_p \quad (11-42)$$

The experimental technique employed is to illuminate a polymerization reaction through open sectors in an opaque disk, which can be made to rotate at different speeds. If the rotation is very slow, so that the time of illumination through each sector is long compared to  $\tau_s$ , the polymerization reaction will progress at essentially the steady-state rate during the light period and be essentially absent during the dark period. Therefore, if the lengths of time of the light and dark periods are equal, the average rate of polymerization will be  $(1/2)R_p$ , that is, one-half of the rate for continuous illumination. On the other hand, if rotation is very rapid and the time of illumination is less than  $\tau_s$ , steady-state conditions will never be attained. At best, the rate of initiation will be  $(1/2)R_{i,s}$ , so that the rate of polymerization will be  $(1/\sqrt{2})R_{p,s}$ . Somewhere between these two extremes of rotation speed, the time of illumination through each sector will exactly equal  $\tau_s$ , and the latter can be obtained from the shape of the curve of  $R_p$  versus time of illumination.

This procedure, combined with a determination of  $k_p^2/k_t$ , has been used to obtain a detailed picture of the polymerization of vinyl acetate at 25°C initiated by the photolytic decomposition of *t*-butyl peroxide. The various observed rates and rate constants, which are more or less typical for a

radical polymerization of unsaturated monomers, are collected in Table 11-5 for two different intensities of illumination.<sup>58</sup> The kinetic chain length,

Table 11-5

Absolute Values of Kinetic Parameters for the Photoinitiated Polymerization of Vinyl Acetate<sup>58</sup>

Parameter	Intensity of illumination		Units
	Low intensity	High intensity	
$R_i$	$1.11 \times 10^{-9}$	$7.29 \times 10^{-9}$	moles liter <sup>-1</sup> sec <sup>-1</sup>
$R_{p,s}$	$0.450 \times 10^{-4}$	$1.19 \times 10^{-4}$	moles liter <sup>-1</sup> sec <sup>-1</sup>
$\tau_s$	4.00	1.50	sec
$k_p$	$0.94 \times 10^3$	$1.01 \times 10^3$	liters mole <sup>-1</sup> sec <sup>-1</sup>
$k_t$	$2.83 \times 10^7$	$3.06 \times 10^7$	liters mole <sup>-1</sup> sec <sup>-1</sup>
$[M\cdot]$	$0.44 \times 10^{-8}$	$0.54 \times 10^{-8}$	moles liter <sup>-1</sup>

$\nu$ , in these reactions as calculated from Equation (11-41) was approximately  $4 \times 10^4$  monomer molecules per radical, but the average degree of polymerization obtained was about  $3.5 \times 10^3$  monomer molecules per polymer, which is much less than  $\nu$ . Therefore, each radical generated must produce about ten polymer chains, apparently as the result of chain transfer. If so, it is interesting to note that a polymer chain containing over 1000 monomer molecules is formed in less than one-half second.<sup>58</sup>

Absolute rate constants for propagation and termination have been

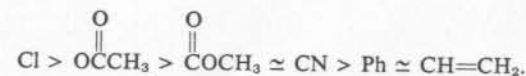
Table 11-6

Absolute Values of Propagation and Termination Rate Constants for Common Monomers<sup>54, 59</sup>

Monomer	Rate constants, liters mole <sup>-1</sup> sec <sup>-1</sup>			
	$k_p$		$k_t \times 10^{-7}$	
	30°C	60°C	30°C	60°C
Methyl acrylate	720	2090	0.22	0.47
Methyl methacrylate	350	705	1.5	1.8
Acrylonitrile	—	1960	—	60
Methacrylonitrile	29	184	1.1	2.3
Styrene	49	145	0.24	0.30
Vinyl acetate	990	2300	2.0	2.9
Vinyl chloride	6800	12,300	1200	2300
1,3-Butadiene	25	100	—	—

determined in this manner and by other less generally applied procedures for most common monomers, as shown in Table 11-6.<sup>54, 59</sup> As expected, the nature of the substituent and the number of substituents on a double bond have a controlling effect on the rate of the radical addition reaction, and over a 300-fold variation is found in Table 11-6 for the rate constants for different monomers. This variation can be explained on the basis of resonance and steric effects caused by the substituents on the transition state of the addition reaction in the propagation step.

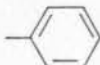
**11.1.3.3. Monomer Reactivities.** The rates of propagation for the monomers in Table 11-6 as determined by the substituent on the double bond are in the order:



This order is caused primarily by a resonance effect which must influence the reactivities of both the monomer molecule and the polymer radical. As will be shown below, there is no doubt that of the two reactivities the more important reactivity is that of the radical, and resonance stabilization of the radical by a particular conjugated substituent is much greater than the stabilization of the monomer. A comparison of the two magnitudes of stabilization by resonance interaction is given in Table 11-7, in which the

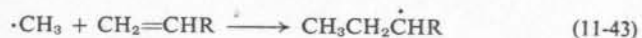
Table 11-7

Resonance Stabilization Energies of Monomers and the Radicals Formed from Them in a Free-Radical Polymerization Reaction<sup>60, 61</sup>

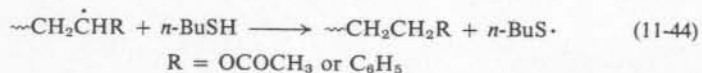
Monomer	Conjugated substituent	Relative value of $k_p$ at 60°C	Resonance stabilization energy, kcal mole <sup>-1</sup>	
			Double bond	Radical
Vinyl acetate	$\text{—O}=\text{CCH}_3$	23.0	1.7	4
Methyl methacrylate	$\text{—COCH}_3$	7.05	4.2	~23
Styrene		1.45	4.2	24.5
1,3-Butadiene	$\text{—CH}=\text{CH}_2$	1	6.0	25

amount of stabilization of the double bond is taken from the heat of hydrogenation,<sup>60</sup> and the amount of stabilization of the radical is based upon bond dissociation energies.<sup>61</sup>

The pattern and extent of variations in  $k_p$  are seen to be more in line with the variations in resonance stabilization of the radical than of the double bond in the monomer. Other patterns of reactivities also support this conclusion in that: (1) methyl radicals react about 25 times faster with styrene than with vinyl acetate at 60°C (11-43),<sup>62</sup> which is opposite to the

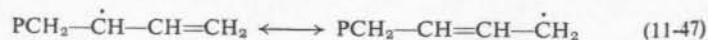
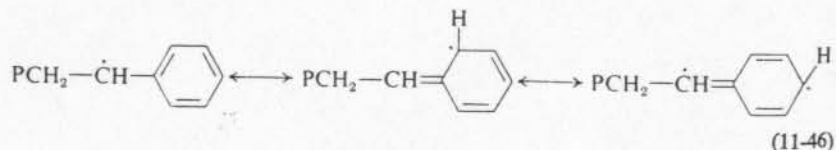
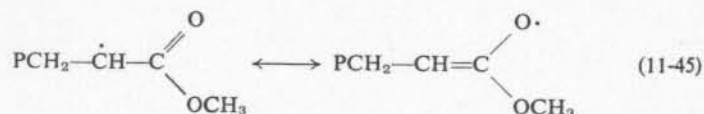


order of propagation reaction rates, while (2) the poly(vinyl acetate) radical reacts 46 times faster with *n*-butyl mercaptan at 60°C (11-44) than

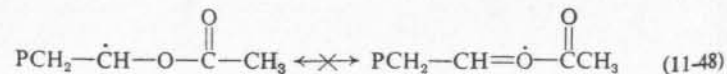


does the polystyrene radical, which is consistent with the order of propagation.<sup>63</sup> The relationship obtained for the former reaction depends upon the relative reactivities of the monomers, while that in the latter reaction depends upon the relative reactivities of the radicals, so it is again apparent that the reactivity of the radical virtually determines the rate of a homopolymerization reaction.

For three of the four monomers above, methyl acrylate, styrene, and butadiene, resonance stabilization of the corresponding polymer radicals, Structures (11-45)–(11-47), respectively, occurs through conjugation of the



carbon atom bearing the unpaired electron with adjacent unsaturated groups. For the fourth monomer, vinyl acetate, the polymer radical (11-48)

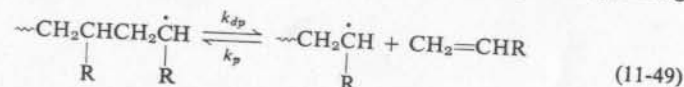


has no such opportunity because the adjacent oxygen atom can only accommodate eight electrons in its outer orbitals.

The decrease in  $k_p$  observed when a methyl group is substituted on the  $\alpha$ -position of olefin monomers, as for both methyl methacrylate versus methyl acrylate and methacrylonitrile versus acrylonitrile, can be attributed to either additional resonance stabilization of the radical (by approximately 4 kcal mole<sup>-1</sup>) or to steric hindrance in the addition reaction caused by this group. Probably both factors contribute to the substantial decreases observed.

Polar effects in free-radical homopolymerization reactions have been observed within a series of *p*-substituted styrene monomers including *p*-methoxy-, *p*-methyl-, *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-cyanostyrene.<sup>64</sup> The styrene monomers with the more electron-attracting substituents have higher overall rate constants, and the rate constants follow a Hammett relationship with a  $\rho$  value of +0.6. The participation of ionic structures in the transition state has been suggested to explain this polar effect.<sup>64</sup>

**11.1.3.4. Depropagation and Ceiling Temperatures.** As discussed in the previous chapter, one of the basic reactions which free radicals undergo is unimolecular elimination. This reaction is particularly important at elevated temperatures, as witnessed by the accelerated rate of decarboxylation of benzoyloxy radicals, which are derived from the dissociation of benzoyl peroxide (11-23), with increased temperature. Similarly, the elimination (11-49) of monomer from the radical endgroup of a growing



polymer chain becomes increasingly important at higher polymerization reaction temperatures. This reaction is the reverse of the propagation reaction and is termed depropagation or depolymerization. For every monomer there is a temperature,  $T_c$ , at which the rate of depropagation becomes equal to the rate of propagation (11-50), and this temperature is

$$k_p[\text{M}][\text{M}\cdot] = k_{dp}[\text{M}\cdot] \quad (11-50)$$

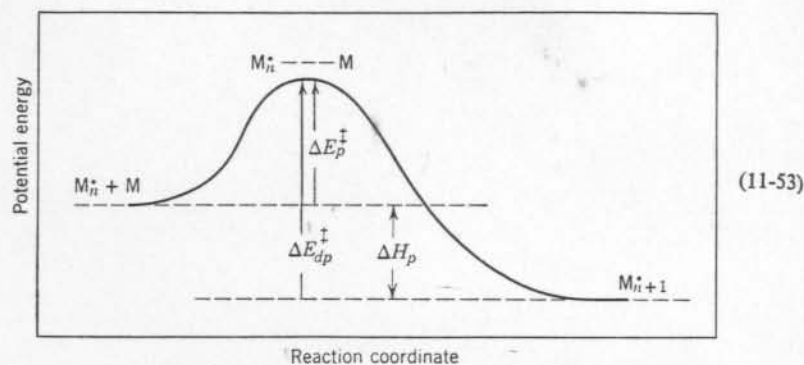
termed the ceiling temperature<sup>58</sup> of the polymerization reaction. The magnitude of this temperature can be obtained in terms of activation energies and frequency factors (11-52) from standard kinetic expressions (11-51) or in terms of the heat of polymerization,  $\Delta H_p$  (11-52), which is

$$A_p \exp(-\Delta E_p^\ddagger/RT_c)[\text{M}] = A_{dp} \exp(-\Delta E_{dp}^\ddagger/RT_c) \quad (11-51)$$

$$T_c = (\Delta E_p^\ddagger - \Delta E_{dp}^\ddagger)/R \ln(A_{dp}[\text{M}]/A_{dp}) = -\Delta H_p/R \ln(A_p[\text{M}]/A_{dp}) \quad (11-52)$$



identical to the difference between the two activation energies as shown by a typical reaction coordinate representation, (11-53).



When the rates of propagation and depropagation are equal, an equilibrium must exist between the two reactions or between monomer molecules and polymer radicals, assuming no termination occurs. Therefore, the ceiling temperature can be expressed in thermodynamic terms (11-54), as well as in terms of kinetic parameters. All known propagation reactions of unsaturated monomers are exothermic because two single bonds are stronger than one double bond. At low temperatures, this negative  $\Delta H_p$  offsets the entropy of propagation, which is also negative because polymerization is an aggregation process. The result is an overall, negative, free-energy change for the propagation reaction. At high temperatures, the negative entropy term,  $T\Delta S_p$ , eventually becomes greater than the  $\Delta H_p$  term, and at that point,  $\Delta F_p$  becomes positive. Beyond this point, polymerization to form high molecular weight polymer is impossible.

The kinetic (11-52) and thermodynamic (11-54) equations can be com-

$$\Delta F_p = \Delta H_p - T_c \Delta S_p = 0 \quad (11-54)$$

$$T_c = \Delta H_p / \Delta S_p$$

bined into an equation, (11-55), which indicates clearly that  $T_c$  increases with increasing  $[M]$ , because both  $\Delta H_p$  and  $\Delta S_p^0$ , the entropy of polymerization at the standard state, are negative. Rearrangement of Equation (11-55) gives a relationship, (11-56), which can be applied experimentally

$$T_c = \Delta H_p / (\Delta S_p^0 + R \ln [M]_c) \quad (11-55)$$

$$\ln [M]_c = \Delta H_p / RT_c - \Delta S_p^0 / R \quad (11-56)$$

for the determination of changes in heat content, entropy, and free energy accompanying polymerization by measurement of equilibrium monomer concentrations at various temperatures. All of these equations apply

equally as well to ionic polymerization reactions as to free-radical reactions, again assuming that active endgroups remain alive long enough for the equilibrium to be established, and to the polymerization of cyclic monomers as well as to unsaturated compounds of all types.<sup>65, 66</sup>

Equation (11-55) reveals that for each monomer concentration there is a specific ceiling temperature, and by the same token, Equation (11-56) indicates that at each polymerization temperature there is a specific monomer concentration,  $[M]_c$ , which will exist in equilibrium with active polymer chains. Because of the latter, no chain-growth polymerization reaction can ever be driven quantitatively to completion. That is, all polymers formed by an addition polymerization reaction will contain a finite amount, however small, of unreacted monomer, assuming no side reactions occur. For most polymers derived from olefin monomers, the concentrations of monomer in equilibrium with the polymer are very low at ordinary temperatures. The estimated values of  $[M]_c$  for some common monomers at 25°C are compiled in Table 11-8.<sup>65</sup> At 132°C, the estimated

Table 11-8

Equilibrium Monomer Concentrations in the  
Polymerization of Various Olefin  
Monomers at 25°C<sup>65</sup>

Monomer	$[M]_c$ moles liters <sup>-1</sup>
Methyl acrylate	10 <sup>-9</sup>
Methyl methacrylate	10 <sup>-3</sup>
Styrene	10 <sup>-6</sup>
Vinyl acetate	10 <sup>-9</sup>

value<sup>67</sup> of  $[M]_c$  for methyl methacrylate is approximately 0.5 mole liter<sup>-1</sup>, so that the polymerization reaction will stop noticeably short of quantitative conversion at this temperature. At 160°C, a monomer-polymer equilibrium mixture from the polymerization of methyl methacrylate contains 2.9% monomer.<sup>68</sup> In contrast to the monomers in Table 11-8, some monomers show remarkably high values of  $[M]_c$  even at room temperature, and  $\alpha$ -methylstyrene is a notable example of this class. For  $\alpha$ -methylstyrene,<sup>65</sup>  $[M]_c = 2.6$  moles liter<sup>-1</sup> at 25°C, and as a result, this monomer is extremely reluctant to polymerize at temperatures above 0°C. However,  $\alpha$ -methylstyrene will polymerize at high pressure because the ceiling temperature is increased from 61°C at 1 atm to 171°C at 6480 atm.<sup>69</sup>

The calculated or observed ceiling temperatures for the bulk polymerization reactions of three monomers of interest are collected in Table

11-9.<sup>70,71</sup> Above these temperatures as stated above, the formation of high molecular weight polymers from these monomers becomes impossible, and only very short chain polymers can be produced. Schematic representations of the effect of temperature on the rate of a polymerization reaction and on the molecular weight as the ceiling temperature is approached are depicted in Figure 11-2.<sup>65</sup> In Figure 11-3 are the calculated curves of the

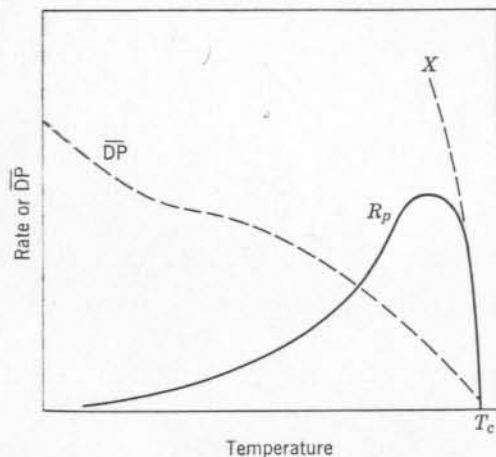


Figure 11-2. Expected shapes of rate-temperature and  $\overline{DP}$ -temperature curves<sup>65</sup>;  $X = \lim_{T \rightarrow T_c} (dR_p/dT)$ .

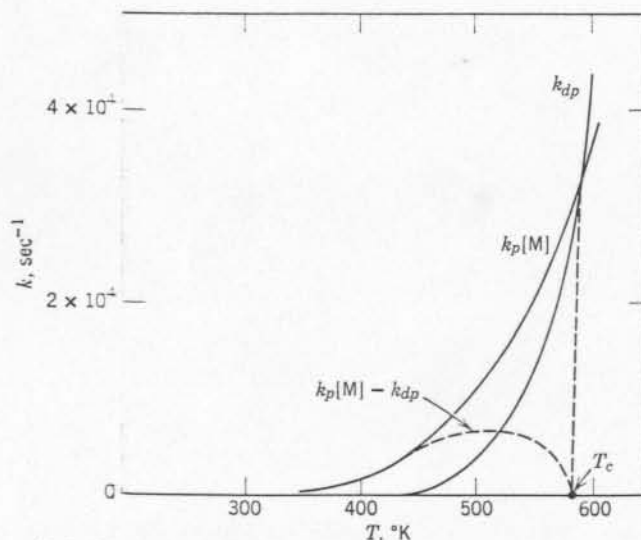


Figure 11-3. Variations of rate constants with temperature for styrene.<sup>65</sup>

Table 11-9  
Ceiling Temperatures for the Polymerization  
Reactions of Common Olefin Monomers<sup>70,71</sup>

Monomer	$T_c$ , °C
Methyl methacrylate	220
Styrene	310
$\alpha$ -Methylstyrene	61

rate constants for propagation and depropagation, and the resultant curve representing the effective rate constant (11-57) for the polymerization of styrene.<sup>65</sup>

$$R_p = (k_p[M] - k_{dp})[M\cdot] \quad (11-57)$$

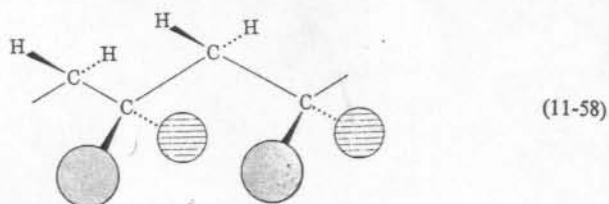
**11.1.3.5. Heat of Polymerization.** The magnitudes of the heat of polymerization for olefin monomers fit into a consistent pattern attributable to the importance of steric effects in addition polymerization reactions. Heats of polymerization for some of the more important monomers are collected in Table 11-10.<sup>72,73</sup> The variations in  $\Delta H_p$  values are determined

Table 11-10  
Heat of Polymerization of Various Olefin Monomers<sup>72-74</sup>

Monomer	$-\Delta H_p$ , kcal mole <sup>-1</sup>	Resonance energy of double bond, kcal mole <sup>-1</sup>
Acrylonitrile	17.3	—
Methyl acrylate	18.7	—
Methyl methacrylate	13.0	4.2
Styrene	16.4	4.2
$\alpha$ -Methylstyrene	8.4	—
Vinyl acetate	21.3	1.7
Vinyl chloride	26.0	—
Vinylidene chloride	14.4	—
Tetrafluoroethylene	33.0	—
Isobutene	12.6	4.4
Acenaphthylene	24.0	—

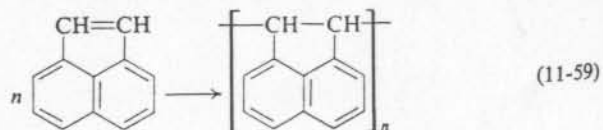
primarily by two effects: (1) differences in resonance stabilization of the double bond in the monomer by the conjugated substituent, estimated in the table from heats of hydrogenation,<sup>61</sup> and (2) steric strains imposed on the newly formed single bonds in the polymer resulting from interactions

between the substituents on alternate carbon atoms along the chain backbone (11-58).



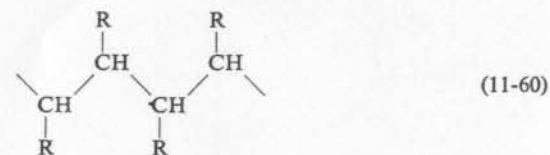
The greater the degree of resonance stabilization of the double bond in the monomer the lower should be the exothermic heat of polymerization. This effect may account for some of the difference between the  $\Delta H_p$  values for styrene and vinyl acetate, but the near identities of resonance stabilization for styrene and isobutene are inconsistent with the significant difference in  $\Delta H_p$  values. Apparently, the degree of steric strain built into the polymer as a result of the addition reaction is much more important and can amount to a residual energy content in the new single bonds of more than 10 kcal mole<sup>-1</sup>, as indicated by a comparison of  $\Delta H_p$  for vinyl chloride and vinylidene chloride. The presence of two chlorine atoms (van der Waal's radius of 1.80 Å.)<sup>75</sup> on every other carbon atom would be expected to result in the formation of steric strains of considerable magnitude within the carbon-carbon bonds along the backbone. The two methyl groups (van der Waal's radius of 2.0 Å.)<sup>75</sup> in isobutene cause even greater strains, and the combination of a methyl and a phenyl group (half-thickness of 1.70 Å.)<sup>75</sup> in  $\alpha$ -methylstyrene produces a strain considerably greater than the additive effect of either one alone. The unusually high steric strain in poly( $\alpha$ -methylstyrene) is responsible for the extreme facility of the depropagation reaction and, consequently, for the low ceiling temperature with this polymer. Surprisingly, two phenyl groups appear to impart less strain than one phenyl group and one methyl group, because the ceiling temperature for 1,1-diphenylethylene is approximately 104°C compared to 61°C for  $\alpha$ -methylstyrene.<sup>66</sup> The lower  $\Delta H_p$  for methyl methacrylate compared to styrene is consistent with the lower  $T_c$  of the former.

The remarkably high value of  $\Delta H_p$  for tetrafluoroethylene apparently results from the much higher carbon-carbon bond strengths in fluorocarbons compared to hydrocarbons. For example, the bond dissociation

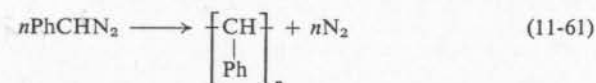


energies for the carbon-carbon bonds in ethane and hexafluoroethane are 83 and 124 kcal mole<sup>-1</sup>, respectively. The unusually high  $\Delta H_p$  for acenaphthylene has been attributed to the relief of steric strain in the five-membered ring in converting the double bond in the monomer to a single bond in the polymer,<sup>72</sup> Reaction (11-59).

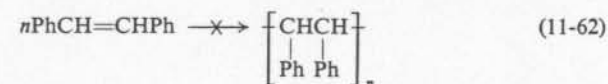
**11.1.3.6. Polymerization of 1,2-Disubstituted Monomers.** The reluctance of 1,1-disubstituted monomers, such as  $\alpha$ -methylstyrene, to polymerize was attributed in the previous section to a ceiling temperature or thermodynamic effect. Similarly, most 1,2-disubstituted monomers show a marked inability to polymerize, but in this case, while the reluctance to react is also caused by steric inhibition, the polymerization reaction does not necessarily have an unfavorable free-energy change. Polymers containing substituents on every carbon atom in the chain (11-60) can be obtained by



other types of polymerization reactions, and these structures once formed are not overly strained but are thermodynamically stable. For example, polyphenylmethylenes can be prepared by the ionic polymerization (11-61)



of phenyldiazomethane,<sup>76</sup> but not by the ionic or radical polymerization (11-62) of stilbene. For many years, maleic anhydride defied polymeriza-

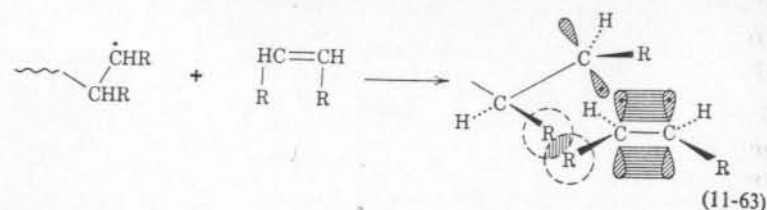


tion, and only recently have techniques been found which would permit this reaction. From the procedures used for this purpose, it now seems that maleic anhydride is best polymerized while in an electronically excited state.<sup>77</sup> Esters of cinnamic acid,  $\text{PhCH=CHCOOR}$ , show little or no tendency to polymerize under normal conditions, but low polymers are formed when the free-radical polymerization reaction is carried out under 10,000 atm pressure.<sup>78</sup>

The failure of 1,2-disubstituted olefin monomers in general to polymerize has been attributed to kinetic, not thermodynamic, effects. The kinetic effect is rationalized on the basis of a steric interaction between one



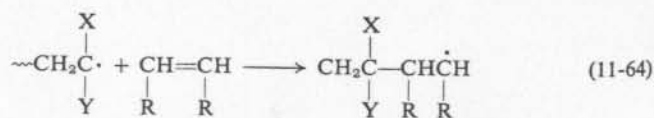
of the two substituents on the olefin and the  $\beta$ -substituent of the endgroup radical on the polymer chain (11-63).<sup>79</sup> This interaction hinders the



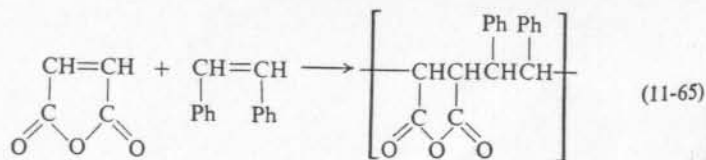
approach of one molecule to the other and, in addition, subsequently imposes a strain on the bonds being established in the transition state. This type of steric hindrance, if significant, would increase the activation energy required for the addition reaction and slow down the rate of propagation to such an extent as to favor the occurrence of a chain transfer or a termination step instead.

Maleic anhydride, for example, has been reported to have a high monomer chain-transfer constant and also a strong tendency towards inducing either chain transfer or induced decomposition of many initiators.<sup>80</sup> Of particular interest in this regard is the fact that the heat of polymerization for this monomer is not low, approximately 14 kcal mole<sup>-1</sup>, which would indicate that its ceiling temperature would be quite favorable for polymerization and would, in fact, be higher than that for the polymerization of methyl methacrylate assuming comparable values of  $\Delta S_p$ .

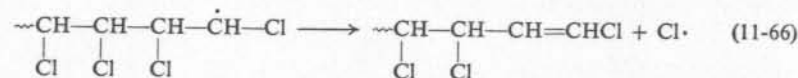
In addition to this observation, further support for the proposal, that the reluctance of 1,2-disubstituted monomers to polymerize is caused by steric hindrance between the  $\beta$ -substituent on the radical and one of the substituents on the monomer (11-63), is provided by the fact that virtually all 1,2-disubstituted olefins which do not homopolymerize will readily copolymerize with 1,1-disubstituted olefins (11-64).<sup>79</sup> An apparent



contradiction to this rationale, however, is that stilbene and maleic anhydride copolymerize (11-65) under conditions for which neither one will



homopolymerize,<sup>81</sup> but this reaction could be aided considerably by a strongly favorable polar effect between the electron-poor anhydride and the electron-rich stilbene, possibly even to the point of the two monomers forming a charge-transfer complex. Symmetrically disubstituted olefins such as 1,2-dichloroethylene may undergo a third type of secondary reaction, other than transfer and termination, which also prevents high polymer formation. This reaction is elimination of a  $\beta$ -substituent (11-66).



It is difficult to make broad generalizations which will apply to predictions of the probable behavior of all 1,2-disubstituted olefin monomers because there are a number of unexplained exceptions, such as the facility of the free-radical polymerization reaction of vinylene carbonate to form high molecular weight polymers.<sup>82</sup> It is apparent that considerably more fundamental information must be gathered in this area.

**11.1.3.7. Chain Transfer.** The effect of chain transfer on reducing initiator efficiency and a quantitative treatment of this effect were discussed in Section 11.1.2.2. Many possibilities or sites for chain transfer, other than the initiator molecule, exist in free-radical polymerization reactions, including transfer to monomer and to polymer and also to solvent in solution polymerization reactions. Unlike transfer to initiator discussed previously, these other transfer reactions often result in a decrease in the rate of the polymerization reaction as well as a decrease in the molecular weight of the polymer produced. A decrease in  $R_p$  is quite common and is attributable to the formation of a relatively stable radical by transfer to the monomer, polymer, or solvent. An exaggerated case of this effect was discussed in Section 10.3.5 for transfer to allylic monomers. In this case, a radical was produced which was too stable to reinitiate the polymerization reaction; this phenomenon has been termed degradative chain transfer.<sup>83</sup> Another extreme case is chain transfer to phenolic or aromatic amine compounds, which are so effective both in scavenging radicals and in preventing reinitiation that  $R_p$  can be reduced to a negligible value. These compounds act, therefore, as inhibitors or retarders for free-radical polymerization reactions.

If the radical formed by chain transfer is active enough to reinitiate the polymerization reaction, then quantitative information can be obtained from determination of the decrease in degree of polymerization by use of an extension of Equation (11-29) to include polymer chain termination caused by transfer to monomer,  $k_{trM}$ , to polymer,  $k_{trP}$  and to solvent,  $k_{trS}$  (11-67),

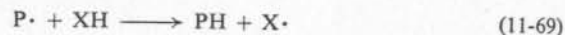
as well as to initiator,  $k_{trI_2}$ . Taking the reciprocal of Equation (11-67), substituting in  $\overline{DP}_0$  (the observed  $\overline{DP}$  in the complete absence of transfer reactions) for the first term on the right hand side, and replacing the rate

$$\overline{DP} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2 + k_{trI_2}[M\cdot][I_2] + k_{trM}[M\cdot][M] + k_{trS}[M\cdot][S]} = \frac{R_p}{R_t} \quad (11-67)$$

constant ratios with the various chain-transfer constants ( $C = k_{tr}/k_p$ ) as before provides the equation, (11-68), and method most generally used for ascertaining chain transfer activity of the various components present in a polymerization reaction.

$$1/\overline{DP} = 1/\overline{DP}_0 + C_i[I_2]/[M] + C_M + C_S[S]/[M] \quad (11-68)$$

The magnitude of the chain transfer constant,  $C_x$ , for a particular polymer radical with a particular substrate, X, is again dependent upon resonance and polar effects in both the radical and substrate. Steric effects are generally of no controlling importance when the chain-transfer step is an abstraction reaction (11-69) of either a hydrogen or halogen atom from



the substrate. The resonance effect on the rate of transfer,  $k_{tr}$ , is determined by the relative strengths of the bond being broken, XH, and the bond being formed, PH. The bond strengths in turn are largely attributable to the stability of the two radicals,  $P\cdot$  and  $X\cdot$ . The more reactive the attacking radical,  $P\cdot$  (that is, the less resonance stabilized) and the more stable the product radical,  $X\cdot$  (that is, the more resonance stabilized) the faster will be the transfer reaction. Therefore, for a particular substrate, the order of reactivity for various polymer radicals in undergoing transfer will parallel the order of homopolymerization rate of the monomer from which the radical is formed, unless polar effects also come into play in the transfer reaction. The propagation rate constants for different monomers increase with decreasing resonance stabilization of the corresponding radicals, as discussed in Section 11.1.3.2, and, for exactly the same reasons, so too do the chain-transfer rate constants.

This effect is shown quantitatively in Table 11-11 by the chain-transfer constants and transfer rate constants for several polymer radicals with toluene as the substrate.<sup>84-86</sup> According to this data, the reactivity of polymer radicals to toluene solvent,  $k_{tr}$ , is strongly determined by the substituent stabilizing the radical, and the ability of substituents to decrease radical reactivity follows the following order:

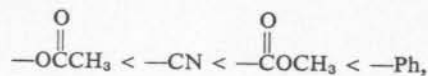


Table 11-11

Chain-Transfer Constants and Rate Constants for Various Polymer Radicals with Toluene Solvent<sup>a</sup>

Polymer radical	$C_s \times 10^4$	$k_{trS}$ , liters mole <sup>-1</sup> sec <sup>-1</sup>
Methyl acrylate	2.7	0.56
Methyl methacrylate	4.0	0.028
Acrylonitrile	4.0	0.785
Styrene	0.16	0.0023
Vinyl acetate	34.0	7.73

<sup>a</sup> At 60°C.<sup>84-86</sup>

which is essentially the order for values of  $k_p$ . Once again the stabilizing influence of a methyl group, which exerts its influence through hyperconjugation with the unpaired electron of the radical, is apparent from a comparison of the much greater reactivity of methyl acrylate compared to methyl methacrylate.

For the chain-transfer reactions with toluene, which is more or less electronically neutral, there is very little polar effect in the transition state, but in cases where the substrate is strongly electronegative or electropositive, the polar effect can become important and can cause inversions in the reactivity order. In cases of this type, the values of  $k_{tr}$  will form a linear relationship with the values of  $k_p$  as is observed with toluene and other nonpolar hydrocarbon substrates. For example, note the inversions in Table 11-12 for the orders of the rate constants in chain-transfer reactions

Table 11-12

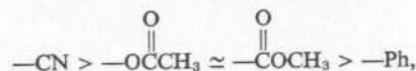
Polar Effects on Chain-Transfer Reactions<sup>a</sup>

Polymer radical	<u>electron rich</u> Et <sub>3</sub> N		<u>electron poor</u> CBr <sub>4</sub>	
	$C_s$	$k_{tr}^b$	$C_s$	$k_{tr}^b$
Methyl acrylate	0.040	84	2.2	4600
Methyl methacrylate	0.00083	0.59	0.27	190
Acrylonitrile	0.59	120	0.19	370
Styrene	0.00071	0.10	0.41	59
Vinyl acetate	0.037	85	> 39	> 90,000

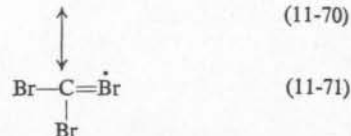
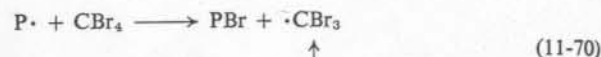
<sup>a</sup> At 60°C.<sup>87,88</sup>

<sup>b</sup> liters mole<sup>-1</sup> sec<sup>-1</sup>.

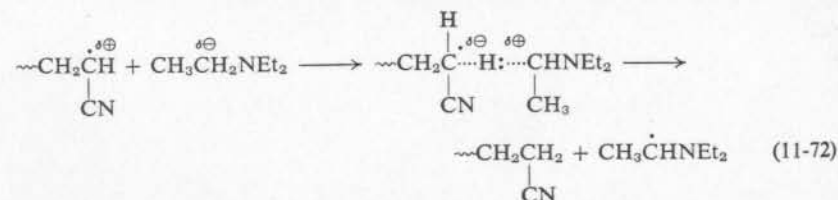
of the polymer radicals in the previous table with an electron-rich solvent, triethylamine, and with an electron-poor solvent, carbon tetrabromide.<sup>87, 88</sup> For the electron-rich solvent, the order of reactivities is



showing the significant alteration due to the polar effect of the substituent. It is of interest to note from the data in Table 11-12 that the chain-transfer rate constants for carbon tetrabromide, Equation (11-70), are as high or higher than the propagation rate constants for the monomers in that table, undoubtedly because of the high stability of the tribromomethyl radical, Equation (11-71).



The large polar effect for solvents such as triethylamine with radicals such as the polyacrylonitrile radical is generally rationalized on the basis of partial charge transfer in the transition state of the reaction (11-72).<sup>89</sup>



Substrates of this type which can donate electrons in the transition state are termed donor solvents, while substrates which attract electrons are termed acceptor solvents. Radicals are classified on the same basis, so that for the previous monomers under discussion, the polystyrene and poly(vinyl acetate) radicals are donor radicals while the polyacrylate and polyacrylonitrile radicals are acceptor radicals. Resonance effects being equal, the reactivity of a donor radical will always be greater with an acceptor solvent than with a donor solvent and vice versa, as shown in Table 11-13 for the polystyrene, PS·, and poly(methyl methacrylate), PMMA·, radicals.<sup>84</sup>

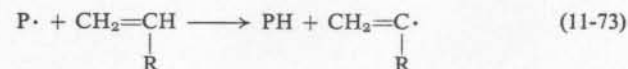
Attempts have been made to treat polar effects quantitatively by use of a linear, free-energy equation similar to the Hammett equation<sup>90</sup> and also by a modification of the *Q-e* treatment used for the correlation of copolymerization rate constants.<sup>88</sup> Both treatments are empirical in nature. The

**Table 11-13**  
Chain-Transfer Reactions between Donor and  
Acceptor Radicals and Solvents<sup>84</sup>

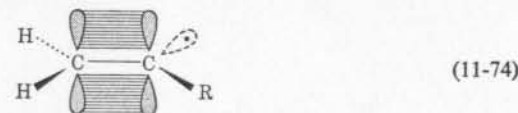
Solvent	Character	Radical, $C_s \times 10^4$	
		PS·(donor)	PMMA·(acceptor)
CCl <sub>4</sub>	Acceptor	170	3.3
(CH <sub>3</sub> ) <sub>2</sub> CO	Acceptor	4.1	0.20
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	Acceptor	5.5	0.13
<i>n</i> -BuSH	Acceptor	220,000	6700
PhCH <sub>3</sub>	Donor	0.16	0.4
PhN(CH <sub>3</sub> ) <sub>2</sub>	Donor	53	430
PhCH(CH <sub>3</sub> ) <sub>2</sub>	Donor	0.82	1.9

former permits predictions of  $k_{tr}$  values within a factor of three, and the latter has been given only limited application but looks promising.<sup>91</sup>

Chain transfer to vinyl monomers involving an abstraction reaction of vinylic hydrogen atoms (11-73) is an inherently slow reaction because of the



high bond energies of these carbon-hydrogen bonds. The high bond energies, in turn, can be attributed to the inability of either the substituent, *R*, or the double bond to delocalize the unpaired electron, and thereby to stabilize the radical by resonance, because the orbital of the unpaired electron is in the nodal plane of the  $\pi$ -bonding system (11-74),



and interaction cannot occur efficiently. Chain-transfer constants of some of the more important vinyl monomers with their own polymer radicals at 60°C are listed in Table 11-14.<sup>92</sup>

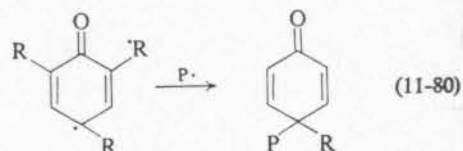
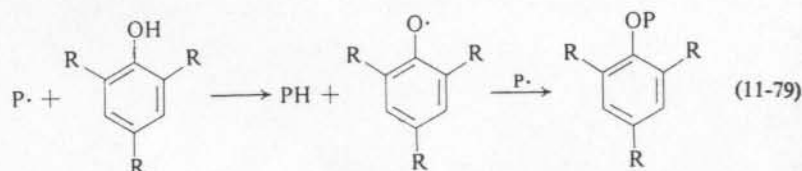
The chain-transfer constant for vinyl acetate is much higher than the others in Table 11-14 because the transfer site is not the vinylic hydrogen atom but the acetoxy hydrogen atom (11-75), which is a reactive site in that the resulting radical is stabilized by resonance interaction with the carbonyl group (11-76). The site is equally reactive in the polymer, as shown in the data in Table 11-15.<sup>84</sup> As a result of this high degree of



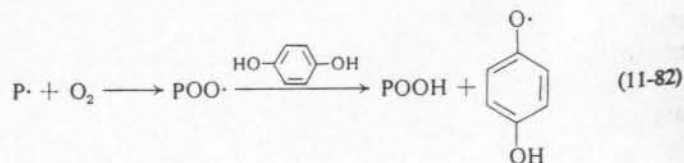
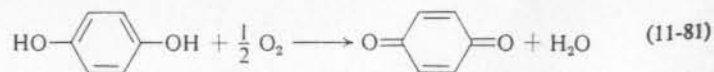


efficient in trapping and stopping kinetic chains will at least cause a significant decrease in the rate of polymerization. Such a compound is termed a retarder. Useful inhibitors for free-radical polymerization reactions must react much faster with radicals than does the monomer because the monomer is almost always present in much larger amounts. This is particularly true in practical applications such as monomer storage, where it is undesirable to have much more than trace amounts of inhibitor present when the monomer is to be used directly in polymerization reactions.

As discussed in Section 10.5, the principal types of chain-transfer inhibitors are the alkyl-substituted phenols and arylamines. There is little quantitative information and much doubt on the mechanism of inhibition and retardation by these compounds. For phenols, it appears most likely that the initial step (11-79) is abstraction of the phenolic hydrogen atom,

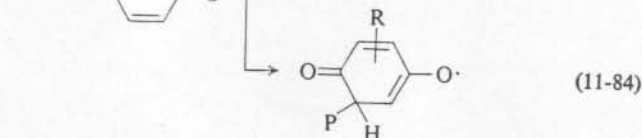
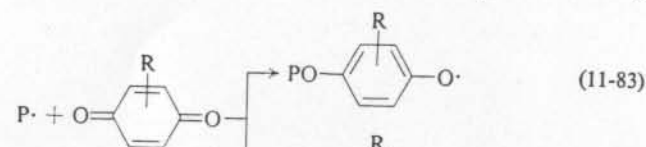


but the site of the subsequent coupling reaction is not firmly established.<sup>101</sup> For hydroquinone, several workers have reported that the presence of oxygen is required for effective inhibition,<sup>102</sup> and similar results have been reported for *t*-butylcatechol.<sup>103</sup> For the former, therefore, either the phenolic compound is first oxidized (11-81) to the quinone, which is the

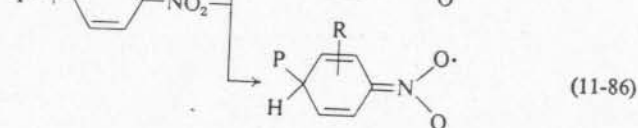
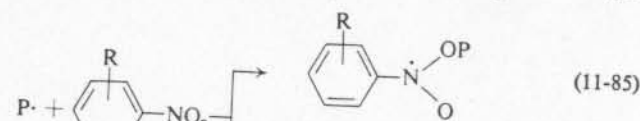


active inhibitor, or hydroquinone is an inefficient scavenger for polymer radicals and only reacts readily with peroxy radicals (11-82). This latter rationale, however, is difficult to accept because peroxy radicals are generally considered to be of low reactivity, and oxygen itself is an efficient inhibitor to the polymerization of many olefin monomers. On the other hand for some monomers, notably styrene, oxygen readily copolymerizes to form a polyperoxide.

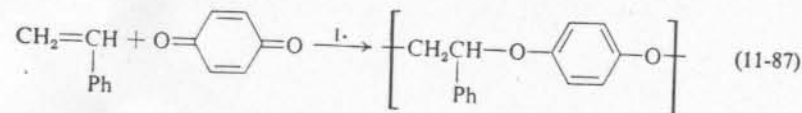
Quinones are an example of another and probably more important class of compounds used for inhibition. This class includes all of the various types of compounds which form unreactive radicals by a radical addition reaction and contains principally, besides quinones, the aromatic nitro compounds.<sup>104</sup> Radicals add to both quinones and nitroaromatic compounds either on an oxygen atom, Reactions (11-83) and (11-85), or on a ring



carbon atom, Reactions (11-84) and (11-86). For both styrene<sup>105</sup> and



methyl methacrylate,<sup>106</sup> addition to benzoquinone (11-83) apparently occurs on an oxygen atom to form a peroxy radical which has essentially no reactivity for the latter compound, but apparently can add (11-87) to the



former to form a styrene-benzoquinone copolymer.<sup>105</sup> For styrene, therefore, benzoquinone acts more as a retarder than an inhibitor, even though

The relative rate of addition to quinone compared to styrene monomer by polymer radical is almost 600:1.<sup>107</sup>

Polynitroaromatic compounds are capable of stopping several kinetic chains per molecule of inhibitor, as indicated by the data in Table 11-16

Table 11-16

### Inhibition of Allyl Acetate Polymerization by Aromatic Nitro Compounds<sup>a</sup>

Inhibitor	Chains stopped per inhibitor molecule
<i>m</i> -Dinitrobenzene	4.1
<i>o</i> -Dinitrobenzene	2.4
1,3,5-Trinitrobenzene	5.9

<sup>a</sup> At 80°C.<sup>103</sup>

for allyl acetate using an initiator-to-inhibitor ratio of 6:1.<sup>108</sup> The relative rates of addition of poly(vinyl acetate) radical to dinitrobenzene,  $k_{\text{inh}}$ , and to monomer,  $k_p$ , are collected in Table 11-17.<sup>109</sup> As would be expected

Table 11-17

### Rate Constant Ratio of Inhibition to Propagation for Poly(vinyl acetate) Radicals with Dinitrobenzene Isomers<sup>a</sup>

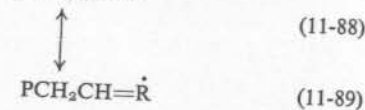
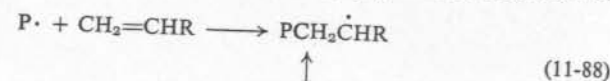
Dinitrobenzene	$k_{inh}/k_p$
<i>ortho</i>	96
<i>meta</i>	105
<i>para</i>	267

<sup>a</sup> At 45°C.<sup>109</sup>

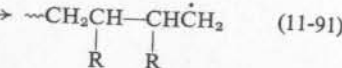
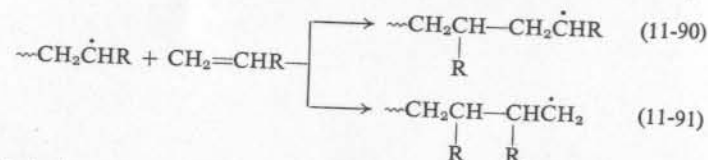
from this data and from the known unreactivity of vinyl acetate with stable radicals, dinitrobenzene compounds are very efficient inhibitors for this monomer. In contrast, the rate constants,  $k_{inh}$ , for addition of poly-(methyl methacrylate) radicals to dinitrobenzene compounds are approximately  $10^5$  lower than those for vinyl acetate,<sup>110</sup> and aromatic nitro compounds are not good inhibitors for this monomer, apparently because of polar effects.

**11.1.3.9. Orientation of Radical Addition Reactions.** As has been discussed in previous sections, the addition (11-88) of a radical to vinyl or

1,1-disubstituted olefin monomers is predominantly if not exclusively on the methylene carbon atom for reasons of both steric and resonance effects. When R in Equation (11-88) is a group containing a multiple bond on the carbon atom immediately adjacent to the carbon atom bearing the unpaired electron, the radical may be stabilized by resonance interaction with delocalization of the electron (11-89).<sup>111</sup> This highly preferred direction of

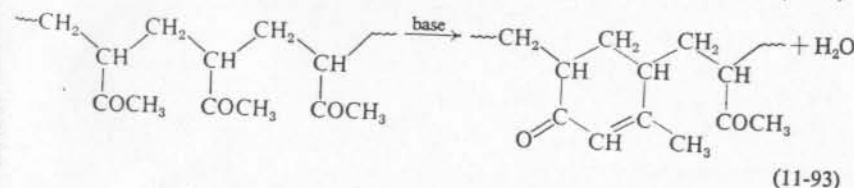
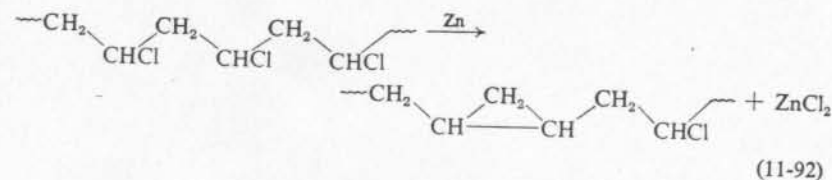


addition of polymer radicals to olefin monomers leads to a high degree of order in the orientation of successive repeating units in the resulting polymer chain. The addition of a secondary or tertiary carbon radical to a methylene group in the polymerization reaction (11-90) is termed head-to-tail addition while the inverse is termed head-to-head addition (11-91).



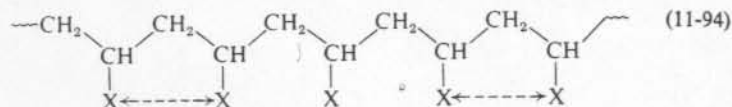
The overwhelming occurrence of head-to-tail addition has been proven chemically for a number of polymers.

(1) *Degree of Head-to-Tail Placement.* Very early studies on the products of the pyrolysis of polystyrene showed that there was no detectable amount of vicinal phenyl substitution in the polymer.<sup>112</sup> Similar conclusions were drawn for poly(vinyl chloride) from the results of dehalogenation reactions with zinc (11-92)<sup>113</sup> and for poly(methyl vinyl ketone) from the results of cyclization reactions by an aldol condensation (11-93).<sup>114</sup> For



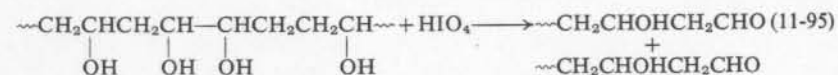


both reactions, it is possible to calculate statistically the number of functional groups which should be converted to the expected products if the polymer has exclusively a 1,3-arrangement of functional groups along the chain. Quantitative conversion is not expected to occur in these cases because occasionally a functional group will be isolated as a result of random reactions of pairs of its neighbors on both sides (11-94). For the



cyclization reaction (11-92) on poly(vinyl chloride), the calculated conversion for a purely head-to-tail polymer is 86.5%,<sup>115</sup> and the observed conversion was 84–86%.<sup>116</sup> For the aldol reaction (11-93), the calculated conversion is 81.6%, while that observed was 79–85%. In both cases, calculated and observed conversions were in very good agreement so that it was possible to conclude that virtually all repeating units in these polymers were in a head-to-tail orientation.

The same conclusion did not hold for poly(vinyl acetate), which on hydrolysis to poly(vinyl alcohol) and oxidation with periodic acid showed a measurable decrease in molecular weight.<sup>117</sup> The decrease in molecular weight was attributed to cleavage (11-95) of the backbone chain at the site



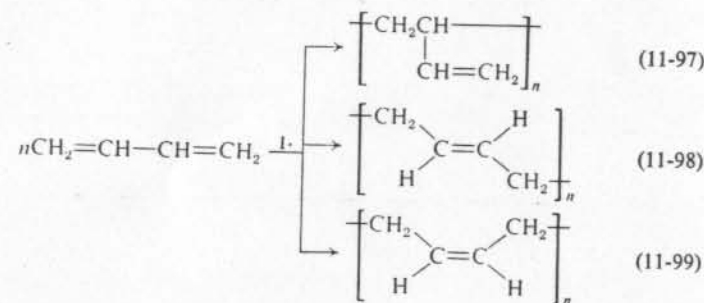
of vicinal glycol groups. By determining the decrease in molecular weight for polymers prepared at various temperatures, it was possible to calculate the ratio of rate constants for head-to-head,  $k_{\text{HH}}$ , and head-to-tail,  $k_{\text{HT}}$ , addition for vinyl acetate, as shown in Equation (11-96). According to the

$$k_{\text{HH}}/k_{\text{HT}} = (A_{\text{HH}}/A_{\text{HT}}) \exp(\Delta E_{\text{HH}}^\ddagger - \Delta E_{\text{HT}}^\ddagger/RT) = 0.1 \exp(-1.3/RT) \quad (11-96)$$

calculations, (11-96), head-to-tail addition is only slightly favored both by steric ( $\Delta S^\ddagger$ ) and energy ( $\Delta E^\ddagger$ ) factors. In contrast, for styrene the difference in activation energies<sup>118</sup> is probably of the order of 8–10 kcal mole<sup>-1</sup>.

Substantial amounts of head-to-head addition have been found in poly(vinylidene chloride),<sup>119</sup> poly(vinylidene fluoride),<sup>120</sup> and poly(vinyl fluoride)<sup>120</sup> by high-resolution nuclear magnetic resonance spectroscopy analysis. Both poly(vinylidene chloride) and poly(vinylidene fluoride) have been found to contain about 10% head-to-head placements, while poly(vinyl fluoride) can contain as much as 30% head-to-head structure. In the latter, the amount of head-to-head structure increases with increasing polymerization temperature.

(2) *Polymerization of Conjugated Dienes.* Conjugated diene monomers have orientation possibilities more complicated than those of vinyl monomers especially for substituted dienes, as discussed in Sections 9.5.2.2 and 9.5.2.3. For 1,3-butadiene, free-radical polymerization yields (11-97) a polymer containing between 15 and 20% of 1,2-structures over a wide range of polymerization temperatures.<sup>121, 122</sup> Low temperature polymerization produces (11-98) predominantly *trans*-1,4 repeating units in the remaining 80–85% of the polymer. The content of *cis*-1,4 units increases (11-99) continuously with increasing temperature to an equilibrium value



of approximately 25% as shown in Table 11-18.<sup>122</sup> An Arrhenius plot ( $\log k_{\text{trans}}/k_{\text{cis}}$  vs.  $1/T$ ) of the data in Table 11-18 yields an activation

Table 11-18  
Repeating Unit Compositions for the Free-Radical Polymerization of 1,3-Butadiene at Various Temperatures<sup>122</sup>

Temperature of polymerization, °C	Repeating unit mole fractions			Polymer melting point, °C
	1,2-	<i>trans</i> -1,4	<i>cis</i> -1,4	
-20	—	0.78–0.84	—	37 ± 1
-10	0.159	0.775	0.066	33 ± 1
0	0.179	0.730	0.091	23 ± 1
25	0.188	0.683	0.129	23 ± 1
50	0.209	0.643	0.148	0 ± 1
75	0.198	0.561	0.241	—
100	0.201	0.545	0.254	—

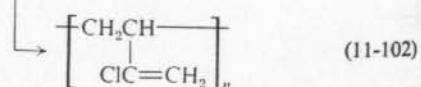
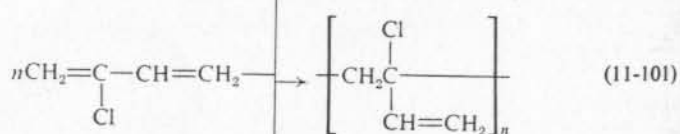
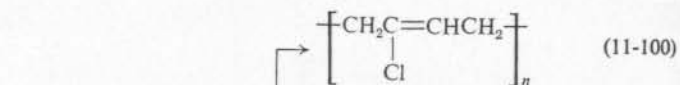
energy difference of approximately 3.1 kcal mole<sup>-1</sup> for *cis*-1,4 addition compared to *trans*-1,4 addition. A similar study has been made on the polymerization of 2-chlorobutadiene (chloroprene) with the results shown in Table 11-19.<sup>123</sup> Application of the Arrhenius equation in this case,

Table 11-19

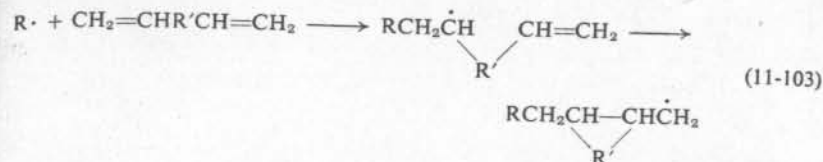
Repeating Unit Composition for the Free-Radical Polymerization of 2-Chloro-1,3-butadiene at Various Temperatures<sup>123</sup>

Temperature of polymerization, °C	1,4-units, %	Composition of 1,4-units, %	
		<i>cis</i>	<i>trans</i>
-40	99	5.0	95.0
-10	—	7.2	92.8
10	93	9.8	90.2
40	96, 91	11.4	88.6
50	87	12.3	87.7
100	84	16.1	83.9

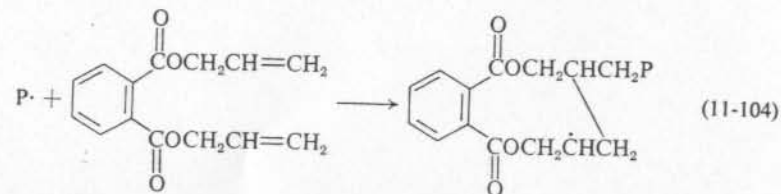
Table 11-19, yields an activation energy difference of 1.6 kcal mole<sup>-1</sup> for *cis*-1,4 addition compared to *trans*-1,4 addition (11-100). At -40°C, the remainder of the repeating units contain a ratio of approximately 3:1 of 1,2-addition (11-101) versus 3,4-addition (11-102), but at temperatures above 10°C, the ratio is close to 1.0.



(3) *Polymerization of Unconjugated Dienes.* The polymerization of unconjugated dienes (divinyl monomers) generally results in the formation of crosslinked polymers because the two vinyl groups react independently and can become incorporated into two different polymer chains. However, if the two vinyl groups are separated by a flexible chain of only two or three atoms, it is possible to form a cyclic structure by an intramolecular addition reaction (11-103). As was discussed in Section 3.9, the formation of 5- and 6-membered rings is a highly favorable occurrence for both kinetic and thermodynamic reasons.

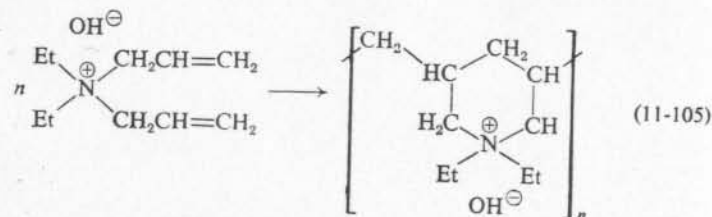


The formation of cyclic structures in the polymerization of divinyl monomers has been proposed as a reason for the poor correlation between predicted and actual degrees of conversion at gelation in the polymerization (11-104) of diallyl phthalate.<sup>124</sup> Calculations indicate that, for this



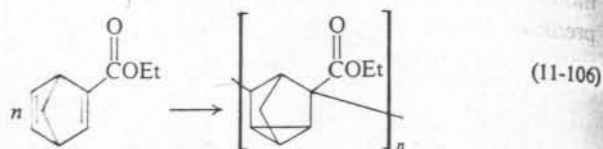
monomer, approximately one-third of the repeating units in the homopolymer are cyclic structures.<sup>125</sup> This type of reaction can occur almost quantitatively in divinyl monomers which can cyclize to form a five- or six-membered ring, rather than the much less probable eleven-membered ring for diallyl phthalate.

One of the first divinyl monomers of this type to be investigated was diethyldiallylammonium hydroxide, Reaction (11-105), which was found



to polymerize by free-radical initiation to yield a water-soluble, non-crosslinked polymer of  $\overline{\text{DP}}$  between 25 and 50 with very little residual unsaturation.<sup>126</sup> The proposal of an alternating intermolecular-intramolecular propagation step for this type of polymerization reaction has since been verified for a large number of other divinyl monomers, including acrylic anhydride,<sup>127</sup> methacrylic anhydride,<sup>128</sup> 2,6-disubstituted-1,6-heptadienes,<sup>129</sup> dimethyl  $\alpha,\alpha'$ -dimethyleneadipate,<sup>129</sup> and vinyl crotonate.<sup>130</sup> In all cases, linear polymers of respectable molecular weights are formed from these monomers. Ionic and heterogeneous cyclopolymerization reactions have also been carried out on diacrylylmethane,<sup>127</sup>

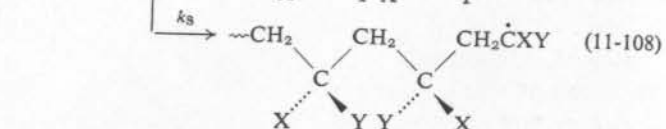
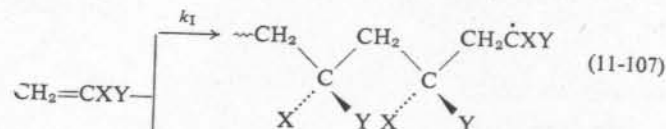
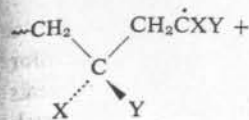
1,6-heptadiene,<sup>131</sup> 1,5-hexadiene,<sup>131</sup> allo-ocimene,<sup>127</sup> diallylsilanes,<sup>132</sup> and others.<sup>133</sup> A cyclopolymerization reaction, in which a high molecular weight, soluble polymer with a three-membered ring is formed, has been observed for 2-carbethoxybicyclo(2,2,1)-2,5-heptadiene.<sup>134</sup> Free-radical polymerization of this diene apparently involves a transannular addition reaction to form a polymer containing nortricyclene repeating units (11-106).



**11.1.3.10. Repeating Unit Configuration.** The possible variations in repeating unit configurations of olefin polymers and the nomenclature applied to these variations are discussed in Section 9.5.2.1. In 1944, it was proposed that there could be a significant difference in the activation energies for the formation of the two different configurations in free-radical polymerization reactions, and that the relative amounts of the two configurations should, therefore, vary with temperature.<sup>135</sup> As a result, a decrease in reaction temperature should cause an increase in the stereoselectivity of the polymerization reaction and, therefore, an increase in the stereoregularity of the polymer. The effect of temperature on one aspect of the stereoregularity of conjugated diene polymers was discussed in the previous section.

Possibly the first conscious attempt to induce a stereospecific polymerization reaction by free-radical initiation at low temperature was that reported for the polymerization of methyl methacrylate in 1958.<sup>136</sup> Free-radical polymerization of this monomer at  $-60^{\circ}\text{C}$  produced a high-melting crystalline polymer, which was later shown to be syndiotactic in structure.<sup>137</sup> Subsequent work showed that stereoregular polymers capable of giving crystalline, x-ray diffraction patterns could be obtained by homogeneous, free-radical polymerization reactions at temperatures as high as  $0^{\circ}\text{C}$ . This phenomena is closely related to the stereospecificity observed for the simple radical-addition reactions of hydrogen bromide to 2-butenes at low temperature discussed in Section 10.2.2, which indicates that activation energies do differ significantly for formation of the two possible stereoisomers.

It is generally believed that this difference in activation energies is caused by steric or polar effects induced by the penultimate repeating unit in the active polymer chain, and the presence of a given configuration in this unit can favor the formation of either a like configuration, Reaction



(11-107), or the opposite configuration, Reaction (11-108), in the adjacent unit on addition of the new monomer molecule. As discussed in Section 9.5.2, the former is termed an isotactic placement and the latter a syndiotactic placement. The extent to which the selectivity of addition should increase with decreasing reaction temperature is shown in Table 11-20 by

**Table 11-20**  
Calculated Rate Constant Ratio and Repeating Unit Composition for Syndiotactic Placement as a Function of Reaction Temperature<sup>138</sup>

Polymerization temperature, $^{\circ}\text{C}$	Calculated rate constant ratio, $k_s/k_i$	Calculated mole fraction of syndiotactic units
-100	17.0	0.94
-50	9.4	0.90
0	6.2	0.86
50	4.7	0.82
100	3.8	0.79

the calculated values of the ratio of rate constants for syndiotactic,  $k_s$ , versus isotactic placement,  $k_i$ . The rate constant ratios in Table 11-20 are obtained by assuming that the syndiotactic placement has a lower activation energy by 1 kcal mole<sup>-1</sup> than the isotactic placement, and that the two types of placement have the same frequency factor or entropy of activation.<sup>138</sup>

Experimentally, an indication of the approximate degree of stereoregularity of a polymer may be gained from x-ray diffraction and broad-line nuclear magnetic observations of the polymer in the solid state, if the stereoregularity of the chain results in crystallization of the polymer.<sup>139</sup>



For the former, however, some polymers which are highly stereoregular do not show crystalline, x-ray diffraction patterns. This problem can arise for any one of a number of reasons, including (1) that steric hindrance prevents the polymer chain from assuming the required conformation for crystallization; (2) that the necessary annealing process to induce crystallization has not been found for the particular polymer; or (3) that the blocks of ordered units are too short to form a crystallite large enough to be observed by x-ray diffraction.<sup>138</sup>

Solubility properties,<sup>140</sup> and the breadth and reproducibility of the crystalline melting point<sup>141</sup> may also be used as semiquantitative measures of stereoregularity and of the resulting degree of solid-state order. A direct measure of the mole fraction of syndiotactic or isotactic units has been provided for several polymers from infrared spectra<sup>142</sup> and by high-resolution nuclear magnetic resonance spectra.<sup>137, 143</sup> The former has been applied to polystyrene,<sup>144</sup> poly(vinyl chloride),<sup>145, 146</sup> poly(methyl methacrylate),<sup>147</sup> and poly(isobutyl vinyl ether).<sup>148</sup> Chemical reactivity such as the hydrolysis of poly(methyl methacrylate), also provides a semiquantitative estimate of the type and degree of tacticity.<sup>147</sup>

The effect of temperature on the stereoselectivity of the radical polymerization reaction of methyl methacrylate has been determined by high-resolution nuclear magnetic resonance spectroscopy. From this study it was found that low temperature, free-radical polymerization reactions favor the formation of syndiotactic units, as shown by the data in Table 11-21.<sup>149</sup> Application of the Arrhenius equation to this data and to data in

Table 11-21

Effect of Reaction Temperature on Tacticity in the Polymerization of Methyl Methacrylate<sup>149</sup>

Polymerization temperature, °C	Rate constant ratios, $k_s/k_i$	Mole fraction of syndiotactic units
-78	7.4	0.88
0	3.8	0.79
50	3.3	0.77
100	2.7	0.73

a closely related investigation yields an activation energy or enthalpy difference between isotactic and syndiotactic placement of approximately 0.8–1.1 kcal mole<sup>-1</sup> with little or no activation entropy difference.<sup>149, 150</sup> A similar result has been obtained for the free-radical polymerization reaction of vinyl chloride, where infrared measurements indicate an

activation energy difference of approximately 0.6 kcal mole<sup>-1</sup> in favor of syndiotactic placement.<sup>146</sup>

High-resolution nuclear magnetic resonance spectroscopy has also been applied to repeating-unit configuration studies on a wide variety of polymers including poly(vinyl chloride), poly( $\alpha$ -methyl styrene), polystyrene, poly( $\beta$ , $\beta$ -dideuterostyrene),<sup>151</sup> poly(vinyl acetate), poly(methacrylic anhydride), poly(methacrylic acid), and poly(trifluorochloroethylene).<sup>143</sup> In the free-radical polymerization of methacrylic acid, it has been observed that increasing the pH of the reaction mixture increases the preference for syndiotactic placement.<sup>137</sup> The ratio of rate constants for isotactic and syndiotactic placements,  $k_i/k_s$  is nearly twice as great when uncharged polymer radicals and uncharged monomer react as when both are negatively charged by having the carboxyl groups in the ionized form. The difference between free energies of activation for isotactic and syndiotactic placements increases from approximately 0.9 kcal at pH 2.0 to 1.3 kcal at pH 10.0. For the free-radical polymerization of trifluorochloroethylene, in marked contrast to that of methyl methacrylate, high-resolution NMR analysis indicates that there is a negligible difference in the activation enthalpies, but a substantial difference in the activation entropies between isotactic and syndiotactic placement, in favor of the latter.<sup>137</sup>

Qualitative studies on the stereoselectivity of free-radical polymerization reactions have also been carried out on isopropyl and cyclohexyl acrylates<sup>152</sup> and on a series of vinyl esters including vinyl acetate, vinyl mono-, di-, and trichloroacetate, and vinyl trifluoroacetate.<sup>153</sup> An indication of the differences in degree of stereoregularity in the five different vinyl acetate polymers, all of which were prepared at 60°C, was obtained by hydrolysis of each to the alcohol and then comparing the solubility properties of the five samples of poly(vinyl alcohol) obtained. Swelling measurements were made on each type of poly(vinyl alcohol), and the results obtained are listed in Table 11-22. The least swollen polymer is assumed to have the

Table 11-22

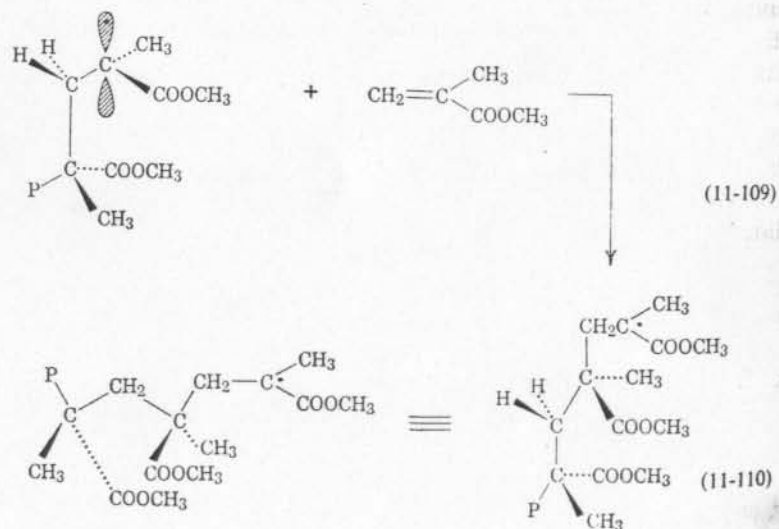
Effect of Monomer Structure on Tacticity in the Polymerization of Vinyl Esters<sup>153</sup>

Monomer, R in CH <sub>2</sub> =CHOCOR	$\eta_{sp}/c$ , dl/g	Degree of swelling at 70°C
CH <sub>3</sub>	4.9	$\infty$
CH <sub>2</sub> Cl	1.5	21
CHCl <sub>2</sub>	0.9	5
CCl <sub>3</sub>	0.9	6
CF <sub>3</sub>	1.2	4

highest degree of crystallinity as a result of having the highest degree of stereoregularity. These results were supported by observations on the sharpness of the halos in the x-ray patterns of the original poly(vinyl esters).

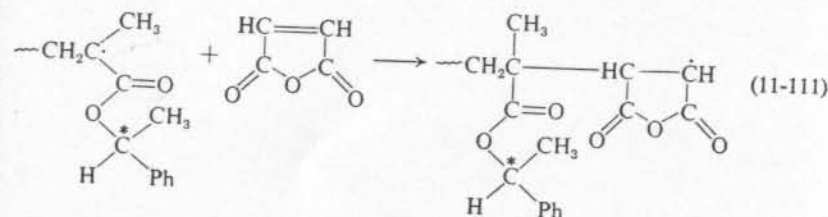
The differences in stereoregularity for the five vinyl ester polymers have been attributed to enhanced stereoselectivity in the polymerization reaction caused by a strong polar effect because the increase in stereoselectivity parallels the increase in dissociation constant of the respective acetic acids. The crystalline repeat distance for poly(vinyl trifluoroacetate) is consistent with a syndiotactic structure for the ordered regions of the polymer.

The stereoregular polymerization of vinyl chloride has been attributed to a combination of steric and polar effects,<sup>154</sup> while that of methyl methacrylate is considered to be mostly owing to a steric effect. A model has been proposed for the latter in which the free-radical endgroup of the growing polymer chain is assumed to have a conformation which most exposes the radical to attack (11-109).<sup>155</sup> This conformation is selected to be the one that permits the lowest degree of steric strain by placing the two bulkiest groups in a *trans* arrangement, assuming that the relative sizes of the groups in poly(methyl methacrylate) are  $P > \text{COOCH}_3 > \text{CH}_3$ . It can be seen from this model that addition of a monomer molecule to the end-group radical results in the formation (11-110) of a syndiotactic placement.

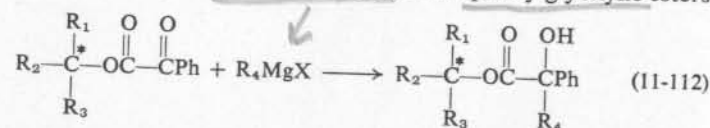


Succeeding addition reactions occur before the terminal radical can rotate and generate an isotactic placement arrangement.<sup>156</sup>

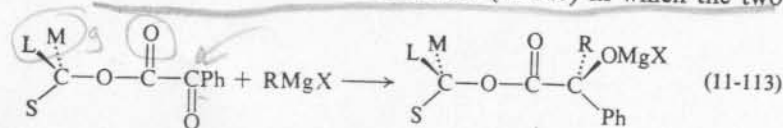
The importance of steric effects in determining the configuration of a newly formed repeating unit has been elegantly revealed by the preparation of optically active polymers through asymmetric induction in a homogeneous, free-radical polymerization reaction. The optically active polymer was obtained by the copolymerization of (-)-1-phenylethyl methacrylate and maleic anhydride as described in Section 9.5.2.2.1. The asymmetric center in the alcohol function of the ester apparently induces (11-111) an asymmetry into the direction of addition of the methacrylate radical to a maleic anhydride unit.



A close analogy can be drawn between this reaction (11-111) and the classical reaction (11-112) of Grignard reagents with phenylglyoxylic esters



of asymmetric alcohols.<sup>157</sup> A large number of reactions of the latter type have been studied to determine the factors which control the extent of asymmetric induction observed. From these investigations, two generalizations have emerged which permit a correlation of the sign of rotation of the lactic acid produced on hydrolysis of the ester to the configuration of the original asymmetric alcohol in the phenylglyoxylic ester. These rules are: (1) the ester will assume a conformation (11-113) in which the two



largest groups (large, L, and medium, M) on the  $\alpha$ -carbon atom of the alcohol are both *gauche* to ester carbonyl, and (2) the Grignard reagent will attack preferentially from that side of the carbonyl group on which the medium group resides.<sup>158, 159</sup>

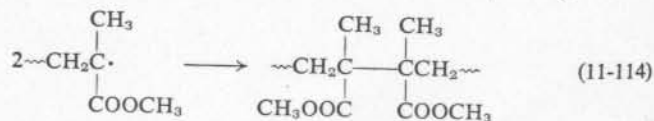
These rules reveal the nature of the steric effects which most probably cause the formation of an excess of one type of asymmetric center both in the copolymerization reaction (11-111) of an optically active methacrylate

ester and in another closely related copolymerization reaction of  $\alpha$ -methylbenzyl vinyl ether with maleic anhydride.<sup>160</sup> A partial asymmetric synthesis in a simple addition reaction involving an optically active methacrylate ester has also been reported, and the optical rotation of the product corresponded to 10% asymmetric synthesis.<sup>161</sup>

#### 11.1.4. Termination

The mode of termination of kinetic chains in a free-radical polymerization reaction determines the applicability of the rate equations derived in Section 11.1.1, as well as the molecular weight of the polymer, Equation (11-17), and the molecular weight distribution. The rate equations are based on the assumption that termination of a kinetic chain of a polymerization reaction occurs exclusively by the bimolecular reaction of two polymer chain radicals, and when other modes of termination become important, the order with respect to monomer becomes some value other than the expected square-root dependency.

The molecular weight average and distribution are determined by the modes of termination for both the polymer chain and kinetic chain. Polymer chain termination by chain transfer may cause very great variations in molecular weight properties, and the relative amount of combination and disproportionation is an important consideration in both polymer and kinetic chain terminations.<sup>162, 163</sup> Very little is known about the latter for most monomers, although studies indicate that styrene polymerization terminates almost entirely by combination at low temperatures and disproportionation at high temperatures.<sup>164</sup> Two important structural factors which affect the ratio of these two termination reactions are the number of hydrogen atoms available for disproportionation (for example, five for methyl methacrylate versus two for styrene) and the number and bulkiness of the substituents on the radical carbon atom. The poly(methyl methacrylate) radical carries two bulky groups, and combination (11-114) of two



polymer radicals creates a strained bond. As a result there is an activation energy difference between the two possible reactions of about 5 kcal mole<sup>-1</sup> in favor of disproportionation. Polar effects are also important in polymer radical-radical termination reactions, and termination in the polymerization of either styrene or *p*-chlorostyrene is by combination, while that with *p*-methoxystyrene is partly by disproportionation. Possibly electrostatic repulsion occurs between two poly(*p*-methoxystyrene) radicals.<sup>165</sup>

Absolute values of termination rate constants are given in Section 11.1.3.2.

**11.1.4.1. Primary Radical Termination.** Another important side reaction, other than chain transfer, which can strongly influence both rate and molecular weight, is termination between a polymer radical and an initiator radical. This reaction is termed primary radical termination. The extent of primary radical termination will increase with both increasing initiator concentration and decreasing monomer concentration because the concentration of primary radicals will increase under these conditions. Primary radical termination will also increase with decreasing temperature because the activation energy for Reaction (11-115) of an initiator radical



with a polymer radical will be lower than that of addition of a primary radical to a monomer in an initiation reaction, (11-116).<sup>164</sup> For the



polymerization reactions of styrene and methyl methacrylate initiated with azobisisobutyronitrile at 60°C, the ratio,  $k_t'/k_i$ , is approximately 100 and the ratio  $k_t'/k_i$  is approximately 10<sup>7</sup>. In contrast, vinyl acetate shows no kinetic evidence of primary radical termination.<sup>166, 167</sup>

Primary radical termination becomes increasingly important as the polymerization reaction progresses in many systems, not only for chemical reasons as discussed above but also for physical reasons. If the progress of a polymerization reaction is accompanied by a large increase in viscosity, as is true in most polymerization reactions carried out in the absence of solvent, then termination reactions between two polymer chain endgroups become increasingly more difficult due to the inability of the endgroups to freely diffuse together.

With the onset of higher viscosities and lower monomer concentrations, the relative importance of primary radical termination reactions can become very great because a primary radical can diffuse into zones where polymer endgroup radicals cannot readily enter. Nevertheless, because the initiator concentration and the concentration of primary radicals also decrease with increasing conversion, the absolute rates of the kinetic and polymer chain terminations reactions decrease, and both the overall rate of polymerization and the molecular weight of the polymer can increase greatly.

This state of affairs, in which the termination reaction between two polymer chains becomes diffusion-controlled because of a marked increase in viscosity in the reaction medium, is termed the gel effect or the



Trommsdorff effect. The latter term is derived from the name of one of the early investigators in the field.<sup>168</sup>

**11.1.4.2. The Gel Effect.** The occurrence of a gel effect in a polymerization reaction is revealed by an autoacceleration in rate of the type shown in Figure 11-4. Because the onset of the gel effect is apparently determined

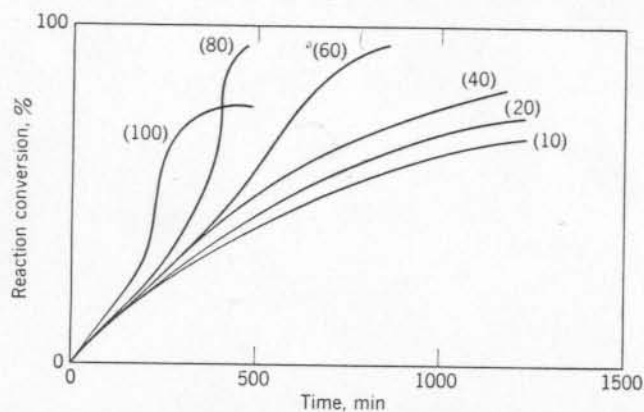


Figure 11-4. Effect of dilution on rate of polymerization of methyl methacrylate at 50°C. Curves are labeled for per cent concentration of monomer in solvent.<sup>174</sup>

primarily by the viscosity of the polymerization mixture, as discussed above, the variables which affect viscosity will determine the importance of the gel effect. The important variables in this respect are temperature, molecular weight of polymer, and presence of solvent for the polymer.

The average molecular weight at the onset of the gel effect is shown in Table 11-23 for the polymerization reactions of four different mono-

Table 11-23

The Average Degree of Polymerization Within a Reaction Mixture at the Start of the Gel Effect<sup>169</sup>

Monomer	Temperature, °C	Conversion at onset of gel effect, %	Initial $\overline{DP}$	$k_{35\%}/k_{0\%}$	
				$k_p$	$k_t$
Methyl acrylate	30	0	> 10,000	—	—
Methyl methacrylate	30	15	5000	1.12	0.0066
Styrene	50	30	4000	0.67	0.075
Vinyl acetate	25	> 40	2400	—	—

mers.<sup>169</sup> The last two columns of Table 11-23 strikingly reveal the cause of the gel effect, namely the large decrease in the rate of the termination reaction with increasing conversion. These columns give the ratios of apparent rate constants for propagation,  $k_p$ , and for termination,  $k_t$ , at 35% conversion relative to the rate constant for each at the start of the polymerization reaction. More detailed data has been collected for the change in apparent  $k_t$  with conversion during the polymerization of vinyl acetate at 25°C, as shown in Table 11-24.<sup>160</sup> The effect of conversion in the

Table 11-24  
Decrease in Apparent Rate Constant for Termination with Increase in Conversion in the Polymerization of Vinyl Acetate<sup>170</sup>

Conversion, %	$k_t \times 10^{-5}$ , liters mole <sup>-1</sup> sec <sup>-1</sup>	$\Delta E_t^\ddagger$ , kcal mole <sup>-1</sup>
4	240	1
23	126	1.4
46	90	3.4
57	6.7	8.6
65	1.15	13

photoinitiated polymerization of methyl methacrylate on a number of important variables, including overall rate of polymerization, average lifetime of a kinetic chain, apparent rate constant for propagation, and apparent rate constant for termination, is shown in Table 11-25.<sup>171</sup> The

Table 11-25

Effect of Conversion on Kinetic Parameters in the Polymerization of Methyl Methacrylate at 22.5°C<sup>171</sup>

Conversion, %	Overall rate, % hr <sup>-1</sup>	Kinetic chain lifetime, sec	Rate constants, liters mole <sup>-1</sup> sec <sup>-1</sup>	
			$k_p$	$k_t$
0	3.5	0.89	384	$4.42 \times 10^7$
10	2.7	1.14	234	$2.73 \times 10^7$
20	6.0	2.21	267	$7.26 \times 10^6$
30	15.4	5.0	303	$1.42 \times 10^6$
40	23.4	6.3	368	$8.93 \times 10^5$
50	24.5	9.4	258	$4.03 \times 10^5$
60	20.0	26.7	74	$4.98 \times 10^4$
70	13.1	79.3	16	$5.64 \times 10^3$
80	2.8	216	1	$7.6 \times 10^2$

data indicate that the apparent rate constant for termination decreases by about 100,000-fold from the start of the polymerization reaction up to 80% conversion.

The onset of the gel effect for vinyl acetate and for methyl methacrylate<sup>172</sup> is believed to occur between 10 and 30% conversion at temperatures of 60°C and below. The limiting reaction conversion for methyl methacrylate at 25°C is approximately 80%, but increasing the reaction temperature to 85°C increases the limiting conversion to approximately 97% because of a decrease in viscosity of the reaction mixtures with increasing temperature.<sup>173</sup> In contrast, the gel effect is important almost from the very start of the polymerization of methyl acrylate at room temperature.<sup>169</sup> For styrene polymerization at 25°C, the overall rate acceleration is a factor of 5.2 at 38% conversion and 16.9 at 60% conversion.

Chain-transfer agents, which reduce the molecular weight of the polymer,<sup>169</sup> and solvents, which directly reduce the viscosity of the medium, both delay or can even eliminate the onset of the gel effect. The effect of solvents on the rate of polymerization of methyl methacrylate at 50°C is shown in Figure 11-4.<sup>174</sup> It can be seen from this data that the autoacceleration effect is completely eliminated when the reaction mixture is diluted with 60% of an inert solvent. The molecular weight of the polymers formed at different dilutions also show a continuous decrease with increasing dilution again because of the increasing importance of bimolecular chain termination reactions.<sup>175</sup>

At very high viscosities even the rate of propagation will become diffusion-controlled, as shown in Table 11-25 for methyl methacrylate and in Table 11-26 for vinyl acetate polymerization. The rate of initiation may also be reduced as a result of an increasingly important contribution of

Table 11-26

Variation in Apparent Rate Constant for Propagation with Reaction Conversion for the Polymerization of Vinyl Acetate<sup>170</sup>

Reaction of conversion, %	$k_p$ , liters mole <sup>-1</sup> sec <sup>-1</sup>
4	895
23	1290
46	1980
57	238
65	87

cage recombination of the two initiator radicals.<sup>176</sup> For methyl methacrylate polymerization, the effect of conversion on kinetic variables has been divided into three distinct stages.<sup>171</sup> Up to 10% conversion, the reaction mixture changes from a mobile liquid to a viscous syrup, but the rate of polymerization adheres closely to steady-state kinetics, as represented by Equation (11-13). Between 10 and 50% conversion, the reaction mixtures change from a very viscous fluid to a soft solid, and large increases are obtained in both the rate of polymerization and the lifetime of the kinetic chain. The energy of activation for termination increases markedly, but this term now includes an energy of activation for diffusion of polymeric radicals. This term is for segmental diffusion of the radical end of the growing polymer chain, not for translational diffusion of the entire polymer chain.<sup>177</sup> As the conversion nears completion, termination appears to become a unimolecular process, and propagation becomes diffusion-controlled as the monomer becomes immobile in a gelled reaction medium. At this stage, kinetic chain termination is merely the cessation of propagation.<sup>171</sup>

Reduction in the rate of termination in a free-radical polymerization reaction can also be brought about by several other physical methods, all of which are based on the principle that termination by the reaction of two polymer chain endgroups can be prevented by isolating the growing chains from each other. In many cases, isolation of growing polymer chains has been accomplished by occlusion of the active endgroup within discrete polymer particles. This phenomenon is responsible for the unusual rate behavior observed in the following physical systems: (1) polymerization reactions initiated in the gas phase; (2) polymerization of a monomer in a medium which is a nonsolvent for the polymer, termed precipitation polymerization; (3) emulsion polymerization; (4) polymerization within a crosslinked network, termed popcorn polymerization; and (5) polymerization of crystalline monomer in the solid state.

## 11.2. PHYSICAL SYSTEMS FOR POLYMERIZATION

As discussed in the previous section, the behavior of a polymerization reaction and the properties of the resulting polymer can vary greatly according to the nature of the physical system in which the polymerization reaction is carried out. The following types of physical systems are considered briefly in this section: (1) bulk polymerization, (2) solution polymerization, (3) suspension polymerization, (4) emulsion polymerization, (5) precipitation polymerization, (6) gas-phase polymerization, and (7) solid-state polymerization.

It is interesting to note that the technique of emulsion polymerization

was first developed in the early 1900's in a deliberate attempt to duplicate the physiological conditions existing during the formation of rubber in the plant.<sup>178</sup> Natural rubber is collected in the form of an aqueous latex, which is stabilized by a protein emulsifying agent. The original emulsion polymerization reactions were carried out by heating, for long periods of time, isoprene or butadiene in water containing protective organic colloids because free-radical initiators were not known at that time.

### 11.2.1. Bulk Polymerization

The simplified kinetics derived in Section 11.1.1 for free-radical polymerization reactions apply best for bulk polymerization at low conversions and for solution polymerization in inert solvents. At high conversions, the kinetics of bulk polymerization become complicated by chain transfer to polymer and by the gel effect. As discussed in Section 11.1.3.7, the extent to which chain transfer occurs depends upon the reactivity of the polymer radical and the activity of the chain-transfer site. For highly reactive radicals, such as the poly(vinyl acetate) radical, chain transfer becomes important at conversions as low as 20%, and branched and crosslinked polymers are formed. For stable radicals, such as the polystyrene radical, chain transfer is of little importance even at high conversions.

Probably the most important problem experienced in bulk polymerizations is the difficulty of dissipating the high exothermic heat of the polymerization reaction which is common to most vinyl or olefin monomers. This problem can become very serious at high viscosities of the reaction mixture in large batch preparations, and localized overheating can often lead to degradation and discoloration of the polymer. To minimize this problem, bulk polymerization may either be terminated at relatively low conversion of 40–60% and excess monomer distilled off or the polymerization reaction may be carried out in two steps. In the first step, a large batch of monomer is polymerized to an intermediate conversion and then, for ease of heat dissipation, the polymerization reaction is completed in thin layers. For example, the reaction may be carried to completion while the monomer-polymer mixture flows either through a small diameter tube or down the walls of a column or simply by free fall in thin streams.<sup>179</sup> Because of this heat dissipation problem, bulk polymerization reactions in large batches are seldom carried out, but instead, if bulk polymerization kinetics are desired, the reaction is conducted either with the monomer dissolved in an inert liquid which is a solvent for both the monomer and polymer, or with the monomer dispersed as very small droplets in water. The latter is termed suspension polymerization.

### 11.2.2. Solution Polymerization

The principal problems encountered in solution polymerization are chain transfer to the solvent and removal of the solvent for isolation of the polymer. Gel effects are also possible depending upon the goodness of the solvent and on the concentration used, as shown in Figure 11-4. Because of the solvent-removal problem, solution polymerization is generally not used on a large scale unless the application in mind involves the direct use of the polymer in solution.<sup>180</sup>

The effect of chain transfer on the overall rate of a polymerization reaction, on induced decomposition of the initiator, and on the molecular weight of the polymer have been covered in previous sections. However, nonreactive solvents which are not susceptible to chain transfer reactions may also influence either the rate of polymerization or the structure of the polymer formed. As an example of the latter, the stereochemistry of polymer formed in the free-radical polymerization of vinyl chloride may be strongly dependent on the dielectric constant of the solvent present.<sup>181</sup> Furthermore, poly(vinyl chloride) prepared in the presence of aldehydes reportedly shows an unusually high order of stereoregularity, although the results, in this case, appear to be strongly dependent on molecular weight.<sup>182</sup>

In some cases, it has been observed that the reduction in the rate of polymerization or in molecular weight of the polymer with certain solvents for certain monomers appears to be greater than can be accounted for by the occurrence of degradative chain transfer. Such is the case, for example, for the polymerization of vinyl acetate in benzene<sup>183</sup> and for styrene in bromobenzene,<sup>184</sup> but the reason for these effects has not been adequately explained. For some highly polar monomers, such as *N*-vinylpyrrolidone and acrylic acid, water is a particularly good solvent for the polymerization reaction because of its nonreactivity and because it permits the use of inorganic redox initiators.

### 11.2.3. Suspension Polymerization<sup>185</sup>

For many nonpolar monomers, polymerization in an aqueous dispersion offers a method of eliminating many of the problems encountered in bulk and in solution polymerization, especially the heat dissipation problem in the former and solvent reactivity and removal in the latter. Another attractive feature for large batch preparations is that the polymeric products obtained from a suspension polymerization, if correctly carried out, are in the form of finely granulated beads which are easily filtered and dried.

Rates and molecular weights for a suspension polymerization reaction



are identical to those expected for bulk polymerizations.<sup>186</sup> The catalyst is dissolved in the monomer, the monomer is dispersed in water, and a dispersing agent is incorporated to stabilize the suspension formed. Emulsion polymerization, which is discussed below, is superficially related to suspension polymerization, but the kinetic relationships are entirely different. The major causes of this difference are, first, that the monomer droplets in suspension polymerization systems are approximately 0.1–1 mm in size, while the particles in an emulsion polymerization are approximately  $10^{-5}$  to  $10^{-6}$  mm in size and second, that the catalyst is dissolved in the aqueous phase in the latter, but is incorporated directly into the droplets in the former.

Suspending agents which are generally used fall into one of two classes: water-soluble organic polymers or water-insoluble inorganic compounds. Examples of the former are poly(vinyl alcohol), poly(acrylic acid), methyl cellulose, gelatin, and various pectins. Examples of the latter are kaolin, magnesium silicates, aluminium hydroxide, and various phosphates. The suspending agents are believed to stabilize the suspension primarily by preventing or reducing the number of direct collisions between droplets.<sup>185</sup> The inorganic compounds are, in general, more easily removed from the final polymer than are the organic polymer agents, and surface active agents are often added with this type of stabilizer. Monomers having significant water solubility, such as acrylic acid or acrylonitrile, may be polymerized efficiently with a suspension process by adding electrolytes to salt out the monomer from solutions.

In general, suspension polymerization reactions show the same rate characteristics as bulk polymerization reactions, including the gel effect, and many of the same initiators are used. Suspension polymerization is used industrially for many monomers including styrene, methyl methacrylate, vinyl chloride, vinylidene chloride, and vinyl acetate.

#### 11.2.4. Emulsion Polymerization<sup>187</sup>

The course of an emulsion polymerization is considerably different from that of the previous three types of physical systems, all of which adhere closely to the rate and  $\overline{DP}$  relationships derived in Section 11.1.1. The principal difference is that, during most of the course of the reaction, the locus of reaction in an emulsion polymerization is in such a small volume (colloidal monomer-polymer particles) that only one free radical can be present at any given time. The initiating and terminating radicals enter from outside the reaction locus through an interfacial boundary.

The monomer is also fed into the reaction locus from the outside by diffusion through the continuous phase (water) from a large reservoir (monomer droplets). For this reason, monomers applicable to emulsion

polymerization must have a finite water solubility, but still not so high as to cause a substantial amount of polymerization in the aqueous phase. Monomers which have suitable solubilities include methyl acrylate, methyl methacrylate, styrene, vinyl chloride, vinylidene chloride, and butadiene. Vinyl acetate and acrylonitrile have such high water solubilities that the normal course of an emulsion polymerization is not followed, and a considerable amount of polymerization occurs in the aqueous phase.

At the start of the reaction, an emulsion polymerization is a three-component system as follows:

1. Colloidally dispersed soap micelles swollen with monomer to an average diameter of approximately 50 Å.
2. Macrodroplets of monomer stabilized by soap molecules around the periphery and approximately 15,000 Å. in diameter.
3. The aqueous phase which usually contains a two-component redox initiator composed of a peroxide and a reducing agent, as well as an electrolyte to stabilize the latex product and to control its particle size, a buffer to control the rate of redox initiation and increase latex stability, and a small amount of dissolved monomer.

The soap micelles swollen with monomer and the monomer particles compete for capture of the radicals generated in the aqueous phase, but because there are approximately  $10^{18}$  micelles  $\text{cc}^{-1}$  compared to  $10^{11}$  droplets  $\text{cc}^{-1}$ , the micelles capture almost all of the radicals generated. The monomer used up by the resulting polymerization reaction in the micelle is quickly replenished by diffusion of new monomer molecules from the aqueous phase, which in turn, is kept saturated with monomer by the macrodroplets.

A radical diffusing into the micelle after being generated in the aqueous phase initiates a polymerization reaction which continues either until all the monomer in the micelle is reacted or until a second radical diffuses in, in which case termination occurs instantly because of the small volume of the reaction locus. This pattern is maintained throughout most of the course of an emulsion polymerization, and consequently, for half the time, on the average, a given micelle will contain a growing polymer chain, and for half the time it will contain no growing polymer chains at all. As a result, the overall rate of polymerization,  $R_p$ , will be a function (11-117)

$$R_p = k_p[M](N/2) \quad (11-117)$$

of both the propagation rate and the number of colloidally dispersed monomer-polymer particles,  $N$ . The factor  $N/2$  appears in the Equation (11-117) because, on the average, only one-half of the particles contain growing chains at any given time.

The most remarkable conclusion to be drawn from this kinetic relationship is that the rate of polymerization is independent of the rate of generation of radicals. To some extent, however, the degree of polymerization is still dependent (11-118) on the rate of radical generation,  $R_i$ , but both  $R_p$

$$\overline{DP} = R_p/R_i = (k_p[M]/R_i)N/2 \quad (11-118)$$

and  $\overline{DP}$  can be readily increased by the physical expedient of increasing the number of particles. Descriptively speaking, increasing the number of particles while maintaining the same rate of initiation increases the time interval between the capture of two radicals, and therefore, increases the lifetime of a given growing polymer chain. This increased lifetime is responsible for the increases in both  $R_p$  and  $\overline{DP}$ . For any given number of particles, increasing the rate of radical generation does not increase the rate of polymerization because one-half of the particles are dead at any given time, regardless of the number of radicals present in the system, due to the facility of the termination reaction.

The number of particles which an emulsion polymerization system will contain is generally determined at the start of the polymerization reaction by the reaction temperature and by the concentrations of soap, catalyst, and other additives. At high conversions or for latexes with very large particles, this simplified kinetic scheme is not followed. In a normal emulsion polymerization, however, the particle size in the final polymer latex is generally of the order of 500–1500 Å.

### 11.2.5. Precipitation Polymerization

If a polymer is insoluble in its own monomer or in a particular monomer-solvent combination, it will precipitate out as it is formed. If the polymer precipitates out in the form of compact small spheres while still containing a live radical endgroup, an increase in the rate of polymerization will be observed because the live endgroups become buried in the spheres, and termination between two growing polymer chains becomes extremely difficult or improbable. This phenomenon is termed precipitation polymerization, and, as in emulsion polymerization, the rate of polymerization follows kinetic relationships considerably different from those for a homogeneous, bulk polymerization reaction.<sup>188</sup>

Polymerization systems in which this phenomenon is believed to occur include styrene in alcoholic solvents,<sup>189</sup> methyl methacrylate in water,<sup>190</sup> acrylonitrile<sup>191</sup> in water, and in the bulk polymerization of both vinyl chloride<sup>192</sup> and vinylidene chloride.<sup>193</sup> Precipitation polymerization occurs for the last two because the polymer is insoluble in its own monomer.

The existence of high concentrations of long-lived free radicals in these

systems has been proven by electron spin resonance spectroscopy.<sup>194</sup> Unlike the case in emulsion polymerization, in precipitation polymerization not only the absolute rate constant for termination but also that for propagation is less than in a homogeneous system.<sup>195</sup> However, the overall rate is still higher because the decrease of the propagation rate is several orders of magnitude less than the decrease of the termination rate. For example, in the homogeneous polymerization of methyl methacrylate in bulk compared to the precipitation polymerization in water, both at 25°C, the rate constants for propagation are 310 and 75 liters mole<sup>-1</sup> sec<sup>-1</sup>, respectively, while the apparent rate constants for termination are  $6.6 \times 10^7$  and  $1.8 \times 10^4$  liters mole<sup>-1</sup> sec<sup>-1</sup>, respectively.<sup>190</sup>

### 11.2.6. Gas-Phase Polymerization

The term gas-phase polymerization is a misnomer in that it refers only to a polymerization reaction initiated on monomer vapors, generally by photochemical means.<sup>196</sup> High molecular weight polymer molecules are not volatile, so a fog of polymer particles containing growing polymer chains quickly forms, and the major portion of the polymerization reaction occurs in the condensed state.<sup>197</sup> Gas-phase polymerization, in this sense, is very similar in mechanism to emulsion and precipitation polymerizations because the polymer particles in the fog can contain only one growing radical and fresh monomer diffuses into the particle from the gas phase.

One of the more unusual features of gas-phase polymerization is that, because the rate of polymerization is often controlled by the rate of absorption of monomer from the gas phase, an increase in reaction temperature may cause a decrease in the rate of reaction. That is, the system may show an apparent negative activation energy. Such is the case for the polymerization reaction of methyl acrylate vapor, which is converted to polymer extremely rapidly on irradiation with ultraviolet light and has an overall energy of activation of  $-8.9$  kcal mole<sup>-1</sup>.<sup>198</sup> However, the latent heat of vaporization for methyl acrylate is approximately 8 kcal mole<sup>-1</sup>, so that the actual overall activation energy is on the order of  $-0.9$  kcal mole<sup>-1</sup>. The fact that  $\Delta E_0^\ddagger$  is still negative can be attributed to an unusually high value for the apparent activation energy of termination,  $\Delta E_t^\ddagger$ , which in turn, is a reflection of the decrease in termination rate caused by isolation of the growing polymer chains.

Other monomers which have been polymerized successfully in the gas phase include methyl methacrylate,<sup>199</sup> vinyl acetate,<sup>199</sup> methyl vinyl ketone,<sup>200</sup> and chloroprene.<sup>201</sup> Advantage has been taken of the long life of the isolated polymer radicals in gas-phase polymerizations to prepare a block copolymer of chloroprene and methyl methacrylate by alternately exposing the particles to pure vapors of the two monomers.<sup>201</sup>

The effect of radical isolation on the rate of termination is clearly shown by the comparison in Table 11-27 of the values of  $k_p/k_t$  for bulk versus gas-

Table 11-27

Comparison of Rate Constant Ratios for Propagation and Termination in Bulk and Gas-Phase Polymerization Reactions<sup>200</sup>

Monomer	Bulk $k_p/k_t$	Gas-phase $k_p/k_t$
Styrene	$0.20 \times 10^{-4}$ (30°C)	0.44 (35°C)
Vinyl chloride	$0.57 \times 10^{-6}$ (30°C)	0.05 (35°C)
Acrylonitrile	$0.25 \times 10^{-5}$ (60°C)	0.88 (20°C)

phase polymerization for several monomers.<sup>200</sup> Kinetic equations for these polymerization reactions are considerably different from those for homogeneous free-radical polymerization and are quite complicated.<sup>198</sup>

### 11.2.7. Solid-State Polymerization

Polymerization reactions have been carried out on a large number of olefin and cyclic monomers in the crystalline solid state. Examples of the former are collected in Table 11-28.<sup>202</sup> As indicated in this table, the reaction is generally initiated by irradiating the crystals with ionizing radiation, and as a result, the exact mechanism of the polymerization is unknown. That is, whether the polymerization reaction follows an ionic or free-radical course or both cannot be ascertained directly because of the wide variety of reaction types which can be induced by ionizing radiation. In two cases, however, for crystalline *p*-acetamidostyrene and *p*-benzamido-styrene, the polymerization reactions are spontaneous, thermally initiated reactions at temperatures well below the melting point.<sup>203</sup>

Five different classifications of solid-state polymerization reactions have been recognized according to their kinetic behavior.<sup>204</sup> The five groups have been defined as follows:

*Group I.* Monomers which polymerize faster in the solid-state than immediately above the melting points, for example, styrene, 2,4-dimethylstyrene, acrylonitrile, methacrylonitrile, and formaldehyde.

*Group II.* Monomers which do not polymerize in the liquid state but do in the solid state, for example, hexamethylcyclotrisiloxane,  $\beta$ -propiolactone, trioxane, diketene, and 3,3-bis(chloromethyl)oxetane.

*Group III.* Monomers which polymerize much slower in the solid state than in the liquid and may not polymerize at all in the crystalline state, for example, methyl methacrylate, methyl acrylate, vinyl acetate, and vinyl chloride.

*Group IV.* Monomers which polymerize equally well in either state, for example, vinyl stearate, vinyl carbazole, and vinyl pyrrolidone.

Table 11-28

Polymerization of Olefin Monomers in the Solid State Initiated by Gamma Radiation<sup>202</sup>

Olefin monomer	Monomer M.P., °C	Irradiation temp., °C	Tendency to polymerize	$V_s/V_l^a$
Styrene	-30	-51 to -78	+	$\gg 1$
$\alpha$ -Methylstyrene	-23	-78 to -196	-	0
2,4-Dimethylstyrene	—	-80	+	—
Vinyl acetate	-159	-196	+	$\ll 1$
Vinyl carbazole	+64	6-20	+	$\approx 1$
Vinyl chloride	-138	-138	-	0
1,3-Butadiene	—	-196	+	—
N-Vinylphthalimide	—	—	-	0
Isobutene	-141	-80, -196	+	$\approx 1$
Acrylic acid	+12	—	+	—
Methacrylic acid <sup>b</sup>	+16	0	+	—
Acrylamide	+85	0-60	+	—
Acrylonitrile	-83	-83 to -135	+	$\gg 1$
Methyl methacrylate <sup>c</sup>	-50	-78, -196	-	0
Octadecyl methacrylate	+17	-10, +30	+	1

<sup>a</sup> Ratio of rates above ( $V_l$ ) and below ( $V_s$ ) the melting point.

<sup>b</sup> Also initiated by ultraviolet light radiation.

<sup>c</sup> Does not polymerize with either ultraviolet light or gamma radiation.

*Group V.* Monomers which exhibit a negative activation energy in the liquid state and a slow reaction rate in the solid, for example, butadiene, and possibly isoprene and isobutene.

The propagation reactions for Group I and II monomers in the solid state are probably ionic in mechanism, while those for Groups III and IV are believed to be free radical in character. Very little information is available on the solid-state polymerization of Group V monomers.



Monomers in Group III have been polymerized both in the crystalline state and as organic glasses.

The most detailed work on the mechanism of solid-state polymerization reactions of olefin monomers reported in the literature has been on salts of acrylic acid and on acrylamide.<sup>205, 206</sup> A free-radical mechanism for the latter is supported by the observation that the number of growing polymer chains calculated from yield and molecular weight data agrees closely with the number of free radicals measured by electron spin resonance spectroscopy.<sup>206, 207</sup>

The structure of the crystal lattice and crystal imperfections play important and sometimes controlling roles in these reactions, and it has been postulated that reactive sites must be no further apart in the monomer crystal than a distance of 4 Å.<sup>208</sup> Evidence that polymerization occurs at crystal imperfections in acrylamide is that if the crystal is scratched the polymerization reaction proceeds rapidly along the scratch.<sup>209</sup> Isolation of growing ends of live polymer chains by the lattice structure and by crystal boundaries permits very high radical concentrations, on the order of  $10^{-4}M$ , and at the same time, results in very low termination rates. Crystallographic data on partially polymerized single crystals of both calcium acrylate dihydrate and barium methacrylate dihydrate indicate that there is no change in the atomic positions of the unreacted monomer, so that the growing end of the active polymer chain is apparently embedded in the crystalline monomer phase with the remainder of the polymer chain forming a separate phase.<sup>210</sup>

Long-lived radicals are the rule and are necessary because the propagation reactions are extremely slow in the solid state compared to homogeneous, liquid-state polymerization reactions. The propagation rate for crystalline acrylamide corresponded to a mean time of approximately 10 sec between successive additions of monomer molecules to a growing polymer chain.<sup>206</sup> In homogeneous bulk polymerization, the mean time between additions is approximately  $10^{-4}$  sec. The extremely slow rate of addition apparently eliminates the possibility that the heat of polymerization causes localized melting in solid-state polymerization reactions.

The importance of crystal lattice structure is shown convincingly by the fact that crystalline methylene bisacrylamide will polymerize at a much slower rate than acrylamide,<sup>211</sup> that many monomers which are highly reactive in liquid form do not polymerize at all in the solid state,<sup>206</sup> and that different salts of acrylic acid polymerize at vastly different rates.<sup>212</sup> Potassium acrylate polymerizes, by initiation of the crystalline monomer with ionizing radiation, many orders of magnitude more rapidly than either sodium or lithium acrylate, while with calcium acrylate the anhydrous crystalline salt and the dihydrate can be polymerized in the solid state but

the monohydrate is inert. The polymerization rates of the anhydrous amorphous salts depend on the hydrate form from which it originates.<sup>210</sup> The role of the crystal lattice has been likened to that of the catalytic surface in heterogeneous polymerization reactions of the Ziegler type.<sup>206</sup> As expected, the usual steady-state assumptions for homogeneous, free-radical polymerization cannot be invoked here, and the kinetics are considerably different.<sup>205</sup>

A unique form of solid-state polymerization, mentioned briefly in Section 15.E.1, has been carried out on vinyl and diene monomers in the canals of urea and thiourea clathrates.<sup>213</sup> The polymerization reaction is initiated by irradiation of the clathrates with high energy electrons and is probably free radical in character.

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