

Copolymerization

I. INTRODUCTION

As indicated in Chapter 1, the polymerization of organic compounds was first reported about the mid-19th century. However, it was not until about 1910 that the simultaneous polymerization of two or more monomers (or copolymerization) was investigated when it was discovered that copolymers of olefins and dienes produced better elastomers than either polyolefins or polydienes alone. The pioneering work of Staudinger in the 1930s and the development of synthetic rubber to meet wartime needs opened the field of copolymerization.

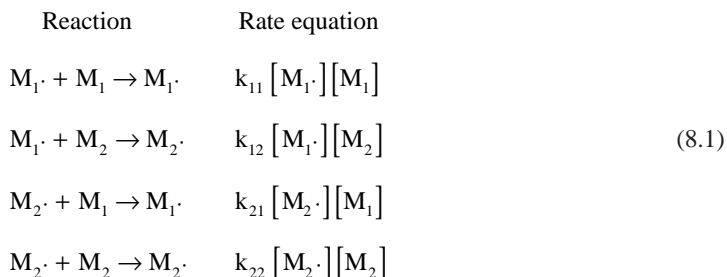
Copolymers constitute the vast majority of commercially important polymers. Compositions of copolymers may vary from only a small percentage of one component to comparable proportions of both monomers. Such a wide variation in composition permits the production of polymer products with vastly different properties for a variety of end uses. The minor constituent of the copolymer may, for example, be a diene introduced into the polymer structure to provide sites for such polymerization reaction as vulcanization; it may also be a trifunctional monomer incorporated into the polymer to ensure cross-linking, or possibly it may be a monomer containing carboxyl groups to enhance product solubility, dyeability, or some other desired property. Copolymerization reactions may involve two or more monomers; however, our discussion here is limited to the case of two monomers.

II. THE COPOLYMER EQUATION

Some observations are relevant to the consideration of copolymerization kinetics are

- The number of reactions involved in copolymerization of two or more monomers increases geometrically with the number of monomers. Consequently, the propagation step in the copolymerization of two monomers involves four reactions.
- The number of radicals to be considered equals the number of monomers. The terminal monomer unit in a growing chain determines almost exclusively the reaction characteristics; the nature of the preceding monomers has no significant influence on the reaction path.
- There are two radicals in the copolymerization of two monomers. Consequently, three termination steps need to be considered.
- The composition and structure of the resulting copolymer are determined by the relative rates of the different chain propagation reactions.

By designating the two monomers as M_1 and M_2 and their corresponding chain radicals as $M_1\cdot$ and $M_2\cdot$, the four propagation reactions and the associated rate equations in the copolymerization of two monomers may be written as follows:



Here the first subscript in the rate constant refers to the reacting radical, while the second subscript designates the monomer. Now, it is reasonable to assume that at steady state, the concentrations of $M_1\cdot$ and $M_2\cdot$ remain constant. This implies that the rates of generation and consumption of these radicals are equal. It follows therefore that the rate of conversion of $M_1\cdot$ to $M_2\cdot$ necessarily equals that of conversion of $M_2\cdot$ to $M_1\cdot$. Thus from Equation 8.1

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \quad (8.2)$$

The rates of disappearance of monomers M_1 and M_2 are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \quad (8.3)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] \quad (8.4)$$

By using Equation 8.2, one of the radicals can be eliminated. By dividing Equation 8.3 by Equation 8.4 we obtain:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1 [M_2] + [M_2]}{[M_1] + r_2 [M_2]} \quad (8.5)$$

where r_1 and r_2 are monomer reactivity ratios defined by

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad (8.6)$$

$$r_2 = k_{22}/k_{21}$$

Equation 8.5 is the copolymer equation. Let F_1 and F_2 represent the mole fractions of monomers M_1 and M_2 in the increment of polymer formed at any instant during the polymerization process, then

$$F_1 = 1 - F_2 = d[M_1]/d([M_1] + [M_2]) \quad (8.7)$$

Similarly, representing the mole functions of unreacted M_1 and M_2 in the monomer feed by f_1 and f_2 , then

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (8.8)$$

Substitution of Equations 8.7 and 8.8 in Equation 8.5 yields:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (8.9)$$

III. TYPES OF COPOLYMERIZATION

By definition, r_1 and r_2 represent the relative preference of a given radical that is adding its own monomer to the other monomer. The physical significance of Equation 8.9 can be illustrated by considering the product of the reactivity ratios,

$$r_1 r_2 = \frac{k_{11} k_{22}}{k_{12} k_{21}} \quad (8.10)$$

The quantity $r_1 r_2$ represents the ratio of the product of the rate constants for the reaction of a radical with its own kind of monomer to the product of the rate constants for the cross-reactions. Copolymerization may therefore be classified into three categories depending on whether the quantity $r_1 r_2$ is unity, less than unity, or greater than unity.

A. IDEAL COPOLYMERIZATION ($r_1 r_2 = 1$)

$$\begin{aligned} r_1 r_2 = 1, \quad \text{then} \\ r_1 = 1/r_2 \quad \text{or} \quad k_{11}/k_{12} = k_{21}/k_{22} \end{aligned} \quad (8.11)$$

In this case the copolymer equation reduces to

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1 [M_1]}{[M_2]} \quad (8.12)$$

or

$$F_1 = \frac{r_1 f_1}{f_1(r_1 - 1) + 1} = \frac{r_1 f_1}{r_1 f_1 + f_2} \quad (8.13)$$

It is evident that for ideal copolymerization, each radical displays the same preference for adding one monomer over the other. Also, the end group on the growing chain does not influence the rate of addition. For the ideal copolymer, the probability of the occurrence of an M_1 unit immediately following an M_2 unit is the same as locating an M_1 unit after another M_1 unit. Therefore, the sequence of monomer units in an ideal copolymer is necessarily random.

The relative amounts of the monomer units in the chain are determined by the reactivities of the monomer and the feed composition. To illustrate this, we note that the requirement that $r_1 r_2 = 1$ can be satisfied under two conditions:

Case 1: $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$. In this case, one of the monomers is more reactive than the other toward the propagating species. Consequently, the copolymer will contain a greater proportion of the more reactive monomer in the random sequence of monomer units. An important practical consequence of ideal copolymerization is that increasing difficulty is experienced in the production of copolymers with significant quantities of both monomers as the difference in reactivities of the two monomers increases.

Case 2: $r_1 = r_2 = 1$. Under these conditions, the growing radicals cannot distinguish between the two monomers. The composition of the copolymer is the same as that of the feed and as we said above, the monomers are arranged randomly along the chain. The copolymer equation becomes:

$$F_1 = \frac{f_1 f_1}{f_1 + f_2} = f_1 \quad (8.14)$$

B. ALTERNATING COPOLYMERIZATION ($r_1 = r_2 = 0$)

When $r_1 = r_2 = 0$ (or $r_1 r_2 = 0$), each radical reacts exclusively with the other monomer; that is neither radical can regenerate itself. Consequently, the monomer units are arranged alternately along the chain irrespective of the feed composition. In this case the copolymer reduces to:

$$\frac{d[M_1]}{d[M_2]} = 1 \quad (8.15)$$

or

$$F_1 = 0.5$$

Table 8.1 Reactivity Ratios of Some Monomers

Monomer 1	Monomer 2	r_1	r_2	T (°C)
Acrylonitrile	1,3-Butadiene	0.02	0.30	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

From Young, L.J., *Polymer Handbook*, 2nd ed., Brandrup, J. and Immergut, H.H., Eds., John Wiley & Sons, New York, 1975. With permission.

Polymerization continues until one of the monomers is used up and then stops. Perfect alternation occurs when both r_1 and r_2 are zero. As the quantity $r_1 r_2$ approaches zero, there is an increasing tendency toward alternation. This has practical significance because it enhances the possibility of producing polymers with appreciable amounts of both monomers from a wider range of feed compositions.

C. BLOCK COPOLYMERIZATION ($r_1 > 1$, $r_2 > 1$)

If r_1 and r_2 are both greater than unity, then each radical would prefer adding its own monomer. The addition of the same type of monomer would continue successively until there is a chance addition of the other type of monomer and the sequence of this monomer is added repeatedly. Thus the resulting polymer is a block copolymer. In the extreme case of this type of polymerization ($r_1 = r_2 = \infty$) both monomers undergo simultaneous and independent homopolymerization; however, there are no known cases of this type of polymerization. Even though cases exist where $r_1 r_2$ approaches 1 ($r_1 r_2 = 1$), there are no established cases where $r_1 r_2 > 1$. Indeed, the product $r_1 r_2$ is almost always less than unity. Table 8.1 lists the reactivity ratios for some monomers.

Example 8.1: The reactivity ratios for the copolymerization of methyl methacrylate (1) and vinyl chloride (2) at 68°C are $r_1 = 10$ and $r_2 = 0.1$. To ensure that the copolymer contains an appreciable quantity (>40% in this case) of the vinyl chloride, a chemist decided to carry out the copolymerization reaction with a feed composed of 80% vinyl chloride. Will the chemist achieve his objective?

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} = \frac{10(0.2)^2 + (0.2)(0.8)}{10(0.2)^2 + 2(0.2)(0.8) + 0.1(0.8)^2}$$

$$= 0.714$$

$$F_2 = 1 - F_1 = 0.286.*$$

If the difference in the reactivities of the two monomers is large, it is impossible to increase the proportion of the less-reactive monomer in the copolymer simply by increasing its composition in the feed.

IV. POLYMER COMPOSITION VARIATION WITH FEED CONVERSION

Since the reactivity ratios r_1 and r_2 are generally of different magnitudes, there are necessarily differences in the rate of possible growth reactions. Consequently, the composition of the feed, f_1 , and that of the

* Although $f_2 = 80\%$, $F_2 = 28.6\%$.

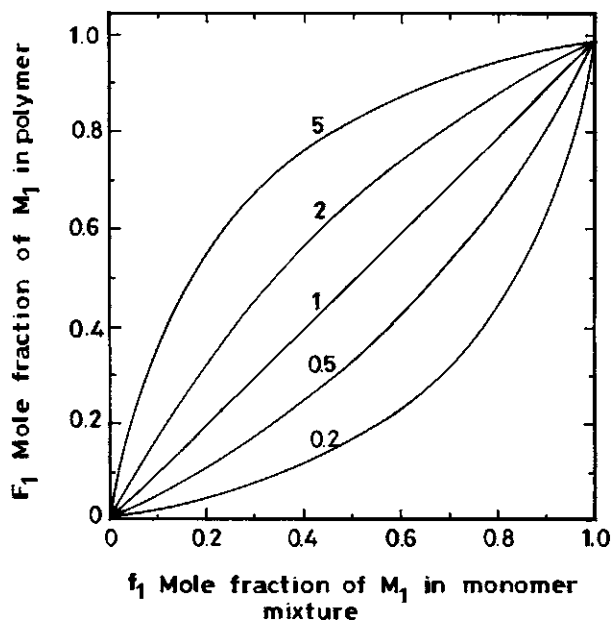


Figure 8.1 Variation of instantaneous composition of copolymer (mole fraction, F_1) with feed composition (mole fraction f_1 for ideal copolymerization with the values of $r_1 = 1/r_2$ indicated).

polymer, F_1 , is neither equal nor constant throughout the polymerization. Therefore, the polymer produced over a finite range of conversion consists of a summation of increments of polymer differing in composition. Consider, for example, the copolymerization of styrene (1) and vinyl acetate (2). The reactivity ratios are $r_1 = 55$ and $r_2 = 0.015$. This means that either radical has a much greater preference to add styrene than vinyl acetate. The first polymer formed consists mainly of styrene. This also means a faster depletion of styrene in the feed. As polymerization proceeds, styrene is essentially used up and the last polymer formed consists mostly of vinyl acetate. However, at 100% conversion, the overall polymer composition must reflect the initial composition of the feed. It follows that the copolymers generally have a heterogeneous composition except in very special cases.

Equations 8.5 and 8.9 give the instantaneous polymer composition as a function of feed composition for various reactivity ratios. Figure 8.1 shows a series of curves calculated from these equations for ideal copolymerization. The range of feed composition that gives copolymers containing appreciable amounts of both monomers is small except the monomers have very similar reactivities.

The curves for several nonideal cases are shown in Figure 8.2. These curves illustrate the effect of increasing tendency toward alternation. With increasing alternation, a wider feed composition yields a copolymer containing substantial amounts of each monomer. This tendency is utilized in practice for the preparation of many important copolymers.

In those cases, where r_1 and r_2 are both either less or greater than unity, the curves of Figure 8.2 cross the line $F_1 = f_1$. The points of interception represent the occurrence of azeotropic copolymerization; that is, polymerization proceeds without a change in the composition of either the feed or the copolymer. For azeotropic copolymerization the solution to Equation 8.5 with $d[M_1]/d[M_2] = [M_1]/[M_2]$ gives the critical composition.

$$\frac{[M_1]}{[M_2]} = \frac{1-r_2}{1-r_1} \quad (8.16)$$

$$(f_1)_c = \frac{1-r_2}{2-r_1-r_2} \quad (8.17)$$

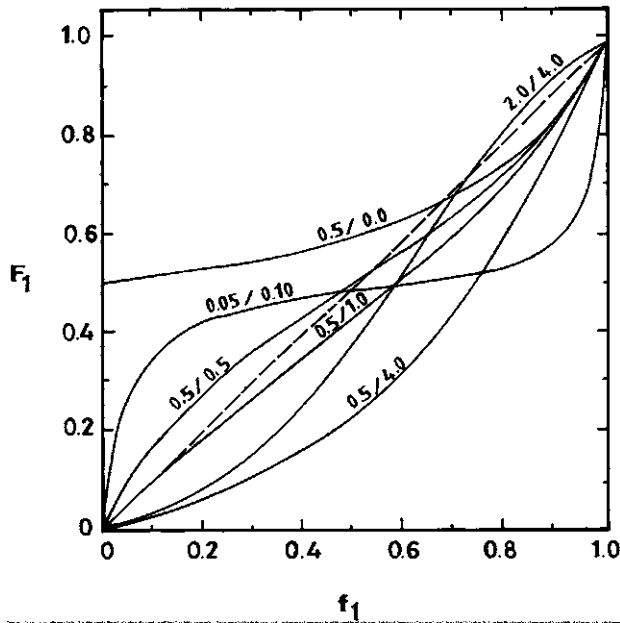


Figure 8.2 Instantaneous composition of copolymer F_1 as a function of monomer composition f_1 for the values of the reactivity ratios r_1/r_2 indicated.

If both r_1 and r_2 are greater than unity or if both are less than unity, then $(f_1)_C$ lies within the acceptable range $0 < f_1 < 1$. If $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, then there will be no critical feed composition, $(f_1)_C$. As we said earlier, cases where both r_1 and r_2 are greater than unity are not known; whereas, there are numerous cases where r_1 and r_2 are less than unity. When $r_1 \ll 1$ and $r_2 \gg 1$ or $r_1 \gg 1$ and $r_2 \ll 1$, the two monomers have a tendency to polymerize consecutively; the first polymer is composed predominantly of the more reactive monomer; the other monomer polymerizes only after almost all of the more reactive monomer has been exhausted. The case of styrene–vinyl acetate discussed above exemplifies this type of copolymerization.

Our discussion thus far has indicated that during copolymerization, the composition of both the feed and the polymer vary with conversion. To follow this composition drift, it is necessary to integrate the copolymer equation — a problem that is complex. Consider a system that is composed initially of M total moles of the two monomers ($M = M_1 + M_2$) and in which the resulting copolymer is richer in M_1 than the feed ($F_1 > f_1$). When dM moles have been polymerized, the polymer will contain $F_1 dM$ moles of M_1 while the feed content of M_1 will be reduced to $(M - dM)(f_1 - df_1)$ moles. Writing a material balance for M_1 :

$$Mf_1 - (M - dM)(f_1 - df_1) = F_1 dM \quad (8.18)$$

Expanding and neglecting the second-order differential yields:

$$dM/M = df_1/(F_1 - f_1) \quad (8.19)$$

On integration, Equation 8.19 becomes

$$\ln M/M_0 = \int_{f_0}^f df_1/(F_1 - f_1) \quad (8.20)$$

where M_0 and f_{10} are the initial values of M and f_1 . Using Equation 8.19, it is possible to calculate F_1 by choosing values for f_1 , and the integral may be evaluated graphically or numerically. This gives the relation between feed composition and the degree of conversion ($1 - M/M_0$). An analytic solution to Equations 8.19 and 8.20 has been obtained. For $r_1 \neq 1$ and $r_2 \neq 1$,

$$\frac{M}{M_0} = \left[\frac{f_1}{(f_1)_0} \right]^\alpha \left[\frac{f_2}{(f_2)_0} \right]^\beta \left[\frac{(f_1)_0 - \delta}{f_1 - \sigma} \right]^\gamma \quad (8.21)$$

where the superscripts are given by:

$$\alpha = \frac{r_2}{1-r_2}; \quad \beta = \frac{r_1}{1-r_1}; \quad \gamma = \frac{1-r_1 r_2}{(1-r_1)(1-r_2)} \quad (8.22)$$

$$\delta = \frac{1-r_2}{2-r_2-r_1}$$

The feed composition variation with conversion gives the instantaneous composition of the copolymer as a function of conversion. It is also useful to know the *overall average composition* $\langle F_1 \rangle$ for a given conversion. This can be obtained through a material balance, say, for M_1 in a batch reactor. Moles M_1 in feed = moles of M_1 in polymer + moles of unreacted M_1 .

$$(f_1)_0 M_0 = \langle F_1 \rangle (M_0 - M) + f_1 M \quad (8.23)$$

On rearrangement Equation 8.23 becomes:

$$\langle F \rangle = \frac{f_{10} - f_1 (M/M_0)}{(1 - M/M_0)} \quad (8.24)$$

Example 8.2: What is the composition of the copolymer formed by the polymerization of an equimolar mixture of butadiene (1) and styrene (2) at 66°C? Which will contain more styrene — the polymer formed first or that formed later in the reaction?

Solution: From Table 8.1, $r_1 = 1.35$ and $r_2 = 0.58$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$= \frac{1.35(0.5)^2 + (0.5)^2}{1.35(0.5)^2 + 2(0.5)^2 + 0.58(0.5)^2}$$

$$= 0.60$$

$$k_{11} = 1.35 k_{12}, \quad k_{22} = 0.58 k_{21}$$

The rate of consumption of butadiene by either radical is greater than the rate of addition of styrene. Therefore the polymer formed first will be richer in butadiene while the polymer formed at the later stages of the reaction will be richer in styrene.

Example 8.3: Estimate the feed and copolymer compositions for the azeotropic copolymerization of acrylonitrile and styrene at 60°C.

Solution: For azeotropic copolymerization:

$$f_{1c} = \frac{1 - r_2}{2 - r_1 - r_2}$$

From Table 8.1

$$f_{1c} = \frac{1 - 0.4}{2 - 0.04 - 0.4}$$

$$f_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$= \frac{0.04(0.38)^2 + (0.38)(0.62)}{0.04(0.38)^2 + 2(0.38)(0.62) + 0.4(0.62)^2}$$

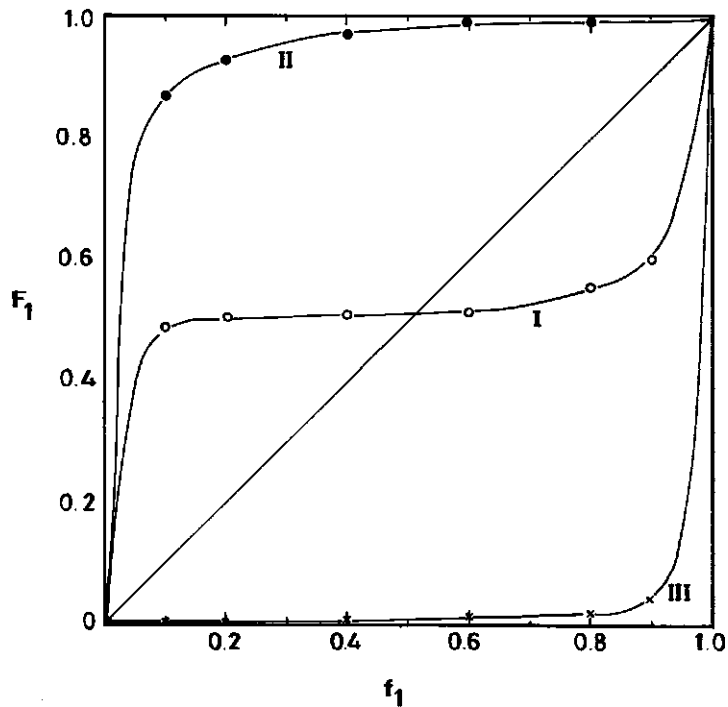
$$= 0.38$$

Example 8.4: Plot graphs showing the variation of the instantaneous copolymer composition F_1 with monomer composition for the following systems:

- I. Vinyl acetate (1), maleic anhydride (2), 75°C, $r_1 = 0.055$, $r_2 = 0.003$.
- II. Styrene (1), vinyl acetate (2), 60°C, $r_1 = 55$, $r_2 = 0.01$.
- III. Vinyl chloride (1), methyl methacrylate (2) 68°C, $r_1 = 0.1$, $r_2 = 10$

Comment on the shapes of the curves.

Solution:



The range of feed composition that gives copolymers with appreciable quantities of both monomers is small for Cases II and III where the differences in reactivity ratios are large. However, in Case I where the reactivity ratios are comparable, copolymers with comparable quantities of both monomers are obtainable.

V. CHEMISTRY OF COPOLYMERIZATION

By definition, monomer reactivity ratios are independent of the initiation and termination steps of copolymerization reaction. In addition, they are virtually independent of the reaction medium, and their dependence on temperature is minimal. The relative reactivities of a series of monomers are determined by the reactivity of the individual monomer and that of the attacking radical. The reactivities of monomers and radicals are themselves dependent on the nature of the substituents on the monomer double bond. The influence of substituents on reactivity is threefold:

- Enhancement of monomer reactivity through activation of the double bond
- Conferment of resonance stabilization on the resulting radical
- Provision of steric hindrance at the reaction site

We now briefly discuss the contribution of these factors to radical copolymerization reactions.

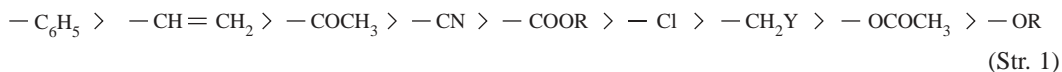
A. MONOMER REACTIVITY

The relative reactivities of monomers to a given radical can be obtained from analysis of the relative reactivity ratios. This can be seen by considering the inverse of the monomer reactivity ratio:

$$1/r_1 = k_{12}/k_{11} \quad (8.25)$$

The inverse of the reactivity ratio (Equation 8.25) is the ratio of the rate of reaction of the given radical with another monomer to its rate of reaction with its own monomer. If the rate of reaction of the reference radical with its own monomer is taken as unity (i.e., $k_{11} = 1$), then the resulting k_{12} values give the relative reactivities of monomers with respect to the reference radical. A list of such values is given in Table 8.2.

Note that a different reference is taken for each column and as such only values in each column can be compared; horizontal comparisons are meaningless. In general, the relative reactivities of monomers decrease from the top to the bottom of each column; the order of decrease is irregular due to the specificity of addition of monomers by radicals. It is evident that the effect of substituents in enhancing monomer reactivity is in the order:



The effect of a second 1-substituent is generally additive.

Table 8.2 *Relative Reactivities of Monomers to Reference Radicals at 60°C*

Monomer	Reference Radical				
	Styrene	Methyl Methacrylate	Acrylonitrile	Vinyl Chloride	Vinyl Acetate
Styrene	(1.0)	2.2	25	50	100
Methyl methacrylate	1.9	(1.0)	6.7	10	67
Acrylonitrile	2.5	0.82	(1.0)	25	20
Vinylidene chloride	5.4	0.39	1.1	5	10
Vinyl chloride	0.059	0.10	0.37	(1.0)	4.4
Vinyl acetate	0.019	0.05	0.24	0.59	(1.0)

From Billmeyer, F.W., Jr., *Textbook of Polymer Science*, 2nd ed., Interscience, New York, 1971. © John Wiley & Sons. Reprinted with permission of John Wiley & Sons.

Table 8.3 Radical–Monomer Propagation Rate Constants at 60°C (l/mol-s)

Monomer	Radical					
	Butadiene	Styrene	Methyl Methacrylate	Methyl Acrylate	Vinyl Chloride	Vinyl Acetate
Butadiene	100	250	2,820	42,000	350,000	—
Styrene	74	143	1,520	14,000	600,000	230,000
Methyl methacrylate	134	278	705	4,100	123,000	150,000
Methyl acrylate	132	206	370	2,090	200,000	23,000
Vinyl chloride	11	8	70	230	12,300	10,000
Vinyl acetate	—	2.6	35	520	7,300	2,300

From Billmeyer, F.W., Jr., *Textbook of Polymer Science*, 2nd ed., Interscience, New York, 1971. © John Wiley & Sons. Reproduced with permission of John Wiley & Sons.

The above order of monomer reactivities corresponds to the order of increased resonance stabilization of the resulting radical by the particular substituent. Substituents with unsaturation leading to a monomer with conjugated bonds are most effective in conferring resonance stabilization on radicals. On the other hand, substituents such as chlorine that have only nonbonding electrons for interaction with the radical show only weak stabilization. In the case of styrene, for example, the resonance stabilization energy is about 20 kcal/mol compared with 1 to 4 kcal/mol for the unconjugated systems. It is important to remember, however, that substituents that stabilize the product radical also stabilize the monomer, albeit to a much lesser extent. Again, using styrene as an example, the monomer is stabilized to about 3 kcal/mol. Therefore a limited compensation is derived from the stabilization of monomers by substituents.

B. RADICAL REACTIVITY

The relative reactivities of radicals to a reference monomer can be obtained from the product of the inverse of the reactivity ratio ($1/r_1 = k_{12}/k_{11}$) and the appropriate propagation rate constants for homopolymerization (k_{11}). Some values are listed in Table 8.3.

The order of enhancement of radical reactivity due to substituents is the reverse of that for the monomers. This should be expected because the enhancement of monomer reactivity by a substituent is due to its stabilization and the consequent decrease of the reactivity of the corresponding radical. The degree of depression of radical reactivity by substituents turns out to be much greater than the extent of enhancement of monomer reactivity. The styrene radical is about 1000 times less reactive than the vinyl acetate radical to a given monomer if the effects of alternation are disregarded, but then the styrene monomer is only about 50 times more reactive than the vinyl acetate to a given radical.

C. STERIC EFFECTS

Monomer–radical reaction rates are also influenced by steric hindrance. The effect of steric hindrance in reducing monomer reactivity can be illustrated by considering the copolymerization reaction rate constants (k_{12}) for di- and tri-substituted ethylene. Table 8.4 lists some of these values.

Table 8.4 Rate Constants (k_{12}) for Radical–Monomer Reactions

Monomer	Polymer Radical		
	Vinyl acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	8.7	720
Vinylidene chloride	23,000	78	2,200
<i>cis</i> -1,2-dichloroethylene	370	0.60	—
<i>trans</i> -1,2-dichloroethylene	2,300	3.9	—
Trichloroethylene	3,450	8.6	29
Tetrachloroethylene	460	0.70	4.1

From Odian, G., *Principles of Polymerization*, McGraw-Hill, New York, 1970. With permission.

We have already alluded to the fact that the addition of a second substituent to the 1- or α -position increases monomer reactivity. However, when the same substituent is in the 2- or β -position (i.e., 1,2-disubstitution), the reactivity of the monomer decreases 2- to 20-fold. This has been attributed to the resulting steric hindrance between the substituent and the attacking radical. The role of steric hindrance in the reduction of the reactivity of 1,2-disubstituted vinyl monomers can be further illustrated by the fact that while these monomers undergo copolymerization with other monomers, say, styrene, they exhibit extreme reluctance to homopolymerize. Homopolymerization is prevented because of the steric hindrance between a 2-substituent on the attacking radical and the monomer. On the other hand, there is no 2- or β -substituent on the attacking styrene radical; consequently, copolymerization is possible.

Example 8.5: Arrange the following monomers in the possible order of decreasing reactivity with an acrylonitrile radical. What is the basis of your arrangement?

- Methacrylate
- Vinyl methyl ether
- Methyl methacrylate
- Vinyl acetate

Solution:

Monomer	Structure
a. Methacrylate	$\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$
b. Vinyl methylether	$\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$
c. Methyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 = \text{C} \\ \\ \text{C} = \text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$
d. Vinyl acetate	$\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{O} \\ \\ \text{C} = \text{O} \\ \\ \text{CH}_3 \end{array}$

Order of reactivity: $c > a > d > b$. Reason: (1) increasing stabilization of resulting radical; (2) second substituent in 1-position increases monomer reactivity.

D. ALTERNATION-POLAR EFFECTS

We indicated in our earlier discussion that the relative reactivities of different monomers were not exactly the same for different radicals. Similarly, the order of reactivity of different radicals is influenced by the

Table 8.5 Product of Reactivity Ratios of Monomers Showing Order of Alternating Tendency

Vinyl acetate								
—	Butadiene							
0.55	0.78	Styrene						
0.39	0.31	0.34	Vinyl chloride					
0.30	0.19	0.24	1.0	Methyl methacrylate				
0.60	0.10	0.16	0.96	0.61	Vinylidene chloride			
0.90	0.04	0.11	0.24	0.96	0.08	Methyl acrylate		
0.21	0.006	0.016	0.11	0.18	0.34	0.84	Acrylonitrile	
0.004	—	0.02	0.06	—	0.56	—	—	Diethyl fumarate

reference monomer. This suggests, therefore, that monomer reactivity is a function of radical reactivity and vice versa. A close examination of monomer reactivity data reveals a tendency toward enhanced copolymerization reactivities for certain pairs of monomers. This is evidently a result of some monomer–radical affinity. This tendency toward enhanced reactivity for certain monomer pairs is a general phenomenon in radical copolymerization and is due to the alternating tendency in comonomer pairs. As the quantity r_1r_2 deviates from unity (ideal behavior) and approaches zero, the tendency for alternation increases. It is possible to arrange monomers in order of their r_1r_2 values such that the farther apart any two pairs of monomers are, the greater their tendency toward alternation. Table 8.5 shows such an arrangement. Notice, however, that there are some exceptions, presumably due to the predominance of steric factors; for example, vinyl chloride and styrene show a greater alternation tendency than vinyl chloride and vinyl acetate, even though the former monomer pair is closer in Table 8.5 than the latter.

The order of occurrence of monomers in Table 8.5 is obviously a reflection of the polarity of the double bond. Observe that the product r_1r_2 approaches unity only in those cases where the substituents on the monomers are either both electron-donating or electron-withdrawing substituents. Expressed differently, alternation tendency increases if the substituents on both monomers exhibit different electron-donating or electron-attracting characteristics. Alternation tendency is enhanced by an increased difference in the polarity of monomer pairs.

Example 8.6: Which of the following pairs of monomers will most probably form an alternating copolymer?

- Butadiene (1), Styrene (2), 60°C, $r_1 = 1.89$, $r_2 = 0.78$.
- Vinyl acetate (1), styrene (2), 60°C, $r_1 = 0.01$, $r_2 = 55$.
- Maleic anhydride (1), isopropenyl acetate (2), 60°C, $r_1 = 0.002$, $r_2 = 0.032$.

Solution:

Monomer	r_1r_2
(a)	1.4742
(b)	0.5500
(c)	0.000064

Alternating tendency increases generally as r_1r_2 approaches zero. Hence monomer pair (c) has the highest alternating tendency.

VI. THE Q-e SCHEME

The Q-e scheme is an attempt to express free radical copolymerization data on a quantitative basis by separating reactivity ratio data for monomer pairs into parameters characteristic of each monomer. Under this scheme, radical–monomer reaction rate constant k_{12} is written as:

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \quad (8.26)$$

Table 8.6 *Q and e Values for Monomers*

Monomer	e	Q
<i>t</i> -Butyl vinyl ether	-1.58	0.15
Ethyl vinyl ether	-1.17	0.032
Butadiene	-1.05	2.39
Styrene	-0.80	1.00
Vinyl acetate	-0.22	0.026
Vinyl chloride	0.20	0.44
Vinylidene chloride	0.36	0.22
Methyl methacrylate	0.40	0.74
Methyl acrylate	0.60	0.42
Methyl vinyl ketone	0.68	0.69
Acrylonitrile	1.20	0.60
Diethyl fumarate	1.25	0.61
Maleic anhydride	2.25	0.23

From Alfrey, T., Jr. and Price, C.C., *J. Polym. Sci.*, 2, 101, 1947. With permission.

where P_1 represents the reactivity of radical $M_1\cdot$ and Q_2 the reactivity of monomer M_2 ; e_1 and e_2 represent the degrees of polarity of the radical and monomer, respectively. Both P and Q are determined by the resonance characteristics of the radical and monomer. It is assumed that both the monomer and its radical have the same e value. Consequently,

$$k_{11} = P_1 Q_1 \exp(-e_1^2) \quad (8.27)$$

Therefore

$$r_1 = k_{11}/k_{12} = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \quad (8.28)$$

Similarly

$$r_2 = k_{22}/k_{21} = Q_2/Q_1 \exp[-e_2(e_2 - e_1)] \quad (8.29)$$

Thus, according to the Q - e scheme, by assigning values to Q and e , it should be possible to evaluate r_1 and r_2 for any monomer pair. A selected list of Q and e values is shown in Table 8.6. Negative values of e indicate electron-rich monomers, while positive e values indicate electron-poor monomers.

The Q - e scheme is subject to criticisms. First, there seems to be no justification for assuming the same e values for the monomer and the radical derived from it. Second, the Q and e values for a particular monomer are not unique; they vary with the monomer to which the monomer is paired (Table 8.7). In spite of these flaws, however, the Q - e scheme provides a semi-empirical basis for correlating the effect of structure on monomer reactivity.

Table 8.7 Variation in Q and e Values

Monomer (M_1)	Comonomer	e_1	Q_1
Acrylonitrile	Styrene	1.20	0.44
	Vinyl acetate	0.90	0.37
	Vinyl acetate	1.0	0.67
	Vinyl chloride	1.3	0.37
	Vinyl chloride	1.6	0.37
Vinyl chloride	Styrene	0.2	0.024
	Methyl acrylate	0.0	0.035

From Odian, G., *Principles of Polymerization*, McGraw-Hill, New York, 1970. With permission.

VII. PROBLEMS

- 8.1. Styrene can undergo copolymerization reaction with either methyl methacrylate or vinyl chloride. It has been suggested that the resulting copolymers become brittle for styrene composition greater than 70%. Explain why even with a feed composition as low as 25% styrene, styrene–vinyl chloride copolymer is brittle, while styrene–methyl methacrylate copolymer is not.
- 8.2. Discuss the composition and structure of the polymer product obtained from the reaction of acrylonitrile (1) and 1,3-butadiene (2) in the molar ratios 25:75, 50:50, and 75:25. $r_1 = 0.02$, $r_2 = 0.3$ at 40°C.
- 8.3. Methyl methacrylate (1) and vinyl chloride (2) form an ideal copolymerization at 68°C. What is the composition of this copolymer for a feed composition $f_1 = 0.75$ and $r_2 = 0.1$?
- 8.4. For a particular application, it has been established that an alternating copolymer is most suitable. Given the following monomers — butadiene, styrene, acrylonitrile, and vinyl chloride — which monomer pair would be best studied for the application?
- 8.5. Arrange the following monomers in *increasing* order of reactivity with a vinyl acetate radical. Explain the basis of your arrangement.
 - a. Acrylonitrile
 - b. Styrene
 - c. α -Methyl styrene
 - d. 2-Methyl styrene
 - e. Vinyl ethyl ether
- 8.6. Maleic anhydride does not homopolymerize, but will readily form alternating copolymer with styrene. Explain.
- 8.7. The following are the Q and e values for monomers A, B, C, and D:

Monomer	Q	e
A	2.39	-1.05
B	0.15	-1.58
C	0.69	0.68
D	0.42	0.60

Monomers A and B; A and C; and C and D are subjected, respectively, to copolymerization reactions. Which of these reactions will most likely result in an alternating polymer? What is the composition of the copolymer formed at low conversion from equimolar mixtures of the pairs of monomers?

- 8.8. Describe the probable proportions and sequences of monomers entering a copolymer chain at the beginning of polymerization of a 1:1 molar mixture of each of the following pairs:
 - a. Vinyl acetate (1) and isopropenyl acetate (2); $r_1 = r_2 = 1$
 - b. Butadiene (1) and styrene (2); $r_1 = 1.89$, $r_2 = 0.78$
 - c. Maleic anhydride (1) and stilbene (2); $r_1 = r_2 = 0.01$

d. Maleic anhydride (1) and isopropenyl acetate (2); $r_1 = 0.002$, $r_2 = 0.032$

In each case, would the composition of polymer formed toward the end of the reaction (where the monomers are nearly consumed) be much different, and if so how?

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