Kinetics of Polymerization: E] Chain copolymerization:

We have so far considered free-radical polymerizations where only one monomer is used and the product is a homopolymer. The same type of polymerization can also be carried out with a mixture of two or more monomers to produce a polymer product that contains two or more different mer units in the same polymer chain. The polymerization is then termed a copolymerization and the product is termed a copolymer. Monomers taking part in copolymerization are referred to as comonomers. The simultaneous polymerization of two monomers is known as binary copolymerization and that of three monomers as ternary copolymerization, and so on. The term multicomponent copolymerization embraces all such cases. The relative proportions of the different mer units in the copolymer chain depend on the relative concentrations of the comonomers in the feed mixture and on their relative reactivities.

It should be noted that the chain copolymerization may be initiated by any of the chain initiation mechanisms, namely, free-radical or ionic chain initiations. While polymerization of a single monomer is relatively limited regarding the number of different products that are possible, copolymerization enables the polymer engineer to synthesize an almost unlimited number of products with different properties by variations in the nature and relative amounts of the two monomers in the feed mixture and to tailor-make polymers with specific properties. Copolymerization is thus very important from a technological viewpoint.

The classification of copolymers according to structural types and the nomenclature for copolymers have already been described. In this section we are primarily concerned with the simultaneous polymerization of two monomers by chain-growth mechanism to produce random, statistical, and alternating copolymers. Copolymers having completely random distribution of the different monomer units along the copolymer chain are referred to as random copolymers. Statistical copolymers are those in which the distribution of the two monomers in the chain is essentially random but influenced by the individual monomer reactivities. The other types of copolymers, namely, graft and block copolymers, are not synthesized by the simultaneous polymerization of two monomers. These are generally obtained by other types of reactions.

The instantaneous copolymer composition - the composition of the copolymer formed at very low conversions (about 5%)—is usually different from the composition of the comonomer feed from which the copolymer is produced, because different monomers have differing tendencies to undergo copolymerization. It was observed early that the relative copolymerization tendencies of monomers often bore little resemblance to their relative rates of homopolymerization. Some monomers are more reactive in copolymerization than indicated by their rates of homopolymerization; other monomers are less reactive. For example, vinyl acetate polymerizes about twenty times as fast as styrene in a free-radical reaction, but the product obtained by free-radical polymerization of a mixture of vinyl acetate and styrene is found to be almost pure polystyrene with hardly any content of vinyl acetate. Further, and most dramatically, a few monomers, such as maleic anhydride and stilbene undergo facile copolymerization with radical initiation, although they have very little or no tendency to undergo homopolymerization under the same condition.

The composition of a copolymer thus cannot be determined simply from a knowledge of the homopolymerization rates of the two monomers. In order to develop a simple model for that purpose one has to assume that the chemical reactivity of the propagating chain (which may be a free radical, carbocation, or carbanion) in a 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. This is referred to as the first order Markov or terminal model of copolymerization. Consider the case for the copolymerization of the two monomers M₁ and M₂. Although radical copolymerization has been more extensively studied and is more important than ionic copolymerization, we will consider the general case without specification as to whether the mode of initiation is by a radical, anionic, or cationic species. Copolymerization of the two monomers leads to two types of propagating species - one with M₁ at the propagating end and the other with M₂. These can be represented by $M₁^*$ and $M₂^*$ where the asterisk represents either a radical, a carboxylation, or a carbanion as the propagating species depending on the particular case. If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain (referred to as the end or ultimate unit), four propagation reactions are then possible. Monomers M₁ and M₂ can each add either to a propagating chain ending in M₁ or to one ending in M₂, that is,

\[
\begin{align*}
M₁^* + M₁ & \rightarrow k_{11} M₁^* \\
M₁^* + M₂ & \rightarrow k_{12} M₂^* \\
M₂^* + M₁ & \rightarrow k_{21} M₁^* \\
M₂^* + M₂ & \rightarrow k_{22} M₂^*
\end{align*}
\]

where $k_{11}$ is the rate constant for a propagating chain ending in M₁ adding to monomer M₁, $k_{12}$ that for a propagating chain ending in M₁ adding to monomer M₂, and so on. The propagation of a reactive centre by addition of the same monomer is often referred to as homopropagation or self-propagation; propagation of a reactive centre by addition of the other monomer is referred to as cross-propagation or a crossover reaction. All propagation reactions are assumed to be irreversible.

Monomer M₁ disappears by the first and the third reaction, while monomer M₂ disappears by the second and the fourth. The rates of disappearance of the two monomers, which are synonymous with their rates of entry into the copolymer, are given by:

\[
\begin{align*}
\frac{d[M₁]}{dt} &= k_{11}[M₁^*][M₁] + k_{21}[M₂^*][M₁] \\
\frac{d[M₂]}{dt} &= k_{12}[M₁^*][M₂] + k_{22}[M₂^*][M₂]
\end{align*}
\]

Dividing the first equation with the second yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

\[
\frac{d[M₁]}{d[M₂]} = \frac{k_{11}[M₁^*][M₁] + k_{21}[M₂^*][M₁]}{k_{12}[M₁^*][M₂] + k_{22}[M₂^*][M₂]}
\]

In order to remove the concentration terms in $M₁^*$ and $M₂^*$ from this equation, a steady-state concentration is assumed for each of the reactive species $M₁^*$ and $M₂^*$ separately. For the concentrations of $M₁^*$ and $M₂^*$ to remain constant, their rates of interconversion must be equal. In other words, the rates of the third and the fourth reactions must be equal:

\[
k_{21}[M₂^*][M₁] = k_{12}[M₁^*][M₂]
\]

Meaning, $[M₁^*] = \frac{k_{21}[M₂^*][M₁]}{k_{12}[M₂]}$
Putting the value of \([M_1,^*]\), we get,

\[
\frac{d[M_1]}{d[M_2]} = \frac{k_{11}k_{21}[M_2']^2[M_1]^2 + k_{21}[M_2']^2[M_1]}{k_{21}[M_2']^2[M_1] + k_{22}[M_2']^2[M_2]}
\]

\[
\frac{d[M_1]}{d[M_2]} = \frac{k_{11}k_{21} [M_1]}{k_{12} [M_2]} + k_{21} \frac{[M_1]}{[M_2]}
\]

Dividing this equation’s numerator and denominator with \(k_{21}\) we get:

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{k_{11} [M_1]}{k_{12} [M_2]} + \frac{1}{k_{21}} \right)
\]

We now define two parameters (called monomer reactivity ratios), \(r_1\) and \(r_2\), as

\[
 r_1 = \frac{k_{11}}{k_{12}} , \quad r_2 = \frac{k_{22}}{k_{21}}
\]

And substituting for \(r_1\) and \(r_2\), we get,

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{[M_1]}{[M_2]} + 1 \right)
\]

The left hand side represents relative molar increment of the two monomers in the copolymer. For copolymerization to low conversions, this may be taken as the molar ratio of the two monomer units incorporated in the copolymer, i.e., \([M_1]/[M_2]_{\text{copolymer}}\), while the ratio \([M_1]/[M_2]\) on the right hand side of the equation relates to the feed monomer ratio, i.e. molar ratio of the two monomers in the feed monomer mixture, \([M_1]/[M_2]_{\text{feed}}\).

Thus we have,

\[
\begin{align*}
\left( \frac{[M_1]}{[M_2]} \right)_{\text{copolymer}} &= \left( \frac{[M_1]}{[M_2]} \right)_{\text{feed}} \left[ \frac{r_1 \left( \frac{[M_1]}{[M_2]} \right)_{\text{feed}} + 1}{\left( \frac{[M_1]}{[M_2]} \right)_{\text{feed}} + r_2} \right]
\end{align*}
\]

The equation can also be rewritten as,

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

This is the so-called copolymer equation or the copolymer composition equation. The ratio representing the ratio of the rates at which the two monomers \(M_1\) and \(M_2\) enter the copolymer gives the molar ratio of the two monomer units in the copolymer (being formed at a given instant), and hence is referred to as the copolymer composition. According to this equation, the copolymer composition depends on the concentrations of the two types of monomers in the feed, namely, \([M_1]\) and \([M_2]\), and on the kinetic parameters \(r_1\) and \(r_2\) (the monomer reactivity ratios, ratios of propagation rate constants). Since initiation
and termination rate constants are not involved in the copolymer equation, the copolymer composition should be independent of the initiator used and of the absence or presence of inhibitors/retarders or chain transfer agents.

Significance of monomer reactivity ratio: As defined by the polymer equation, the monomer reactivity ratio can be looked upon as the relative tendency for homopropagation and cross-propagation. If for a given monomer pair, \( r_1 = 0 \) and hence \( k_{11} = 0 \), it would mean that \( M_1 \) does not homopolymerize in the presence of \( M_2 \). Similarly, \( r_1 > 1 \), i.e., \( k_{11} > k_{12} \) means that \( M_1 \) preferentially adds \( M_1 \) instead of \( M_2 \) and \( r_1 < 1 \), i.e., \( k_{12} > k_{11} \) means that \( M_1 \) preferentially adds \( M_2 \). For example, an \( r_1 \) value of 0.5 would mean that \( M_1 \) adds \( M_2 \) twice as fast as \( M_1 \). It is evident from the copolymer equation that the values of \( r_1 \) and \( r_2 \) refer only to a pair of monomers undergoing copolymerization. Thus the same monomer can have different values of \( r_1 \) in combination with different monomers, e.g., acrylonitrile has \((r_1, r_2)\) values of \((0.35, 1.15)\), \((0.02, 1.8)\), \((1.5, 0.84)\), and \((4.2, 0.05)\) at 50°C in free-radical copolymerization with acrylic acid, isobutylene, methyl acrylate, and vinyl acetate, respectively, each being designated as \( M_2 \) and the other monomer, acrylonitrile, as \( M_1 \).

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,

\[
f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]}
\]

and

\[
F_1 = 1 - F_2 = \frac{[dM_1]}{[dM_1] + [dM_2]}
\]

Using these relations, the copolymer equation becomes,

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

\[
F_2 = \frac{r_2 f_2}{f_1 (r_2 f_2 + f_1)}
\]

This equation gives the copolymer composition as the mole fraction of monomer \( M_1 \) in the copolymer and is often more convenient to use than the previous form of the copolymerization equation.

Applicability of the copolymer equation: The copolymerization equation has been experimentally verified in innumerable comonomer systems. The copolymerization equation is equally applicable to radical, cationic, and anionic chain copolymerizations, although the \( r_1 \) and \( r_2 \) values for any particular comonomer pair can be drastically different depending on the mode of initiation. Ionic copolymerizations are predictably much more selective than radical copolymerizations. Almost any pair of monomers undergoes radical copolymerization, in line with the reactivity of almost all monomers in radical polymerization. However, only certain comonomer pairs undergo cationic or anionic copolymerization. For example, both styrene–acrylonitrile and styrene–ethyl vinyl ether undergo radical copolymerization, but there is great selectivity in ionic copolymerizations. Styrene–acrylonitrile undergoes anionic polymerization, but not cationic copolymerization. Styrene–ethyl vinyl ether undergoes cationic copolymerization, but not anionic copolymerization.
For any specific type of initiation (i.e., radical, cationic, or anionic) the monomer reactivity ratios and therefore the copolymer composition equation are independent of many reaction parameters. Since termination and initiation rate constants are not involved, the copolymer composition is independent of differences in the rates of initiation and termination or of the absence or presence of inhibitors or chain-transfer agents. Under a wide range of conditions, the copolymer composition is independent of the degree of polymerization. The only limitation on this generalization is that the copolymer be a high polymer. Further, the particular initiation system used in a radical copolymerization has no effect on copolymer composition. The same copolymer composition is obtained irrespective of whether initiation occurs by the thermal homolysis of initiators such as AIBN or peroxides, redox, photolysis, or radiolysis. Solvent effects on copolymer composition are found in some radical copolymerizations. Ionic copolymerizations usually show significant effects of solvent as well as counterion on copolymer composition.

Types of copolymerization behaviour:

Different types of copolymerization behaviour are observed depending on the values of the monomer reactivity ratios. Copolymerizations can be classified into three types based on whether the product of the two monomer reactivity ratios \( r_1 r_2 \) is unity, less than unity, or greater than unity.

a) **Ideal (random) copolymerization:** \( r_1 r_2 = 1 \)

A value of unity (or nearly unity) for the monomer reactivity ratio signifies that the rate of reaction of the growing chain radicals towards each of the monomers is the same, i.e., \( k_{11} \approx k_{12} \) and \( k_{22} \approx k_{21} \) and the copolymerization is entirely random. In other words, both propagating species \( M_1 \) and \( M_2 \) have little or no preference for adding either monomer. For \( r_1 r_2 = 1 \),

\[
\frac{r_1}{r_2} = 1, \text{ meaning } r_2 = \frac{1}{r_1}
\]

Under this condition,

\[
\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}}
\]

and the relative rates of incorporation of the two monomers into the copolymer are independent of the identity of the unit at the end of the propagating species. This equation also implies that \( k_{11}/k_{12} \) and \( k_{21}/k_{22} \) will be simultaneously either greater or less than unity, or in other words, that both radicals prefer to react with the same monomer.

For an ideal copolymerization this equation is combined with the different forms of the copolymer equation to obtain:

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

And

\[
F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}
\]

Most ionic copolymerizations (both anionic and cationic) are characterized by the ideal type of behaviour.
When \( r_1 = r_2 = 1 \), the two monomers show equal reactivities toward both propagating species. The copolymer composition is the same as the comonomer feed with a random placement of the two monomers along the copolymer chain. Such behavior is referred to as 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 species. The copolymer will contain a larger proportion of the more reactive monomer in random placement.

The following figure shows the variation in the copolymer composition as a function of the comonomer feed composition for different values of \( r_1 \). The term ideal copolymerization is used to show the analogy between the curves in this figure and those for vapor–liquid equilibria in ideal liquid mixtures. The copolymer is richer in \( M_1 \) when \( r_1 > 1 \) and is poorer in \( M_1 \) when \( r_1 < 1 \).

For \( r_1 = 1 \), the composition curve reduces to a straight line given by the diagonal and representing a special case in which \( r_1 = r_2 = 1 \) and hence \( F_1 = F_2 \). For \( r_1 = r_2 = 1 \), \( k_{11} = k_{12} \) and \( k_{22} = k_{21} \) or in other words, the two monomers are equally reactive with each radical and the copolymer composition arising out of a random placement of the two monomers along the chain molecule, is equal to the feed monomer composition over the full range of monomer composition. In case of \( r_1 \) or \( r_2 \neq 1 \), i.e., for \( r_1 > 1 \) and \( r_2 < 1 \), or \( r_1 < 1 \) and \( r_2 > 1 \), one of the reacting monomers is more reactive than the other toward the two propagating species, and consequently, the copolymer formed will incorporate randomly a higher proportion of the more reactive monomer in its chain structure. The copolymer is proportionately richer in \( M_1 \) in comparison with the feed monomer mixture for \( r_1 > 1 \), and just the opposite composition characteristics would result for \( r_2 > 1 \), i.e., for \( r_1 < 1 \). With large differences in the reactivities of the two monomers, (i.e., in the \( r_1 \) and \( r_2 \) values) the formation of copolymer sequences becomes progressively difficult as a consequence of very fast depletion of the more reactive monomer from the monomer mixture. Thus, for \( r_1 = 0.1 \) and \( r_2 = 10 \), giving \( r_1 r_2 = 1.0 \) copolymers incorporating good amounts of \( M_1 \) in its structure is difficult to obtain.

One can distinguish between extreme and moderate ideal behaviour depending on the difference between \( r_1 \) and \( r_2 \). Extreme ideal behaviour occurs when \( r_1 \) and \( r_2 \) are very different (e.g., 10 and 0.1). Moderate ideal behaviour occurs when \( r_1 \) and \( r_2 \) are not too different, (e.g., 0.5 and 2). The term ideal copolymerization does not in any sense connote a desirable process. An important consequence of ideal copolymerizations is that it becomes progressively more difficult to produce copolymers containing appreciable amounts of both monomers as the difference in \( r_1 \) and \( r_2 \) increases, that is, as one progresses from moderate to extreme ideal behaviour. When, for example, \( r_1 = 10 \) and \( r_2 = 0.1 \), copolymers containing appreciable amounts of \( M_2 \) cannot be obtained. Thus a comonomer feed composition of 80 mol% \( M_2 \) (\( f_2 = 0.8 \)) would yield a copolymer containing only 18.5 mol% \( M_2 \) (\( F_2 = 0.185 \)). It is only when \( r_1 \) and \( r_2 \) do not differ markedly (e.g., \( r_1 = 0.5-2 \)) that there will exist a larger range of comonomer feed compositions, which yield copolymers containing appreciable amounts of both monomers.
b) Alternate copolymerization: $r_1r_2 = 0$

A zero, or a nearly zero, value for the reactivity ratio means that the monomer is incapable of undergoing homopolymerization and its radical prefers to add exclusively to the other monomer. As with ideal behaviour, there are two types of alternating behaviour – extreme and moderate alternating behaviour. Both $r_1$ and $r_2$ are zero in extreme alternating behaviour, and the two monomers enter into the copolymer in equimolar amounts in a non-random, alternating arrangement along the copolymer chain. Each of the two types of propagating species preferentially adds the other monomer, that is, $M_1^*$ adds only $M_2$ and $M_2^*$ adds only $M_1$. The copolymerization equation reduces to:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) = 1$$

The copolymer has the following alternating structure irrespective of the commonomer feed composition.

$$\sim M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1\sim$$

Moderate alternating behavior occurs when either (1) both $r_1$ and $r_2$ are small ($r_1r_2 = $ very small, close to 0) or (2) one $r$ value is small and the other $r$ is zero ($r_1r_2 = 0$). The copolymer composition tends toward alternation but is not the perfectly alternating structure, as described above.

The behaviour of most commonomer systems lies between the two extremes of ideal and alternating copolymerization. As the $r_1r_2$ product decreases from one toward zero, there is an increasing tendency toward alternation. Perfect alternation occurs when $r_1$ and $r_2$ are both zero. The tendency toward alternation and the tendency away from ideal behaviour increases as $r_1$ and $r_2$ become progressively less than unity. The range of behaviour can be seen by considering the situation where $r_2$ remains constant at 0.5 and $r_1$ varies between 2 and 0.

This figure shows the copolymer composition as a function of the feed composition in these cases. The curve for $r_1 = 2$ shows the ideal type of behaviour described previously. As $r_1$ decreases below 2, there is an increasing tendency toward the alternating behavior with each type of propagating species preferring to add the other monomer. The increasing alternation tendency is measured by the tendency of the product $r_1r_2$ to approach zero. Of great practical significance is the fact that a larger range of feed compositions will yield copolymers containing sizable amounts of both monomers. However, when $r_1r_2$ is very small or zero the alternation tendency is too great and the range of copolymer compositions that can be obtained is again limited. In the extreme case where both $r_1$ and $r_2$ are zero, only the 1:1 alternating copolymer can be produced. This would show in this figure as a horizontal line at $F_1 = 0.5$ (but the line would not touch either the left or right ordinates).

The plots in the preceding figure illustrate an interesting characteristic of copolymerizations with a tendency toward alternation. For values of $r_1$ and $r_2$ both less than unity, the $F_1/F_2$ plots cross the line representing $F_1 = F_2$ (the diagonal line). At these intersections or crossover points the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition. Such copolymerizations are termed azeotropic copolymerizations. The condition under
which azeotropic copolymerization occurs, obtained by combination of the copolymerization equation with \( d[M_1]/d[M_2] = [M_1]/[M_2] \), is

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

Or

\[
f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)}
\]

A special situation arises when one of the monomer reactivity ratios is much larger than the other. For the case of \( r_1 \gg r_2 \) (i.e., \( r_1 \gg 1 \) and \( r_2 << 1 \)), both types of propagating species preferentially add monomer \( M_1 \). There is a tendency toward consecutive homopolymerization of the two monomers. Monomer \( M_1 \) tends to homopolymerize until it is consumed; monomer \( M_2 \) will subsequently homopolymerize. An extreme example of this type of behaviour is shown by the radical polymerization of styrene-vinyl acetate with monomer reactivity ratios of 55 and 0.01.

c) Block copolymerization: \( r_1 > 1, r_2 > 1 \)

If both \( r_1 \) and \( r_2 \) are greater than unity (and therefore, also \( r_1, r_2 > 1 \)) there is a tendency to form a block copolymer (vide structure below) in which there are blocks of both monomers in the chain.

\(~M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2~\)

If \( r_1 > 1 \), an \( M_1 \) propagating species would add many units of \( M_1 \) in succession until the growing chain happens to add an \( M_2 \) unit changing itself from \( M_1 \) type to \( M_2 \) type. Since \( r_2 \) is also more than 1, the \( M_2 \) propagating species would then preferentially add many \( M_2 \) units in succession until an \( M_1 \) unit happens to add, converting the chain again to the \( M_1 \) type. A block copolymer consisting of long sequences of each monomer in the copolymer chain would thus be expected. The length of each block will be some statistical average with the statistical length dependent on how large the reactivity ratios are. In general, the larger the value of the reactivity ratio, the larger the block will be. However, if both \( r_1 \) and \( r_2 \) are quite large, the two types of monomers would only undergo simultaneous homopolymerization in each other's presence. Such combinations of reactivity ratios are, however, rare in free-radical copolymerizations, but they can be found in other systems.
In batch reactions where the yield is high and no additional monomer is added, at the end of the reaction, the average content of each monomer unit in the total copolymer formed will (normally) necessarily be directly related to the initial ratio of the two monomers. Thus, the copolymer content will vary depending on which the particular chains are formed but the final overall product will have an average of units in it, reflective of the initial monomer concentrations. The values for \( r_1 \) and \( r_2 \) are used to help guide the ratio of reactants necessary to achieve a specific copolymer composition. When a desired copolymer composition is required and either reactivity ratio is unlike and not near zero, continuous flow processes or batch processes where a monomer is continuously added are employed. Considering the reaction between \( \text{VAc} \) and \( \text{VC} \), \( r_1 = 0.23 \), meaning growing chains with \( \text{VAc} \) radicals at their ends have a greater tendency to react with a \( \text{VC} \) monomer than a \( \text{VAc} \) monomer. The value for
$r_2$ is 1.68, meaning that there is a tendency for growing chains with VC radical ends to add to the VC monomer rather than the VAc monomer.

Thus, given that both monomers are present in equal molar amounts, the beginning polymer formed will be rich in VC-derived units. As the amount of VC is depleted, the forming copolymer chains will have greater amounts of VAc until all of the VC is almost used up and chains with almost only VAc units will be formed. If a copolymer composition that favours a copolymer rich in VC is desired, then the concentration of VC will have to be maintained sufficient to give copolymers that have high VC-derived unit content. This is done by simply adding VC as the reaction proceeds. The resonance stability of the macroradical is an important factor in polymer propagation. Thus, for free radical polymerization, a conjugated monomer such as styrene is at least 30 times as apt to form a resonance-stabilized macroradical as VAc, resulting in a copolymer being rich in styrene-derived units when these two are copolymerized. Strongly electrophilic or nucleophilic monomers will polymerize exclusively by anionic or cationic mechanisms. However, monomers that are neither strongly electrophilic nor nucleophilic generally polymerize by ionic and free radical processes. The contrast between anionic, cationic, and free radical methods of addition copolymerization is clearly illustrated by the results of copolymerization of styrene and methyl methacrylate utilizing the three modes of initiation:

![Copolymerization diagram](image)

Such results illustrate the variations of reactivities and copolymer composition that are possible from employing the different initiation modes. The free radical "tieline" resides near the middle since free radical polymerizations are less dependent on the electronic nature of the comonomers relative to the ionic modes of chain propagation. As noted before, the copolymerization can be controlled by control of the monomer feed in accordance with the copolymer equation:

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

**Recommended texts:**


