

Chapter 10

Chain Copolymerization

Copolymers [1, 2] contain two or more repeating monomer structures in the polymer chain. The copolymer can be synthesized by chain polymerization using two or more type of monomers. It is called chain copolymerization. The process can be depicted as



The amount of each monomer in the copolymer is determined by their relative concentration and reactivities. The simultaneous chain polymerization can also be carried out with more than two type of monomers. Such polymerizations are generally referred to as *multicomponent copolymerizations*; the term *terpolymerization* is specifically used for systems of three kind of monomers.

Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the chemical structure and relative amounts of two monomer units or higher in the copolymer product. Thus, polymer can be tailor made into product with specifically desired properties. Most of commercial polymers are copolymers. Copolymers are different from polymer blends. Polymer blends are that polymers mixed physically without chemical bonds. Whereas copolymers are that polymers contain more than one kind of monomer repeating unit.

There are three different types of copolymer structures—alternating, block, and graft. The *alternating* copolymer (I) contains the two monomer units in equimolar amounts in a regular alternating distribution:



Copolymers are named by following the prefix *poly* with the names of the two repeating units. The copolymer is specified by inserting *-alt-* for alternate, *-stat-* for statistic, or *-ran-* for random in between the names of the two repeating units, but *-co-* is used for nonspecific copolymer. A block copolymer (II) is a linear copolymer with one or more long uninterrupted sequences of each polymeric species.

copolymerization is dependent only on the identity of the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit. All propagation reactions are irreversible.

Monomer M_1 disappears by reactions in Eqs. 10.2 and 10.4, while monomer M_2 disappears by reactions in Eqs. 10.3 and 10.5. The rates of disappearance of the two monomers are given by

$$-d[M_1]/dt = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \quad (10.6)$$

$$-d[M_2]/dt = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] \quad (10.7)$$

Dividing Eq. 10.6 by Eq. 10.7 yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]} \quad (10.8)$$

In order to remove the concentration terms in $M_1\cdot$ and $M_2\cdot$ from Eq. 10.8, a steady-state concentration is assumed for each of the propagating chains $M_1\cdot$ and $M_2\cdot$ separately. For the concentrations of $M_1\cdot$ and $M_2\cdot$ remain constant, their rates of interconversion must be equal. In other words, the rates of reactions in Eqs. 10.3 and 10.4 must be equal:

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \quad (10.9)$$

Equation 10.9 can be rearranged and combined with Eq. 10.8 to yield

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2\cdot][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2\cdot][M_1]}{k_{22}[M_2\cdot][M_2] + k_{21}[M_2\cdot][M_1]} \quad (10.10)$$

Dividing the top and bottom of the right side of Eq. 10.10 by $k_{21}[M_2\cdot][M_1]$ and combining the result with the parameters r_1 and r_2 , which are defined as

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21} \quad (10.11)$$

One finally obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (10.12)$$

Equation 10.12 is known as the *copolymerization equation* or the *copolymer composition equation*. The copolymer composition, $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units in the copolymer which is related to the concentrations of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2 . The parameters r_1 and r_2 are called the *monomer reactivity ratios*. Each r defines as the ratio of the rate constant for a propagating chain adding its own type of monomer to the rate constant for its addition of the other monomer. The tendency of two monomers to copolymerize is expressed by r values between zero and unity.

A r_1 value greater than unity means that $M_1\cdot$ preferentially adds M_1 instead of M_2 , while an r_1 value less than unity means that $M_1\cdot$ preferentially adds M_2 . A r_1 value of zero would mean that M_1 is incapable of undergoing homopolymerization.

The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, then

$$f_1 = 1 - f_2 = [M_1]/([M_1] + [M_2]) \quad (10.13)$$

and

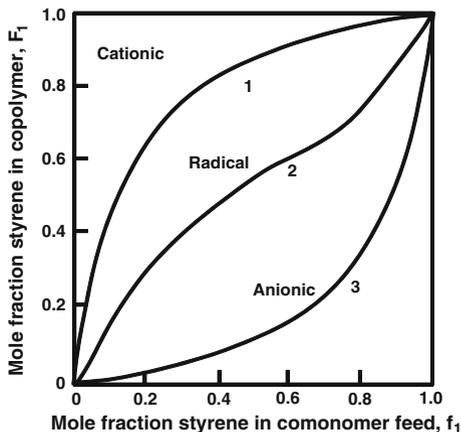
$$F_1 = 1 - F_2 = d[M_1]/(d[M_1] + d[M_2]) \quad (10.14)$$

Combining Eqs. 10.13 and 10.14 with Eq. 10.12 yields

$$F_1 = (r_1f_1^2 + f_1f_2)/(r_1f_1^2 + 2f_1f_2 + r_2f_2^2) \quad (10.15)$$

The copolymerization equation has been experimentally verified in numerous co-monomer systems. The copolymerization equation is equally useful to radical and ionic chain copolymerizations, although the r_1 and r_2 values for any particular co-monomer pair can be drastically different depending on the mode of initiation. Thus the r_1 and r_2 values for the co-monomer pair of styrene (M_1) and methyl methacrylate (M_2) are 0.52 and 0.46 in radical copolymerization, 10 and 0.1 in cationic polymerization, and 0.1 and 6 in anionic copolymerization [1]. Figure 10.1 shows that these different r_1 and r_2 values give rise to large differences in the copolymer composition depending on the mode of initiation. The ionic copolymerizations are expected to be more selective than radical copolymerization. Methyl methacrylate shows increased reactivity in anionic copolymerization and decreased reactivity in cationic copolymerization, while the opposite is observed for styrene. Thus, for an equimolar styrene—methyl methacrylate feed the copolymer is approximately a 1:1 copolymer in the radical polymerization but

Fig. 10.1 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for styrene-methyl methacrylate in cationic (plot 1), radical (plot 2), and anionic (plot 3) copolymerizations initiated by SnCl_4 , benzoyl peroxide, and $\text{Na}/\text{liquid NH}_3$, respectively [1]



is mostly styrene in the cationic copolymerization and mostly methyl methacrylate in the anionic copolymerization.

Radical copolymer is more useful than cationic or anionic copolymer, because about all the monomers are reacted in the radical copolymer. Since termination and initiation rate constants are not involved in the copolymer composition equation, the copolymer composition is independent of difference in the rates of initiation and termination. Thus, the particular initiation system used in a radical copolymerization has no effect on copolymer composition. The copolymer composition is also independent on the absence or presence of inhibitions or chain transfer agents. Therefore, under a wide range of conditions, the copolymer composition is independent of the degree of polymerization.

10.1.1 Types of Copolymerization Behavior

Different types of copolymerization behavior are observed depending on the reactivity ratios of monomers [4]. Copolymerizations can be classified into three types: (1) $r_1 r_2 = 1$, (2) $r_1 r_2 < 1$, (3) $r_1 r_2 > 1$. When the $r_1 r_2$ product is unity, the reaction is called ideal copolymerization. Ideal copolymerization occurs when the two types of propagating chains $M_1\cdot$ and $M_2\cdot$ show the same preference for adding one or the other of the two monomers. Under these conditions

$$k_{22}/k_{21} = k_{12}/k_{11} \text{ or } r_2 = 1/r_1 \quad (10.16)$$

and the relative rates of incorporation of the two monomers into the copolymer is independent of the identity of the unit at the end of the propagating chains. Thus, by combination Eq. 10.16 with Eqs. 10.12 or 10.15 reduces the copolymerization equation to

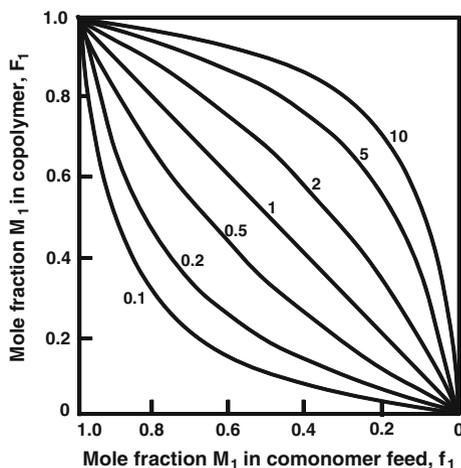
$$d[M_1]/d[M_2] = r[M_1]/[M_2] \quad (10.17a)$$

or

$$F_1 = r_1 f_1 / (r_1 f_1 + f_2) \quad (10.17b)$$

Most of ionic copolymerizations are ideal type. When $r_1 r_2 = 1$, the two monomers show equal reactivity toward both propagating chains. The copolymer composition is the same as the two monomers along the copolymer chain. This behavior is called *random* or *Bernoullian*. For the case, where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating chains. The copolymer will contain a larger proportion of the more reactive monomer in random placement. Figure 10.2 shows the variation in the copolymer composition as a function of the co-monomer feed composition for different value of r_1 . When, for example, $r_1 = 10$, $r_2 = 0.1$, copolymer cannot contain appreciable amounts of M_2 . Thus, a co-monomer feed composition of 80 mol% M_2 ($f_2 = 0.8$) would yield

Fig. 10.2 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for the indicated values of r_1 where $r_1 r_2 = 1$ [1]



a copolymer containing only 18.5 mol% M_2 ($f_2 = 0.185$). It is only $r_1 \approx r_2$, a large range of co-monomer feed compositions which gives copolymer contain appreciable amount of both monomers.

The term ideal copolymerization does not mean it is a desirable process. It is used to explain the process becomes progressively more difficult to produce copolymers containing appreciable amounts of both monomers as the difference in r_1 and r_2 increases. For example, $r_1 = 10$ and $r_2 = 0.1$, the *extreme ideal behavior* occurs when r_1 and r_2 are very different, the obtained copolymers do not contain appreciable amounts of M_2 . To yield copolymers containing appreciable amounts of both monomers, a larger range of co-monomer feed compositions, can be used only for r_1 and r_2 do not differ markedly (e.g., $r_1 = 0.5$, $r_2 = 2$).

When $r_1 r_2 = 0$, the two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain. This type of copolymerization is referred to as *alternating copolymerization*. Each of the two types of propagating chains preferentially adds to the other monomer, that is, $M_1 \cdot$ adds only M_2 and $M_2 \cdot$ adds only M_1 , the copolymerization equation reduces to

$$d[M_1]/d[M_2] = 1 \quad (10.18a)$$

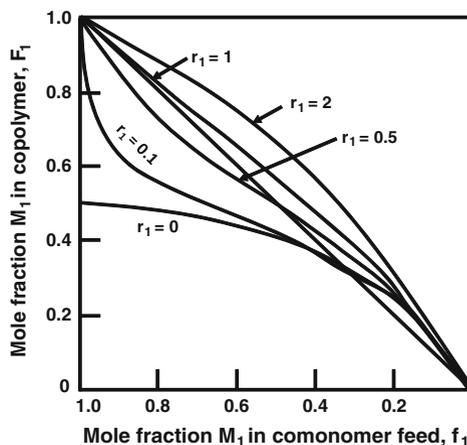
or

$$F_1 = 0.5 \quad (10.18b)$$

The copolymer has the alternating structure irrespective of the co-monomer feed composition. The behavior of most co-monomer systems lies between the two extremes of ideal and alternating copolymerization.

As the $r_1 r_2$ product decreases from unity toward zero, there is an increasing tendency toward alternation. Perfect alternation will occur when r_1 and r_2 become progressively less than unity. The range of behaviors can be seen by considering the

Fig. 10.3 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for the indicated values of r_2 being constant at 0.5 [1]



situation where r_2 remains constant at 0.5 and r_1 varies between 2 and 0. Figure 10.3 shows the copolymer composition as a function of the feed composition in these cases. The curve for $r_1 = 2$ is ideal copolymerization. As r_1 decreases below 2, there is an increasing tendency toward the alternating behavior with each type of propagating chains preferring to add to the other monomer. The increasing alternation tendency is measured by the tendency of the product $r_1 r_2$ to approach zero. When $r_1 r_2$ is very small or zero, the alternation tendency is very large and the range of copolymer compositions that can be obtained is again limited. In the extreme case, only the 1:1 alternating copolymer can be produced for $r_1 r_2 = 0$.

For values of $r_1 r_2 < 1$, the F_1 versus f_1 curves are across the line of $F_1 = f_1$. At these intersections or *crossover points* the copolymer and feed composition are the same. The copolymerization occurred without a change in the feed composition is called “*azeotropic copolymerization*”. The copolymerization Eq. 10.12 can be reduced to

$$\begin{aligned} d[M_1]/d[M_2] &= [M_1]/[M_2], \text{ as} \\ [M_1]/[M_2] &= (r_2 - 1)/(r_1 - 1) \end{aligned} \quad (10.19a)$$

or

$$f_1 = (1 - r_2)/(2 - r_1 - r_2) \quad (10.19b)$$

For the special case of $r_1 \gg r_2$ (i.e. $r_1 \gg 1$ and $r_2 \ll 1$), both types of propagating chains preferentially add to monomer M_1 . There is a tendency toward “*consecutive homopolymerization*” of the two monomers to form block copolymer. For example, the radical polymerization of styrene and vinyl acetate with monomer reactivity ratios of 55 and 0.01 produces block copolymer.

For all copolymerizations except azeotropic copolymerization, the co-monomer feed and copolymer compositions are different. There is a drift in the co-monomer

composition toward the less reactive monomer as the degree of conversion increases. Skeist [5] developed a useful method to analyze copolymer composition as a function of conversion. Consider a system initially containing a total of M moles of the two monomers and in which the copolymer formed is richer in monomer M_1 than is the feed (that is, $F_1 > f_1$). When dM moles of monomers have been copolymerized, the polymer will contain $F_1 dM$ moles of monomer 1 and the feed will contain $(M - dM)(f_1 - df_1)$ moles of monomer 1. A material balance for monomer 1 requires that the moles of M_1 copolymerized is equal to the difference in the moles of M_1 in the feed before and after reaction, or

$$Mf_1 - (M - dM)(f_1 - df_1) = F_1 dM \quad (10.20)$$

Equation 10.20 can be rearranged and converted to the integral form

$$\int_{M_0}^M \frac{dM}{M} = \ln \frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)} \quad (10.21)$$

where M_0 and $(f_1)_0$ are the initial values of M and f_1 .

Equation 10.15 allows the calculation of F_1 as a function of f_1 for a given set of r_1 and r_2 values. These can then be employed as $(F_1 - f_1)$ to allow the graphical or numerical integration of Eq. 10.21 between the limits of $(f_1)_0$ and f_1 . In this manner, one can obtain the variations in the feed and copolymer compositions with the degree of conversion as shown in Eq. 10.22.

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0} \right]^\alpha \left[\frac{f_2}{(f_2)_0} \right]^\beta \left[\frac{(f_1)_0 - \delta}{f_1 - \delta} \right]^\gamma \quad (10.22)$$

The zero subscripts indicate initial quantities and the other symbols are given by

$$\alpha = \frac{r_2}{(1 - r_2)} \quad (10.23a)$$

$$\beta = \frac{r_1}{(1 - r_1)} \quad (10.23b)$$

$$\gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)} \quad (10.23c)$$

$$\delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \quad (10.23d)$$

Equation 10.22 or its equivalent has been used to correlate the drift in the feed and copolymer compositions with conversion for a number of different copolymerization systems.

Fig. 10.4 Variations in feed and copolymer compositions with conversion for styrene (M_1), methyl methacrylate (M_2) with $(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$ and $r_1 = 0.53$, $r_2 = 0.56$ [1]

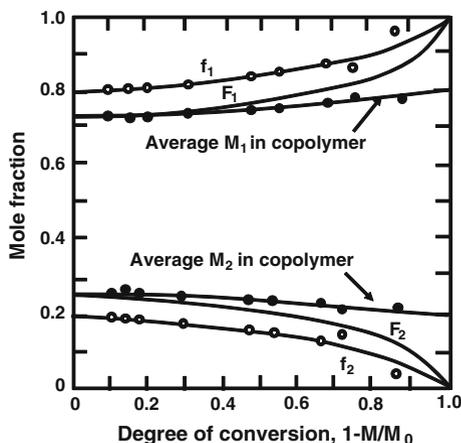


Figure 10.4 shows the variations in feed and copolymer composition with conversion for styrene and methyl methacrylate. The average composition of the copolymer is slightly richer in methyl methacrylate than the feed, because methyl methacrylate has a slightly larger monomer reactivity ratio than styrene. The feed becomes richer in styrene with conversion which leads to an increase in the styrene content of the copolymer with conversion. The average copolymer composition becomes richer in styrene than methyl methacrylate, but less so than the instantaneous copolymer composition.

10.1.2 Effect of Reaction Conditions on Radical Copolymerization

Monomer reactivity ratios are generally (but not always) independent of the reaction medium in radical polymerization. For nonhomogeneous conditions, sometime, the reaction medium affects the monomer reactivity ratio. For instance, the emulsion polymerization of styrene and acrylonitrile, co-monomer feed composition at the reaction site is different from that in the bulk of the reaction system [1]. Deviations are also observed in some copolymerization where the formed copolymer is poorly soluble in the reaction medium. For the copolymerization of methyl methacrylate (M_1) and *N*-vinyl carbazole (NVC) (M_2), $r_1 = 1.80$, $r_2 = 0.06$ in benzene but $r_1 = 0.5$, $r_2 = 0.75$ in methanol. The propagating copolymer chains are completely soluble in benzene, but are marginal in methanol. NVC is preferentially absorbed by the copolymer compared to methyl methacrylate, so NVC enters the copolymer to a greater extent than expected based on the feed composition. The viscosity of solution has effect on r value. Copolymerization of styrene (M_1) and methyl methacrylate (M_2) in bulk leads to a

copolymer containing less styrene than that is carried out in benzene solution. The gel effect in bulk polymerization decreases the mobility of styrene resulting in a decrease in r_1 and an increase in r_2 [6].

Copolymerization involving the combination of polar M_1 and nonpolar M_2 monomers often shows different behavior depending on the polarity of the reaction medium. The copolymer composition is richer in the less polar monomer for reaction in a polar solvent compared to nonpolar solvent for the copolymerization of styrene with acrylamide, acrylonitrile, 2-hydroxyethyl methacrylate, respectively. The result is due to the feed composition in the domain of the growing polymer radical being richer in the less polar monomer. The polar solvent complexes with the polar monomer thus reduces its reactivity [1].

The r_1 and r_2 are relatively insensitive to temperature, for example, the r_1 and r_2 values for styrene and 1,3-butadiene are 0.64 and 1.4 at 5°C, and 0.60 and 1.8 at 45°C, respectively. The r_1 and r_2 values for styrene and methyl methacrylate are 0.52 and 0.46 at 60°C, and 0.59 and 0.54 at 131°C [7]. The monomer reactivity ratio is the ratio of two propagation rate constants, and its variation with temperature will depend on the difference in propagation activation energies according to

$$r_1 = k_{11}/k_{12} = A_{11}/A_{12} \exp [(E_{12} - E_{11})/RT] \quad (10.24)$$

where E_{11} and A_{11} are the propagation activation energy and frequency factor for M_1 radical adding M_1 monomer, respectively, and E_{12} and A_{12} are the corresponding values for M_1 radical adding M_2 monomer. The effect of temperature on r is not large, since the activation energies for radical propagation are relatively small and fall in a narrow range such that $E_{12} - E_{11} \ll 10$ kJ/mol for most pairs of monomers. An increase in temperature results in a less selective copolymerization as the two monomer reactivity ratios of a co-monomer pair each tends toward unity with decreasing preference of either radical for either monomer. Temperature has large effect on those systems, r deviates markedly from unity: especially for ionic polymerization [1].

The pressure effect [1] on the monomer reactivity ratio can be expressed by

$$d \ln r_1 / dP = -(\Delta v_{11}^\ddagger - \Delta v_{12}^\ddagger) / RT \quad (10.25)$$

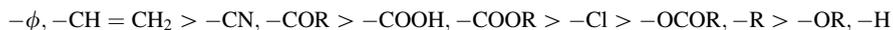
where Δv_{11}^\ddagger and Δv_{12}^\ddagger are the propagation activation volumes for radical M_1 adding monomers M_1 and M_2 , respectively. Although propagation rates increase considerably with pressure, r is less sensitive to pressure, since $(\Delta v_{11}^\ddagger - \Delta v_{12}^\ddagger)$ is smaller than either Δv_{11}^\ddagger or Δv_{12}^\ddagger . The effect of pressure tends to decrease the direction of selectivity of ideal copolymerization. For example, the $r_1 r_2$ product for the copolymerization of styrene and acrylonitrile changes from 0.026 at 1 atm to 0.077 at 1000 atm, while $r_1 r_2$ for the copolymerization of methyl methacrylate and acrylonitrile changes from 0.16 to 0.91. The ideal copolymerization remains so regardless the change of pressure.

10.1.3 Reactivity and Composition of Free Radical Copolymerization

Table 10.1 shows the monomer reactivity ratios of monomers in radical copolymerization [1]. With the same monomer, such as acrylic acid, its r_1 can be varied from 0.25 to 8.7 by changing reaction with styrene radical to vinyl acetate radical. The data are useful for a study of the relation between structure and reactivity in radical addition reactions. The reactivity of monomer toward a radical depends on the reactivities of both of the monomers and radicals. The relative reactivities of monomers and their corresponding radicals can be obtained from an analysis of the monomer reactivity ratios. The reactivity of a monomer can be seen by considering the inverse of the monomer reactivity ratio ($1/r$). The inverse of the monomer reactivity ratio gives the ratio of the rate of reaction of a radical with another monomer to its rate of reaction with its own monomer.

Table 10.2 shows $1/r$ values calculated from the data in Table 10.1. The data in each vertical column show the *monomer reactivities* of a series of different monomers toward the same reference polymer radical. Thus the first column shows the reactivities of the monomers toward the butadiene radical, the second column shows the reactivities of the monomers toward the styrene radical, and so on. It is important to note that the data in Table 10.2 cannot compare the reactivity by horizontal row.

Table 10.2 is organized according to the general decrease order of monomer reactivity in each column. The order of monomer reactivities is approximately the same in each vertical column irrespective of the reference radical. There are few exceptions where the strong alternating tendency of certain co-monomer pairs is present. The data [1] show the substitution effect on the reactivity of monomer toward radical attack in a general order of



The order of monomer reactivities corresponds to the order of increased resonance stabilization by the particular substituent of the radical formed from the monomer. The order of *radical reactivity* can be obtained by multiplying the $1/r$ by the appropriate propagation rate constants of homopolymerization (k_{11}) that is equal to k_{12} , reaction rate of radical-monomer combination. The k_{12} values in any vertical column in Table 10.3 give the order of monomer reactivities as shown in Table 10.2.

Table 10.3 gives the order of radical reactivities toward a reference monomer in the horizontal row. The order of substituent in enhancing radical reactivity is the opposite of their order in enhancing monomer reactivity. A substituent on the monomer can increase or decrease its reactivity depends on the ability of substituent to stabilize or destabilize the corresponding radical. For example, vinyl acetate radical is about 100–1000 times more reactive than styrene radical toward a given monomer, while styrene monomer is only 50–100 times more reactive than

Table 10.1 Monomer reactivity ratios in radical copolymerization [1]

M_1	r_1	M_2	r_2	T (°C)
Acrylic acid	0.24	<i>n</i> -Butyl methacrylate	3.5	50
	0.25	Styrene	0.15	60
	8.7	Vinyl acetate	0.21	70
Acrylonitrile	0.86	Acrylamide	0.81	40
	0.046	1,3-Butadiene	0.36	40
	0.69	Ethyl vinyl ether	0.060	80
	0.98	Isobutylene	0.020	50
	1.5	Methyl acrylate	0.84	50
	0.14	Methyl methacrylate	1.3	70
	0.020	Styrene	0.29	60
	5.5	Vinyl acetate	0.060	70
	3.6	Vinyl chloride	0.044	50
	0.92	Vinylidene chloride	0.32	60
	0.020	2-Vinylpyridine	0.43	60
0.11	4-Vinylpyridine	0.41	60	
Allyl acetate	0	Methyl methacrylate	23	60
	0	Styrene	90	60
	0.70	Vinyl acetate	1.0	60
1,3-Butadiene	0.75	Methyl methacrylate	0.25	90
	1.4	Styrene	0.58	50
	8.8	Vinyl chloride	0.040	50
Diethyl fumarate	0	Acrylonitrile	8.0	60
	0.070	Styrene	0.30	60
	0.44	Vinyl acetate	0.011	60
	0.48	Vinyl chloride	0.13	60
Diethyl maleate	0	Acrylonitrile	12	60
	0	Methyl methacrylate	20	60
	0.010	Styrene	6.1	70
	0.040	Vinyl acetate	0.17	60
	0.046	Vinyl chloride	0.90	70
Ethylene	0	Acrylonitrile	7.0	20
	0.010	<i>n</i> -Butyl acrylate	14	150
	0.38	Tetrafluoroethylene	0.10	25
	0.79	Vinyl acetate	1.4	130
Fumaronitrile	0.019	<i>n</i> -Dodecyl vinyl ether	0.004	60
	0	Methyl methacrylate	6.7	79
	0.006	Styrene	0.29	65
Maleic anhydride	0	Acrylonitrile	6.0	60
	0.045	<i>n</i> -Butyl vinyl ether	0	50
	0.012	Methyl acrylate	2.8	75
	0.010	Methyl methacrylate	3.4	75
	0.08	<i>cis</i> -Stilbene	0.07	60
	0.03	<i>trans</i> -Stilbene	0.03	60
	0.005	Styrene	0.050	50
	0	Vinyl acetate	0.019	75
0	Vinyl chloride	0.098	75	

(continued)

Table 10.1 (continued)

M_1	r_1	M_2	r_2	T (°C)	
Methacrylic acid	2.4	Acrylonitrile	0.092	70	
	0.60	Styrene	0.12	60	
	24	Vinyl chloride	0.064	50	
	0.58	2-Vinylpyridine	1.7	70	
Methacrylonitrile	0.46	Ethyl methacrylate	0.83	80	
	0.25	Styrene	0.25	80	
	12	Vinyl acetate	0.01	70	
Methyl acrylate	0.84	Acrylonitrile	1.5	50	
	0.070	1,3-Butadiene	1.1	5	
	3.3	Ethyl vinyl ether	0	60	
	2.8	Maleic anhydride	0.012	75	
	0.40	Methyl methacrylate	2.2	50	
	0.80	Styrene	0.19	60	
	6.4	Vinyl acetate	0.030	60	
	4.4	Vinyl chloride	0.093	50	
	0.17	2-Vinylpyridine	1.7	60	
	0.20	4-Vinylpyridine	1.7	60	
	Methyl methacrylate	0.36	Acenaphthylene	1.1	60
		0.46	Styrene	0.52	60
		9.0	Vinyl chloride	0.070	68
α -Methylstyrene	2.4	Vinylidene chloride	0.36	60	
	0.14	Acrylonitrile	0.030	75	
	0.040	Maleic anhydride	0.080	60	
	0.27	Methyl methacrylate	0.48	60	
Methyl vinyl ketone	0.14	Styrene	1.2	60	
	0.35	Styrene	0.29	60	
	8.3	Vinyl chloride	0.10	70	
Styrene	1.8	Vinylidene chloride	0.55	70	
	90	Ethyl vinyl ether	0	80	
	42	Vinyl acetate	0	60	
	15	Vinyl chloride	0.010	60	
Vinyl acetate	1.8	Vinylidene chloride	0.087	60	
	3.4	Ethyl vinyl ether	0.26	60	
	0.24	Vinyl chloride	1.8	60	
	0.030	Vinylidene chloride	4.7	68	

vinyl acetate monomer toward a given radical as summarized in Table 10.4. Thus, styrene has higher reactivity than vinyl acetate toward same radical. However, its corresponding radical has lower reactivity toward same monomer.

The interaction of radical reactivity and monomer reactivity in determining the rate of a radical-monomer reaction can be illustrated by potential energy changes accompanying the radical-monomer reaction as a function of the separation between the atoms forming the new bond as shown in Fig. 10.5.

Table 10.2 Relative reactivities ($1/r$) of monomers with various polymer radicals^a[1]

Monomer	Polymer radical									
	Butadiene	Styrene	Vinyl acetate	Vinyl chloride	Methyl methacrylate	Methyl acrylate	Methyl methacrylate	Methyl acrylate	Acrylonitrile	
Butadiene	–	1.7	–	29	4	20	–	–	50	
Styrene	0.7	–	100	50	2.2	5	–	–	2.5	
Methyl methacrylate	1.3	1.9	67	10	–	2	–	–	6.7	
Methyl vinyl ketone	–	3.4	20	10	–	–	–	–	1.7	
Acrylonitrile	3.3	2.5	20	25	0.82	1.2	–	–	–	
Methyl acrylate	1.3	1.3	10	17	0.52	–	–	–	0.67	
Vinylidene chloride	–	0.54	10	–	0.39	–	–	–	1.1	
Vinyl chloride	0.11	0.059	4.4	–	0.1	0.25	–	–	0.37	
Vinyl acetate	–	0.019	–	0.59	0.05	0.11	–	–	0.24	

^a $1/r$ values calculated from data of Table 10.1

Table 10.3 Rate constants (k_{12}) for radical-monomer reactions [1, 2]

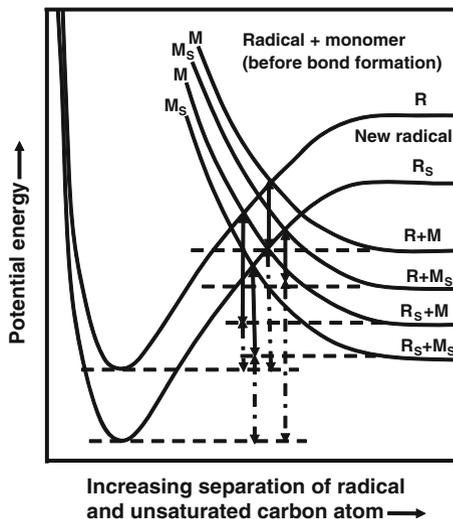
Monomer (M_2)	Polymer radical							
	Butadiene	Styrene	Methyl methacrylate	Acrylonitrile	Methyl acrylate	Vinyl acetate	Vinyl chloride	
Butadiene	100	280	2,060	98,000	41,800	—	319,000	
Styrene	70	165	1,130	49,000	10,045	230,000	550,000	
Methyl methacrylate	130	314	515	13,100	4,180	154,000	110,000	
Acrylonitrile	330	413	422	1,960	2,510	46,000	225,000	
Methyl acrylate	130	215	268	1,310	2,090	23,000	187,000	
Vinyl chloride	11	9.7	52	720	520	10,100	11,000	
Vinyl acetate	—	3.4	26	230	230	2,300	6,490	

^a k_{12} values calculated from data in Table 10.2

Table 10.4 The reactivity comparison between monomer and its corresponding radical

Reactant	Reactivity	Toward
Vinyl acetate radical	100–1,000 x	Same monomer
Styrene radical	1	Same monomer
Styrene monomer	50–100 x	Same radical
Vinyl acetate monomer	1	Same radical

Fig. 10.5 Reaction coordination diagram for the reaction of a polymer radical with a monomer. The dependence of the potential energy of the system (radical + monomer) on the separation between the radical and the unsaturated carbon atom of the monomer is shown. The subscript s indicates the presence of a substituent that is capable of resonance stabilization. Activation energies are represented by the *solid-line arrows*; heats of reaction by the *broken-line arrows* [1]



These energy changes are shown for four possible reactions between resonance-stabilized and nonstabilized monomer and radicals are



where the presence or absence of the subscript s indicates the presence or absence, respectively, of a substituent that is capable of resonance stabilization. Vinyl acetate and styrene monomers are examples of M and M_s , respectively; vinyl acetate and styrene radicals are examples of $R\cdot$ and $R_s\cdot$, respectively. There are two sets of potential energy curves in Fig. 10.5. One set of four repulsion curves represents the energetic approach of a radical to a monomer; the other set of two Morse curves represents the stability of the bond finally formed. The intersections of the curves represent the transition states for the monomer-radical reactions. The

Table 10.5 Rate constants (k_{12}) for radical-monomer reactions involving chlorine substituted ethylenes [1]

Monomer	Polymer radical		
	Vinyl acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	9.7	725
Vinylidene chloride	23,000	89	2,150
<i>cis</i> -1,2-Dichloroethylene	365	0.79	–
<i>trans</i> -1,2-Dichloroethylene	2,320	4.5	–
Trichloroethylene	3,480	10.3	29
Tetrachloroethylene	338	0.83	4.2

order of reaction rate constants for the various monomer-radical reaction is the following which is the opposite order of activation energy of reaction.

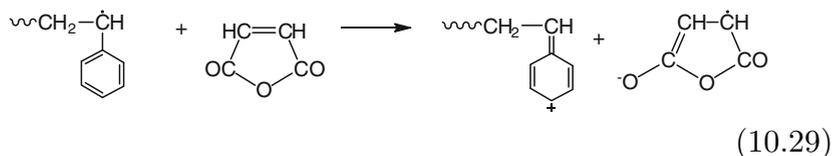


This order of reactivity is consistent with the data in Tables 10.2 and 10.3 as well as many homopolymerization data. The monomers without stabilizing substituents (e.g., vinyl chloride or vinyl acetate) will self-propagate faster than those with stabilizing substituents. Copolymerization will occur primarily between two monomers with stabilizing substituents or between two monomers without stabilizing substituents.

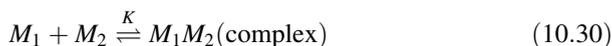
The rates of radical-monomer reactions are also affected by the presence of steric hindrance [1]. Table 10.5 shows the k_{12} values for the reactions of various chlorine substituted ethylenes with vinyl acetate, styrene, and acrylonitrile radicals. The k_{12} of vinylidene chloride is two times higher as compared with vinyl chloride toward vinyl acetate polymer radical which is due to more resonance structure available from vinylidene chloride. The k_{12} of *trans*-1,2-dichloroethylene is six times higher as compared with *cis*-1,2-dichloroethylene toward vinyl acetate polymer radical which is due to the less steric hindrance from the *trans*-1,2-dichloroethylene reacting with vinyl acetate polymer radical. The k_{12} of trichloroethylene is higher than *trans*-1,2-dichloroethylene toward vinyl acetate polymer radical, because the trichloroethylene can provide more resonance structure after the reaction. The trend is similar for the polymer radical of styrene and acrylonitrile.

Table 10.6 lists the monomers in order of their $r_1 r_2$ value with other monomers. The further apart two monomers are, the greater is their tendency toward alternation. Thus, acrylonitrile undergoes ideal copolymerization with methyl vinyl ketone ($r_1 r_2 = 1.1$) and alternating copolymerization with butadiene ($r_1 r_2 = 0.006$).

The order of monomers in Table 10.6 is based on polarity of the double bond. Monomers with electron-donating substituents are located at the top (left) of the table and those with electron-withdrawing substituents at the bottom (right). The $r_1 r_2$ value decreases progressively as one considers two monomers further apart in the table. Monomers on the left are less polar monomers, on the right are more polar. The tendency toward alternation increases as the difference in polarity



The second mechanism suggests the formation of a 1:1 complex between donor and acceptor monomers first, then the complex undergoes homopolymerization to obtain alternating copolymer.



The reactions have been studied by the UV and NMR. The results indicate the formation of charge transfer complexes between electron-donor and electron-acceptor monomers which supports the second mechanism.

Various attempts have been made to place the radical–monomer reaction on the quantitative aspects of the correlation between structure and reactivity. Alfry and Price proposed *Q-e* Scheme [8] that is a useful correlation. The rate constant for a radical–monomer reaction $M_1\cdot$ and M_2 can be expressed by

$$k_{12} = P_1Q_2 \exp(-e_1e_2) \quad (10.32)$$

where P_1 and Q_2 are measures of the resonance stabilization of $M_1\cdot$ radical and M_2 monomer, respectively, and e_1 and e_2 are measures of their polarities. By assuming that the same e value applies to both a monomer and its corresponding radical, one can write expression of k_{11} , k_{22} , k_{21} similar to Eq. 10.32. These can be appropriately combined to yield the monomer reactivity ratios in the forms as below

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \quad (10.33)$$

$$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)] \quad (10.34)$$

which correlate monomer–radical reactivity with the parameters Q_1 , Q_2 , e_1 , and e_2 . The reactivity of monomers is described by a resonance factor “ Q ” and polar factor “ e ”. Table 10.7 lists the Q , e values of some monomers. Therefore, we can use the *Q-e* Scheme to predict monomer reactivity ratios. Values of Q and e have been assigned to monomers based on their r values. For styrene, $Q = 1$, $e = -0.80$ are assigned. The accurately quantitative prediction of monomer reactivity ratio using *Q-e* scheme is limited to the copolymerization that has been experimentally carried out before. Therefore, it is a semi-experimental prediction. The precision of the predicted value, sometime is questionable, if the experimental data of known reactivity ratio are not accurate. The Q , e values do not consider the steric effect.

Table 10.7 Q and e values for various monomers [1]

Monomer	Q	e
Acenaphthalene	0.720	-1.88
Ethyl vinyl ether	0.018	-1.80
Propene	0.009	-1.69
<i>N</i> -Vinylpyrrolidone	0.088	-1.62
<i>n</i> -Butyl vinyl ether	0.038	-1.50
<i>i</i> -Butyl vinyl ether	0.030	-1.27
<i>p</i> -Methoxystyrene	1.53	-1.40
Isobutylene	0.023	-1.20
Allyl acetate	0.24	-1.07
Vinyl acetate	0.026	-0.88
α -Methylstyrene	0.97	-0.81
Styrene	1.00	-0.80
Indene	0.13	-0.71
<i>p</i> -Bromostyrene	1.30	-0.68
Allyl chloride	0.026	-0.60
Isoprene	1.00	-0.55
1,3-Butadiene	1.70	-0.50
2-Vinylpyridine	1.41	-0.42
Ethylene	0.016	0.05
Vinyl chloride	0.056	0.16
<i>m</i> -Nitrostyrene	2.19	0.20
Vinylidene chloride	0.31	0.34
Methyl methacrylate	0.78	0.40
Acrylamide	0.23	0.54
Methacrylic acid	0.98	0.62
Methyl acrylate	0.45	0.64
Methacrylonitrile	0.86	0.68
Vinyl fluoride	0.008	0.72
4-Vinylpyridine	2.47	0.84
<i>n</i> -Butyl acrylate	0.38	0.85
Acrylic acid	0.83	0.88
1-Hexene	0.035	0.92
Methyl vinyl ketone	0.66	1.06
Diethyl maleate	0.053	1.08
Acrylonitrile	0.48	1.23
Tetrafluoroethylene	0.032	1.63
<i>o</i> -Chlorostyrene	2.66	1.57
Diethyl fumarate	0.25	2.26
Fumaronitrile	0.29	2.73
Maleic anhydride	0.86	3.69

The assumption of same e value for monomer and radical is inadequate. However, the Q - e Scheme still useful prediction tool for the structure-reactivity relationship. It can be used to give a general idea of the behavior to be expected from a co-monomer pair that has not been studied.

10.1.4 Rate of Polymerization of Free Radical Copolymerization

The rate of copolymerization depends on the rate of initiation, termination, and propagation. Two different approaches have been used to derive expressions for the rate of copolymerization basis on how the termination reactions are proceeded: (1) by chemical control [4] or (2) by diffusion control [9]. For the first approach, the copolymerization consists of four propagation reactions and three termination reactions

Propagation



Termination



The overall rate of copolymerization from the rate of propagation is

$$\begin{aligned} R_p &= -(d[M_1] + d[M_2])/dt \\ &= k_{11}[M_1\cdot][M_1] + k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] + k_{21}[M_2\cdot][M_1] \end{aligned} \quad (10.42)$$

To eliminate $[M\cdot]$ in Eq. 10.42, a steady-state concentration is assumed for each type of radical,

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \quad (10.43)$$

The overall rate of copolymerization from the rate of termination is

$$R_t = 2k_{t11}[M_1\cdot]^2 + 2k_{t12}[M_1\cdot][M_2\cdot] + 2k_{t22}[M_2\cdot]^2 \quad (10.44)$$

By combining Eq. 10.42 with Eqs. 10.43 and 10.44, then using r_1 , r_2 definitions, one can obtain the rate of copolymerization as

$$R_p = \left(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2 \right) R_t^{1/2} / \left\{ \left(r_1^2 \delta_1^2 [M_1]^2 \right) + (2\phi r_1 r_2 \delta_1 \delta_2 [M_1][M_2]) + \left(r_2^2 \delta_2^2 [M_2]^2 \right) \right\}^{1/2} \quad (10.45)$$

where

$$\delta_1 = (2k_{t11}/k_{11}^2)^{1/2} \quad (10.46a)$$

$$\delta_2 = (2k_{t22}/k_{22}^2)^{1/2} \quad (10.46b)$$

$$\phi = k_{t12}/2(k_{t11}k_{t22})^{1/2} \quad (10.46c)$$

The δ_1 and δ_2 values are obtained from homopolymerization and the r_1 and r_2 from copolymerization data. The rate of copolymerization is experimentally determined, then the ϕ is calculated from Eq. 10.45. Table 10.8 shows the values of ϕ and $r_1 r_2$ of several monomer pairs. There is a general trend of ϕ values greater than unity that indicates the cross-termination is favored. When the ϕ increases with $r_1 r_2$ approaching zero, the tendency toward cross-termination is in parallel with the tendency toward cross-propagation. This leads to the conclusion that polar effects are responsible for the tendency toward cross-termination. The reaction between radicals of dissimilar polarity is enhanced because of stabilization of the transition state for termination by electron-transfer effects.

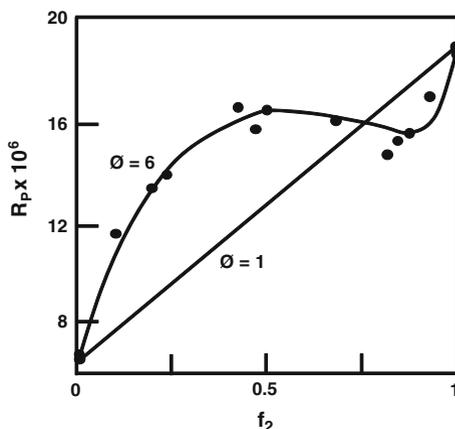
Alternating copolymerization proceeds with enhanced propagation (r_1 and $r_2 < 1$) and enhanced termination ($\phi > 1$). The rate composition plot will depend on the values of ϕ , r_1 and r_2 . Figure 10.6 shows two plots of R_p versus feed for the copolymerization of styrene and methacrylonitrile using ϕ values of 1 and 6 for calculation. The experimental data follow the plot for $\phi = 6$ quite well. The copolymerization of styrene ($r_1 = 42$) and vinyl acetate ($r_2 = 0$) presents a typical example of this case. The value of r_2 is very small and Eq. 10.45 can be reduced to

$$R_p = ([M_1] + 2[M_2]/r_1) R_t^{1/2} / \delta_1 \quad (10.47)$$

Table 10.8 Values of ϕ and $r_1 r_2$ in radical copolymerization of several monomer pairs [1]

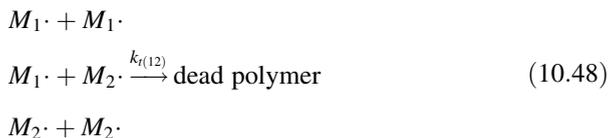
Comonomer	ϕ	$r_1 r_2$
Styrene-butyl acrylate	150	0.07
Styrene-methyl acrylate	50	0.14
Methyl methacrylate- <i>p</i> -methoxystyrene	24	0.09
Styrene-methyl methacrylate	13	0.24
Styrene-methacrylonitrile	6	0.16 ^c
Styrene-methoxystyrene	1	0.95

Fig. 10.6 Dependence of the rate of radical copolymerization of styrene-methacrylonitrile at 60 °C on the co-monomer feed composition. The two plots are the theoretical plots calculated for ϕ values of 1 and 6; the circles represent the experimental data [1]



The addition of very small amount of styrene to vinyl acetate, styrene inhibits the polymerization of vinyl acetate. Vinyl acetate radicals are rapidly converted to styrene radicals. The styrene radicals react very slowly with vinyl acetate monomer. The net effect is an almost complete cessation of polymerization. R_p is very small according to Eq. 10.47.

For the second approach, diffusion controlled termination, the following reactions are considered to obtain the kinetic expression for the rate of copolymerization



where the termination rate constant $k_{t(12)}$ is a function of the copolymer composition. The condition for the steady state for the total concentration of radicals can be expressed by Eq. 10.49 instead of Eq. 10.44.

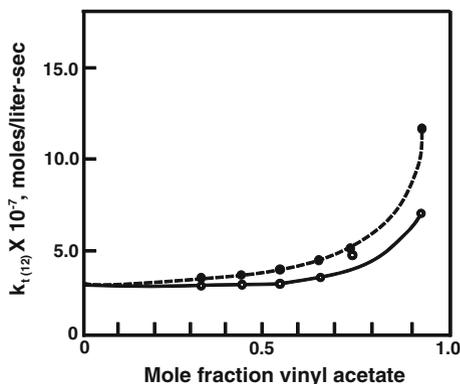
$$R_t = 2k_{t(12)}([M_1\cdot] + [M_2\cdot])^2 \tag{10.49}$$

By combining Eqs. 10.42, 10.43, and 10.49 with the definitions of r_1 and r_2 , one obtains the rate of copolymerization as

$$R_p = \frac{(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)R_i^{1/2}}{k_{t(12)}^{1/2} \left\{ \left[\frac{r_1[M_1]}{k_{11}} \right] + \left[\frac{r_2[M_2]}{k_{22}} \right] \right\}} \tag{10.50}$$

In the ideal situation, one would expect the termination rate constant $k_{t(12)}$ to be a function of the termination rate constants for the corresponding two homopolymerizations as the following:

Fig. 10.7 Dependence of the termination rate constant $k_{t(12)}$ on the mole fraction of vinyl acetate in the radical copolymerization of vinyl acetate-methyl methacrylate. The *solid-line* plot and *open circles* represent calculations by Eq. 10.51; the *broken-line* plot and *solid circles* represent calculations by Eq. 10.50 [1]



$$k_{t(12)} = F_1 k_{t11} + F_2 k_{t22} \quad (10.51)$$

where $k_{t(12)}$ is the average of k_{t11} and k_{t22} each weighted on the basis of the copolymer composition in mole fractions. Equations 10.50 and 10.51 have been validated by experimental data as shown in Fig. 10.7. The lines are calculated data and circles are experimental data. They are fitted quite well except the slight deviation obtained from Eq. 10.51 calculation. The result indicates the weighting the k_{t11} and k_{t22} values directly with the copolymer composition may not be correct.

10.2 Cationic Copolymerization

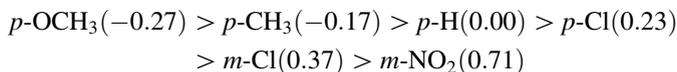
The reactivity of monomer in cationic copolymerization [1] will be increased by (1) increasing the electron density on the double bond and (2) resonance stabilization on the carbocation from the substituent on the monomer. However, it will be affected by the reaction conditions, e.g., solvent, counterion, temperature, and so forth. The relative reactivities of various substituted styrenes have been correlated by the Hammett sigma-rho ($\rho\sigma$) relationship

$$\log(1/r_1) = \rho\sigma \quad (10.52)$$

For example, $\log(1/r_1)$ values for a series of *meta*- and *para*-substituted styrenes copolymerized with styrene were plotted against the sigma substituent constants to yield a straight line with slope ρ of negative sign. The sigma value of a substituent is a quantitative measure of the total electron-donating or electron-withdrawing effect of substituent. Electron-withdrawing and electron-donating substituents have positive and negative sigma constants, respectively. A negative value of ρ means $1/r_1$ is increased by electron-donating substituents as expected for cationic polymerization. Substituents increase the reactivity of styrene in the following order of

Table 10.9 Steric effects in copolymerization of α - and β -methylstyrenes (M_1) with *p*-chlorostyrene (M_2) [1]

M_1	r_1	r_2
Styrene	2.31	0.21
α -Methylstyrene	9.44	0.11
<i>trans</i> - β -Methylstyrene	0.32	0.74
<i>cis</i> - β -Methylstyrene	0.32	1.0



The Hammett-type approach is very useful for the quantitative correlation of monomer reactivity with structure semi-experimentally, but it is applicable only to substituted styrenes. The generally observed order of monomer reactivity is



which is the order expected on the basis of the electron-donating ability of various substituents. Monomers with electron-withdrawing substituent such as acrylonitrile, methyl methacrylate, and vinyl chloride show negligible reactivity in cationic copolymerization. Steric effect is also important in cationic copolymerization. Table 10.9 shows the effect of methyl substituents in the α - and β -positions of styrene. The reactivity of α -methylstyrene is higher than that of styrene due to the presence of electron-donating group of methyl group at α -position to have stabilized cationic propagating chain. On the other hand, the reactivity of β -methylstyrene is lower than that of styrene due to the presence of methyl group at β -position to have steric hindrance effect to retard the copolymerization with *p*-chlorostyrene. The steric effect is to outweigh the electronic effect of methyl group on the double bond. The *trans*- β -methylene is higher reactivity than *cis*- β -methylene as expected from the retardation of the later, although the amount is not large. It is interested to note that the 1,2-disubstituted alkene have some finite reactivity ratio which is zero in free radical copolymerization. Furthermore, the 1,2-disubstituted alkene can self propagate in cationic copolymerization but it is negligible in free radical reaction.

The effect of solvent or counterion on the monomer reactivity ratios is expected as we have observed in the cationic homopolymerization [1]. Actually, the effects are more complicated and difficult to predict than the homopolymerization, since changes in solvent or counterion often result in alternations in relative amounts of different types of propagating center, each of which may be differently affected by solvent. Table 10.10 illustrates these kind of effects for the copolymerization of isobutylene and *p*-chlorostyrene. The AlBr_3 initiated copolymerization shows $r_1 = 1.01$, $r_2 = 1.02$ in hexane but $r_1 = 14.7$, $r_2 = 0.15$ in nitrobenzene. Because the polar characteristic of *p*-chlorostyrene, the calculation of r values using the bulk comonomer feed composition results in a lower value of r_1 together with a

Table 10.10 Effect of solvent and initiator on r values in cationic polymerization [1]

$r_1 = k_{11}/k_{12}$ isobutylene	$r_2 = k_{22}/k_{21}$ <i>p</i> -chlorostyrene	Solvent	Initiator
1.01	1.02	<i>n</i> -C ₆ H ₁₄ (ϵ 1.8)	AlBr ₃
14.7	0.15	C ₆ H ₅ -NO ₂ (ϵ 36)	AlBr ₃
8.6	1.2	C ₆ H ₅ -NO ₂ (ϵ 36)	SnCl ₄

Table 10.11 Effects of solvent and counterion on copolymer composition in the copolymerization of styrene and *p*-methylstyrene[1]

Initiator system	% Styrene in copolymer ^a		
	Toluene (ϵ 2.4)	1,2-Dichloroethane (ϵ 9.7)	Nitrobenzene (ϵ 36)
SbCl ₅	46	25	28
AlX ₃	34	34	28
TiCl ₄ , SnCl ₄ , BF ₃ ·OEt ₂ , SbCl ₃	28	27	27
Cl ₃ CCO ₂ H	–	27	30
I ₂	–	17	–

^a Co-monomer feed = 1:1 styrene and *p*-methylstyrene

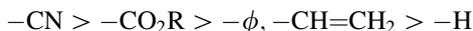
higher value of r_2 . By changing the polarity of solvent, the r value is varied. In the nonpolar solvent, hexane, the polar monomer *p*-chlorostyrene solvates the propagating center, so the r_2 is increased. However, in the polar solvent, nitrobenzene, the propagating center is solvated by solvent which makes the reaction of polar monomer decreased with a reduced r_2 . The solvent effect cannot be considered independent of counterion effect. The AlBr₃ is a stronger initiator than SnCl₄ that produces a higher concentration of propagating center. Thus, a stronger solvent effect is observed for polar *p*-chlorostyrene with an order decrease in r_2 (1.2 vs. 0.15) using AlBr₃ initiator.

Table 10.11 illustrates another example of the effects of solvent and counterion on the copolymerization of styrene with *p*-methylstyrene. The data indicate the copolymer composition to be (1) insensitive to the type of initiator for high polarity solvent such as nitrobenzene or 1,2-dichloroethane and (2) insensitive to solvent polarity for any initiator except the strongest SbCl₅. The styrene content decreases with decreasing initiator strength for the low-polarity solvent of toluene. In the poor solvent, the monomers compete, against the solvent, with each other to solvate the propagating center. The more polar *p*-methylstyrene preferentially solvates the propagating chains, so it is preferentially incorporated into the copolymer. For the polar solvent, the counterion does not appreciably influence the reaction, because the monomer cannot compete with the solvent to solvate the propagating chain. For the strong initiator of SbCl₅, the concentration of propagating center is high, the less polar monomer of styrene can be incorporated more into copolymer when the reaction is in the less polar solvent of toluene.

Temperature has a greater influence on monomer reactivity ratios in cationic copolymerization than in radical copolymerization because of the greater spread of propagation activation energies for the ionic process [10]. The ratio of any two rate constants is expected to toward unity when temperature increases. Since the smaller rate constant (larger activation energy) will increase faster with increasing temperature than the larger rate constant (smaller activation energy).

10.3 Anionic Copolymerization

The reactivity of anionic copolymerization is enhanced by electron-withdrawing substituent that decreases the electron density on the double bond and resonance stabilizes the formation of carboanion [1]. The reactivity is generally increased by the increasing of electron-withdrawing power of the substitute as the following:



There is a tendency toward ideal behavior in most anionic copolymerizations. Steric effects give rise to an alternating tendency for certain co-monomer pairs. Thus the styrene-*p*-methylstyrene pair shows ideal behavior with $r_1 = 5.3$, $r_2 = 0.18$, $r_1r_2 = 0.95$, while the styrene- α -methylstyrene pair shows a tendency toward alternation with $r_1 = 35$, $r_2 = 0.003$, $r_1r_2 = 0.11$, respectively. The steric effect of the additional methyl substituent in the α -position hinders the addition of α -methylstyrene to α -methylstyrene anion and results in lower reactivity ratio.

Monomer reactivity ratios and copolymer compositions of anionic copolymerizations are also altered by changes in the solvent or counterion. Table 10.12 shows data for styrene-isoprene copolymerization at 25°C by *n*-butyl lithium. As in the case of cationic copolymerization, the effects of solvent and counterion cannot be considered independently of each other. For the tightly bound lithium counterion, there are large effects due to the solvent. In a poor solvent such as benzene, the copolymer is rich in the less reactive isoprene (contains 15 % styrene), because isoprene is preferentially complexed by lithium ion. In a good

Table 10.12 Effect of solvent and counterion on copolymer composition in styrene-isoprene copolymerization [1]

Solvent	% Styrene in copolymer for counterion	
	Na ⁺	Li ⁺
None	66	15
Benzene	66	15
Triethylamine	77	59
Ethyl ether	75	68
Tetrahydrofuran	80	80

solvent triethylamine, preferential solvation by monomer is much less important and the inherent greater reactivity of styrene presents high concentration of 59 % in the copolymer.

10.4 Copolymerization Involving Dienes

Diene monomers contain two double bonds that are used in the copolymerization to have crosslinkable functionality, so a cross-linked polymers can be obtained. The reaction is similar to the step polymerization where tri or tetra functional reactants are used. The cross-linking reaction occurs early or late in the copolymerization depends on the relative reactivities of the two double bonds of the diene. The extent of cross-linking depends on (1) the reactivity of the two double bonds of the diene and (2) the amount of diene relative to the other monomer. Therefore, there are usually three types of copolymerization between monomer and diene that are discussed in the following.

The first type is the copolymerization of monomer A with diene BB where all of the double bonds have the same reactivity [1]. Methyl methacrylate-ethylene glycol dimethacrylate (EGDM), vinyl acetate-divinyl adipate (DVA), and styrene-*p*- or *m*-divinylbenzene (DVB) are examples of this type of copolymerization system. Since $r_1 = r_2$, $F_1 = f_1$. At the extent of reaction p , there are $p[A]$ reacted A double bonds, $p[B]$ reacted B double bonds, and $p^2[BB]$ reacted BB monomer units. $[A]$ and $[B]$ are the concentrations of A and B double bonds, $[BB]$ is the concentration of BB , and $[B] = 2[BB]$. The number of cross-links is simply the number of BB monomer molecules in which both B double bonds are reacted that is, $p^2[BB]$. The number of polymer chains is the total number of A and B double bonds reacted divided by the weight average degree of polymerization, $([A] + [B])p/\bar{X}_w$. The critical extent of reaction at the gel point p_c occurs when the number of cross-links per chain is 1/2 and thus is given by

$$p_c = \frac{[A] + [B]}{[B]\bar{X}_w} \quad (10.53)$$

Table 10.13 Cross-linking in the copolymerization of styrene-divinylbenzene [1]

Mole fraction DVB	Gel point (p_c)	
	Calculated from Eq. 10.53	Observed
0.004	0.210	0.160
0.008	0.100	0.140
0.020	0.042	0.076
0.032	0.026	0.074
0.082	0.010	0.052
0.300	0.004	0.045

The equation holds best for systems containing low concentrations of the diene monomer. With increasing diene concentration, the equation predicts gel points at conversions that are increasingly lower than those found experimentally as shown in Table 10.13. This general behavior has been attributed to the wastage of the diene monomer due to (1) intramolecular cyclization, and (2) the reactivity of the second double bond in BB is decreased on reaction of the first double bond as a consequence of its presence in a polymer chain [1].

A second case is the copolymerization of A and BB with reactivities r_1 and r_2 , respectively [1]. In the case, the critical extent of reaction at gelation is given by

$$p_c = \frac{\left(r_1[A]^2 + 2[A][B] + r_2[B]^2\right)^2}{\bar{X}_w[B]([A] + [B])(r_2[B] + [A])^2} \quad (10.54)$$

If $[A] \gg [B]$, then

$$p_c = \frac{[A]r_1^2}{[B]\bar{X}_w} \quad (10.55)$$

When the double bonds of the diene are more reactive than that of the other monomer ($r_2 > r_1$), cross-linking occurs in the early stages of the copolymerization. Cross-linking is delayed until the later stages if $r_1 > r_2$.

The third case is the copolymerization of a monomer A with the diene BC where groups A and B have equal reactivity, but group C has a much lower reactivity [1]. The copolymerization of methyl methacrylate(A)-allyl(C)-methacrylate(B) is an example. If r is the reactivity ratio of C and B groups, then the rate constant for A and B will have the following relationship:

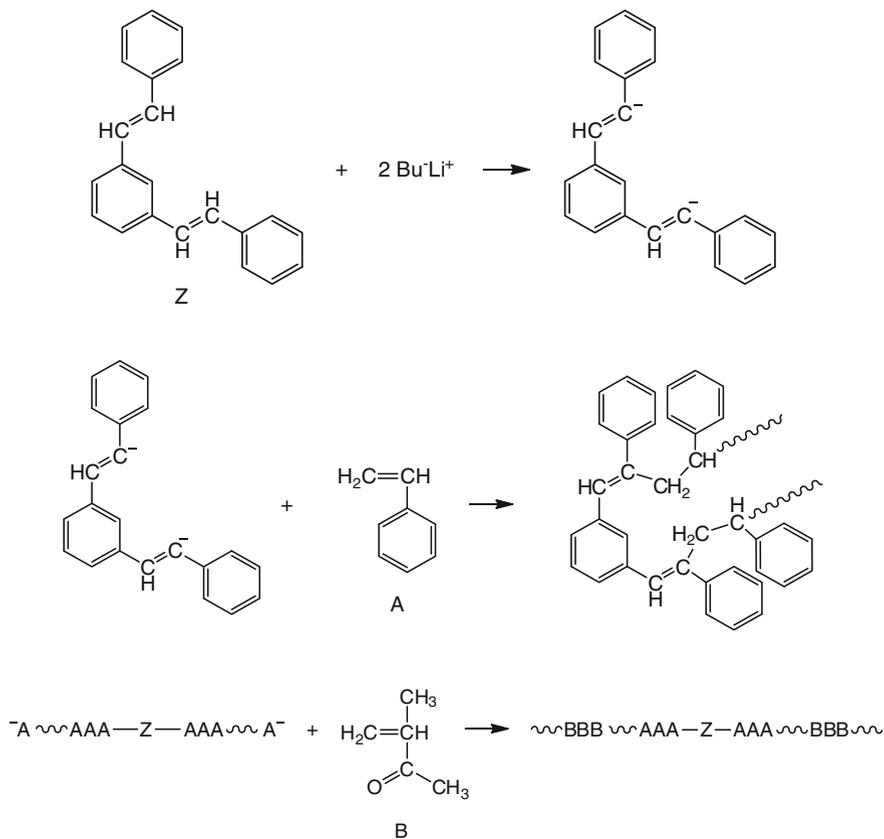
$$r = k_{AC}/k_{AA} = k_{AC}/k_{AB} = k_{BC}/k_{BA} = k_{BC}/k_{BB} \quad (10.56)$$

The copolymer will consist of copolymerized A and B groups with pending C groups that will react later into cross-linking. The critical extent of reaction at gelation is given by

$$p_c = 1 - \exp \frac{-1}{2q\bar{X}_wr} \quad (10.57)$$

where q is the mole fraction of the diene in the initial co-monomer feed.

From the discussion above, one can control the gelation of diene copolymerization and the extent of cross-linking by reducing the amount of diene, the degree of polymerization by using chain transfer agents, proper choice of the reactivity of diene.



10.5 Block Copolymers

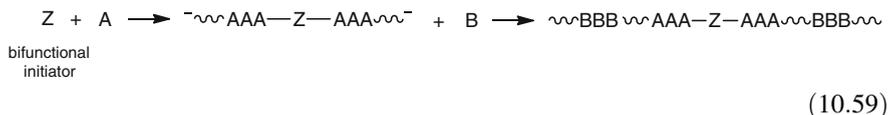
Block copolymers offer the potential to have product having desired and balanced properties of two or more homopolymers. The block copolymer can be synthesized via sequential monomer addition and then terminates with water using anionic polymerization as following



However, the additional sequency of monomer is very important to determine the success of this kind copolymerization. For example, polystyryl carbanion will initiate polymerization of methyl methacrylate, but the reverse does not occur due to the reactivity difference in carbanion. Sequencing is not a problem in synthesizing block copolymers of styrene with isoprene or 1,3-butadiene due to similar reactivity of the monomer. The length of each segment in the block copolymer is determined by the

amount of each monomer added relative to the amount of initiator. The overall properties of the product are various with the block lengths of the different monomers.

Difunctional initiators such as sodium naphthalene can be used to synthesize ABA, BABAB, CABAC, and other symmetrical block copolymers. Difunctional initiators can also be prepared by reacting a diene with two equivalents of *s*- or *t*-butyl lithium.



Triblock copolymer is able to be prepared using a difunctional initiator to initiate the first monomers and result in a homopolymer with two head carbanions. Following by introducing the second monomers and then the ABA triblock copolymer such as methyl methacrylate–styrene–methyl methacrylate is formed as following:

Triblock copolymers such as styrene-isoprene-styrene and styrene-1,3-butadiene-styrene are useful thermoplastic elastomers. They behave as elastomers at ambient temp. However, they are thermoplastic at elevated temperature. Styrene is a hard segment, and butadiene is soft. Diblock copolymers do not show good elastomer behavior but the triblock copolymer with the hard blocks at both ends of the polymer chain bearing rubbery behavior. Higher level block structures do not offer any performance advantage over triblock copolymer.

10.6 Commercial Copolymers

Many commercial copolymers are synthesized basis on polystyrene. Polystyrene itself is brittle and low impact resistance, but it can be copolymerized with rubber-based polymer to have both properties of strength and impact resistance [1]. Examples of styrene copolymers are styrene butadiene rubber (SBR) for tire which contains 25 % styrene, 75 % 1,3-butadiene; Latex paint which has 50–70 % styrene, 30–50 % 1,3-butadiene. Carboxylated SBR is a backing material for the usage of carpets and styrene/divinyl benzene is used for size-exclusion chromatography. The copolymer containing 50–90 % styrene, 10.40 % acrylonitrile (SAN) is widely used in houseware and packaging. The ABS consists of a glassy polymer (SAN) dispersed in a rubbery matrix (grafted rubber) for houseware, housing. The HIPS (high impact polystyrene) is produced by polymerization of styrene in the presence of a rubber of poly-1,4-butadiene.

Other important commercial copolymers are based on polyethylene. Ethylene polymer has the properties of crystallinity, high glass transition temperature, high T_m , high chemical resistance and vinyl acetate polymer has the properties of optical clarity, impact and stress crack resistance, flexibility, and adhesion. By copolymerization of ethylene with vinyl acetate (2–18 %), the merits of both

polymers can be achieved. They are called EVA and widely used in food packaging, stretch and shrink film, drum liner, and so on. The copolymers of ethylene/methyl methacrylate (15–30 %) or ethyl, butyl, methyl acrylates exhibit improved thermal stability, low temperature flexibility. Ethylene-acrylate-alkenoic acid (small amount crosslinker) elastomer has excellent oil resistance and stability over a wide temperature range (-50 to 200°C). The copolymer of ethylene-acrylic acid (15–20 %) has improved adhesion, abrasion resistance, toughness, and low temperature flexibility.

10.7 Problems

1. Define the reactivity ratios r_1 and r_2 and indicate their values for (a) ideal, (b) alternating, (c) azeotropic, and (d) block copolymerization.
2. Derive the copolymer equations, stating the assumptions used.
3. Consider the following monomer reactivity ratios for the copolymerization of various pairs of monomers:

Case	r_1	r_2
1	0.1	0.2
2	0.1	10
3	0.1	3
4	0	0.3
5	0	0
6	0.8	2
7	1	15

What is the composition of the copolymer that would be formed at low conversion from equimolar mixtures of the two monomers in each case? What kind of copolymer will be formed for each case?

4. Using the r_1 and r_2 values from Table 10.1, construct plots showing the initial copolymer composition as a function of the co-monomer feed composition for the radical copolymerizations of methyl acrylate-methyl methacrylate and styrene-maleic anhydride. Are these examples of ideal or alternating copolymerization?
5. Consider the radical copolymerization of a benzene solution that is 1.5 M in styrene and 3.0 M in methyl acrylate.
 - a. What is the initial copolymer composition if the polymerization is carried out at 60°C using benzoyl peroxide at a concentration of 5.0×10^{-4} M? How is the copolymer composition affected if 3.0×10^{-3} M benzoyl peroxide is used?
 - b. How will the presence of 5.0×10^{-5} M *n*-butyl mercaptan affect the initial copolymer composition?

6. Using the Q and e values in Table 10.7, calculate the monomer reactivity ratios for the co-monomer pairs styrene-butadiene and styrene-methyl methacrylate. Compare the results with the r_1 and r_2 values in Table 10.1.
7. Discuss qualitatively the course of the radical copolymerization for each of the following co-monomer pairs in terms of the degree of reaction at which gelation would be expected to occur:
 - a. Styrene-divinylbenzene
 - b. Methyl methacrylate-allyl methacrylate
 - c. Vinyl acetate-EGDM
 - d. Methyl methacrylate-DVA
 - e. Styrene-butadiene
8. Carbonyl monomers can be copolymerized with either carbonyl monomer or alkene. Please write the chemical reactions, reaction condition and reaction products of acetaldehyde copolymerized with chloral, formaldehyde and styrene, respectively. What kind of copolymer of each monomer pair, random, alternate, or block will be obtained for each copolymerization? Explain your answer.
9. 1,3-Butadiene is copolymerized with the following monomers by radical, cationic and anionic initiation, respectively. Please discuss the expected qualitatively copolymer composition in order of their increasing butadiene content and what kind of copolymer would be formed for each of the comonomer pairs using those three different initiation conditions respectively.
 - a. n-Butyl vinyl ether, b. methyl methacrylate, c. methyl acrylate, d. styrene, e. maleic anhydride, f. vinyl acetate, and g. acrylonitrile
10. Discuss the general effects of temperature, solvent, and catalyst on the monomer reactivity ratios in radical copolymerization; compare the differences between the radical copolymerization and ionic copolymerization with the corresponding effects.

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