6

COPOLYMERIZATION

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6.1 INTRODUCTION

6.1.1 What Are Copolymers?

It often occurs that it is desirable to modify the properties of a homopolymer to achieve certain application-specific characteristics that are perhaps not possible by solely manipulating the polymer molecular weight or by chemical modification of the final product. Perhaps one is interested in achieving properties that are intermediate to two homopolymers. Properties of interest could include crystallinity, flexibility, tensile strength, melting point, glass-transition temperature, and many others.

One option would be to blend one homopolymer with another. This would result in a physical mixture prepared via mechanical means such as screw compounding and extrusion. Polymer blending is not straightforward as there is a tendency toward phase separation owing to the inherent incompatibility between most polymers. Thus, one can introduce specific interactive functionalities on the homopolymer pairs (e.g., hydrogen bondings, acid–base interactions, and ion–dipole interactions) and use processing aids and compatibilizing compounds such as ionomers to maintain a uniform blend. There are estimates that 36% of worldwide polymer consumption is accounted for by polymer blends [1].

An alternative to physical blending is the polymerization of two or more monomers referred to as *copolymerization*. When more than two monomers are used, the product is referred to as a *multicomponent copolymer*, and in the special case of three monomers, the term *terpolymer* is used. Of course, adding more than one monomer type to the reaction mixture results in added complexity in the kinetic reaction mechanisms. This complexity arises due to the relative rates of polymerization that depend on the structure of each monomer as well as that of the radicals. This affects the polymer composition (relative amounts of each monomer unit incorporated into the copolymer chain), the monomer sequence distribution (the arrangement of the comonomers in the polymer chain backbone), and the polymer molecular weight. Despite this added complexity, a broad range of application properties that are simply not possible via homopolymerization can be achieved.

6.1.2 Commercial Copolymer Examples

Copolymerization products are widespread. Several important commercial examples are presented below: [2, 3]

Ethylene-Vinyl Acetate (*EVA*). The addition of vinyl acetate to ethylene imparts flexibility, impact and stress crack resistance, optical clarity, and melt adhesive properties. EVA copolymers are used extensively as hot-melt adhesives, in biomedical applications as drug delivery devices, and as a foam in a broad range of sports equipment.

Ethylene-Acrylic Acid (*EAA*). The addition of acrylic acid (15–20%) to ethylene results in a copolymer with an ionic nature, which offers improved adhesive properties. It is used in applications similar to that of EVA and primarily as a hot-melt adhesive.

Styrene-Butadiene Rubber (*SBR*). The homopolymer of styrene is relatively brittle and has a low resistance to impact and solvents. The addition of butadiene significantly increases the abrasion resistance resulting in a copolymer that is most widely used as tire

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rubber. Other applications include automotive belts and gaskets, flooring, shoe heels and soles, electrical insulation, and chewing gum.

Styrene-Acrylonitrile (*SAN*). The addition of acrylonitrile to styrene improves the polymer's resistance to oils and grease, stress cracking, and crazing, leading to a transparent copolymer with high impact strength. SAN copolymers find application in a broad range of household items including packaging, furniture, and electronics.

Acrylonitrile-Butadiene-Styrene (*ABS*) *Terpolymer*. The acrylonitrile and styrene copolymer is grafted onto polybutadiene. The properties of SAN are combined with a greatly improved impact resistance and heat distortion resistance. ABS terpolymers find application as engineering plastics, in household appliances, luggage, telephone housings, automotive parts, and many more.

Butadiene-Acrylonitrile (*Nitrile Rubber* (*NBR*)). Acrylonitrile imparts resistance to hydrocarbon oil and gasoline. NBR finds use as an adhesive (low molecular weight), in nonlatex gloves for the health-care industry, and in automotive parts such as fuel tanks, O-rings, gaskets, belts, and hoses. NBR is also commonly blended with other polymers.

Vinylidene Chloride–Vinyl Chloride (*VDC/VCM*). VDC/VCM copolymers are tough, flexible, and durable. As a film, they find significant use in the food packaging industry. They are also manufactured as a fiber used in car upholstery and garden furniture fabrics.

Ethylene-Propylene-Diene-Monomer (*EPDM*) *Rubber*. The main properties of EPDM are its outstanding heat, ozone and weather resistance, as well as its electrical insulating properties. EPDM rubber finds use in vehicles (weather seals in windows and trunks, cooling system hoses), in safety equipment (seals in respirators), roofing (waterproofing of roofs), and playground surfacing.

6.1.3 Step-Growth Copolymerization

As a last point, let us consider how copolymerization relates to the polymer growth mechanism. First, most step-growth polymerizations (e.g., the production of nylon 6/6 by the reaction of hexamethylene diamine with adipic acid) use two monomers to produce the final polymer. One can say that these are inherently copolymerizations. Considering the copolymer composition in a step-growth polymerization, we expect to achieve a final composition more or less identical to the monomer feed composition. This is due to the one-to-one ratio of functional groups required for step growth as well as the need to achieve nearly 100% conversion to yield high molecular weight polymer. The focus of this chapter is primarily on chain growth copolymerization. In certain cases (e.g., copolymer microstructure, composition measurement methods), applicability of the topic to step-growth copolymerization should be obvious.

6.2 TYPES OF COPOLYMERS

Copolymers composed of two monomers can be classified according to the relative arrangement of the two types of monomer units along the chain or, in other words, according to the monomer distribution. For linear chains, one can have four types of copolymers: statistical/random, alternating, block, and gradient.

6.2.1 Statistical Copolymers

Statistical copolymers are those in which the monomer sequence follows a specific statistical law (e.g., Markovian statistics of order zero, one, two). Random copolymers are a special case of statistical copolymers in which the nature of a monomeric unit is independent of the nature of the adjacent unit (Bernoullian or zero-order Markovian statistics). They exhibit the structure shown in Figure 6.1. If A and B are the two monomers forming the copolymer, the nomenclature is poly (A-*stat*-B) for statistical copolymers and poly (A-*ran*-B) for the random case. It should be noted that sometimes the terms random and statistical are used indistinctly. The commercial examples of these copolymers include SAN: poly (styrene-*ran*-acrylonitrile) [4] and poly (styrene-*ran*-methyl methacrylate) (MMA) [5].

6.2.2 Alternating Copolymers

Alternating copolymers contain the two monomers in equimolar composition following a regularly alternating pattern (Fig. 6.2). The nomenclature for this type of structure is poly (A-*alt*-B). A commercial example of this type of copolymers is poly (styrene-*alt*-maleic anhydride).

Random and alternating copolymers have been usually synthesized by traditional techniques (free radical, anionic, and cationic); however, in the past two decades, many copolymers have been synthesized using the relatively new

Figure 6.1 Schematic representation of a random copolymer.

Figure 6.2 Schematic representation of an alternating copolymer.

controlled/living radical polymerization (or CRP for short; see Chapter 4 for a discussion of this topic), which has expanded the ability of polymer chemists to synthesize macromolecules with defined microstructural characteristics. The most popular CRP techniques are as follows: stable radical polymerization or nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation transfer (RAFT) polymerization. Random copolymerizations have recently been reported by using NMP [6], ATRP [7], and RAFT [8]. Alternating copolymers have also been obtained by NMP [9], ATRP [10], and RAFT [11].

6.2.3 Block Copolymers

Block copolymers contain long sequences of each of the monomer types [12, 13]. At least one long sequence of each of the monomers must be present, but in the so-called multiblock copolymers [14, 15], several long alternating sequences can be present. The recommended nomenclature for these copolymers is poly A-*block*-poly B, although sometimes they are named as poly (A-*block*-B) or simply poly (A-*b*-B) [16]. Figure 6.3 shows an illustration of a multiblock copolymer. Commercial examples of theses copolymers include several products prepared by anionic polymerization [12]: diblock polystyrene-*block*-polybutadiene (SB) rubbers and triblock poly (styrene-*b*-butadiene-*b*-styrene). Another interesting family of triblock copolymers has the structure polyethylene oxide-*block*-poly propylene oxide-*block*-polyethylene oxide; they find many applications as surfactants, as well as in pharmacy and drug delivery [17]. Since the synthesis of block copolymers usually requires living processes (with reduced or null termination reactions), CRP techniques such as NMP [18], ATRP [19], and RAFT [20] have also been used to this end.

6.2.4 Gradient Copolymers

Gradient copolymers are those in which an initial portion of the chain is rich in one monomer and poor in the other, and the concentration of this monomer gradually decreases along the chain length, while the concentration of the second monomer gradually increases, as shown in Figure 6.4. There is no recommended nomenclature for this type of structure. Because of the control required in the synthesis of gradient copolymers, NMP [21], ATRP [22], and RAFT [23] have been successfully used recently to build these structures.

6.2.5 Graft Copolymers

Branched chains formed of a main chain of homopolymer of one monomer type and one or several branches of homopolymer of a second monomer type are called *graft copolymers*; they are illustrated in Figure 6.5. The nomenclature for these copolymers is polyA-*graft*-polyB [24]. They are sometimes referred to as poly(A-*graft*-B). Chapter 10 reviews the topic of graft copolymers, and the reader is also referred to the review by Hadjichristidis [25] for example. CRP has also been used to synthesize this kind of polymer via NMP [26], ATRP [27], and RAFT [28].

6.2.6 Notes on Nomenclature

For linear copolymers in which the sequence distribution is not specified, the recommended notation is poly (A-*co*-B).

The general naming rules given above define the source-based nomenclature recommended by IUPAC [29]. There is another more detailed structure-based nomenclature that can be used when the exact copolymer structure is known, but this is rarely used, mainly because of the difficulty of experimentally determining the exact structure of a synthesized copolymer.

6.3 COPOLYMER COMPOSITION AND MICROSTRUCTURE

6.3.1 Terminal Model Kinetics

The following discussion is valid for chain copolymerization, regardless of the type of mechanism (radical, anionic, or cationic). The prediction of the copolymerization rate for

Figure 6.3 Schematic representation of a block copolymer.

Figure 6.4 Schematic representation of a gradient copolymer.

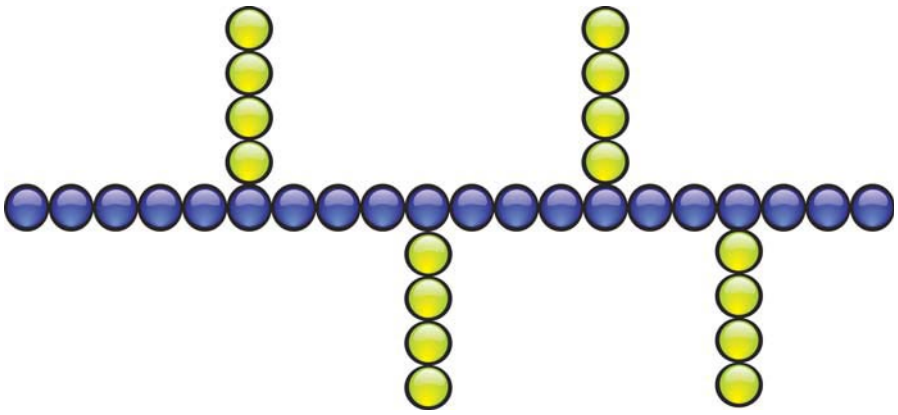

Figure 6.5 Schematic representation of a graft copolymer.

a given system is still an open question in polymer science. In general, it is very difficult to predict the rate of copolymerization of two monomers based on the knowledge of the individual homopolymerization rates of the monomers. However, for most copolymerization systems, it is possible to determine and model the copolymer composition using the so-called terminal model. This model, originally proposed by Mayo and Lewis in 1944 [30], postulates that the chemical reactivity of a propagating chain depends only on the chemical nature of the active monomer unit at the chain end. According to the terminal model, if R_i is a growing chain ending in monomer i (or type i propagating chain), and k_{pij} is the rate constant for the propagation of monomer j with a type i propagating chain, there are four possible propagation reactions in a copolymerization system:

$$R_i + M_j \xrightarrow{k_{pij}} R_j \quad \text{for } i = 1, 2; \quad j = 1, 2 \tag{6.1}$$

From the mass balance for each monomer type, assuming that long chains are formed (long chain hypothesis or LCH), the monomers are mainly consumed in propagation reactions:

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}t} = -k_{p11}[R_1][M_1] - k_{p21}[R_2][M_1] \tag{6.2}$$

$$\frac{\mathrm{d}[M_2]}{\mathrm{d}t} = -k_{p12}[R_1][M_2] - k_{p22}[R_2][M_2] \tag{6.3}$$

From Equations 6.2 and 6.3 and by using the chain rule, it is possible to write the following differential equation:

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}[M_2]} = \frac{k_{p11}[R_1][M_1] + k_{p21}[R_2][M_1]}{k_{p12}[R_1][M_2] + k_{p22}[R_2][M_2]} \tag{6.4}$$

To eliminate the concentrations of the propagating radicals from Equation 6.4, the quasi-steady-state assumption (QSSA) for propagating chains can be used. By virtue of this, the rate of conversion of a type 1 propagating chain into one of type 2 is exactly the same as the rate of conversion of a type 2 propagating chain into one of type 1. This implicitly assumes that the rates of chain type interconversion are much faster than the rates of formation or termination of a chain or, in other words, that the reaction environment (in particular, the relative concentration of the two monomers) does not change significantly during the growth of a chain. Mathematically, this results in

$$k_{p12}[R_1][M_2] = k_{p21}[R_2][M_1] \tag{6.5}$$

or

$$[R_1] = \frac{k_{p21}[R_2][M_1]}{k_{p12}[M_2]} \tag{6.6}$$

Replacement of the concentration of Equation 6.6 in Equation 6.4, followed by division of the resulting numerator and denominator by $k_{p21}[R_2][M_1]$, rearrangement, and writing of the result in terms of the parameters r_1 and r_2 defined by Equation 6.8 result in

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \tag{6.7}$$

where

$$r_1 = \frac{k_{p11}}{k_{p12}} \quad r_2 = \frac{k_{p22}}{k_{p21}} \tag{6.8}$$

The parameters r_1 and r_2 are known as the *reactivity ratios of monomers* 1 and 2, respectively. They represent the tendency of a given propagating chain type toward homopropagation divided by the tendency toward cross-propagation with the other monomer. There are extensive literature reports of values of reactivity ratios for many copolymerization systems. Table 6.1 lists some illustrative values, but extended lists have been compiled and published

TABLE 6.1 Reactivity Ratios

M_A \ M_B	Acrylic acid	Acrylonitrile	Butadiene	Ethylene	Styrene	Maleic anhydride	Methacrylic acid	Methyl methacrylate	Methyl acrylate	Butyl acrylate	Vinyl acetate
Acrylic acid					0.35 [33] 0.22			1.22 [34] 0.83			2.39 [35] 0.03
Acrylonitrile			0.03 [36] 0.20	7.00 [37] 0.00	0.55 [38] 0.22	6.0 [39] 0.0	0.26 [40] 3.44	0.14 [41] 0.19	1.27 [42] 0.87	1.08 [42] 0.83	9.32 [43] 10^{-4}
Butadiene		0.20 [36] 0.03			1.55 [44] 0.37			0.70 [45] 0.32	1.09 [46] 0.07	1.04 [46] 0.07	
Ethylene		0.00 [37] 7.00			0.05 [47] 14.88	0.04 [48] 0.0			0.02 [49] 19.40	0.01 [50] 13.94	0.79 [51] 1.40
Styrene	0.22 [33] 0.35	0.22 [38] 0.55	0.37 [44] 1.55	14.88 [47] 0.05		0.04 [52] 0.02	0.14 [53] 0.67	0.43 [54] 0.49	0.72 [55] 0.17	0.354 [56] 0.119	48.0 [57] 0.05
Maleic anhydride		0.0 [39] 6.0		0.0 [48] 0.04	0.02 [52] 0.04			0.01 [58] 3.4	0.012 [59] 2.79		0.06 [59] 0.019
Methacrylic acid		3.44 [40] 0.26			0.67 [53] 0.14			0.63 [60] 0.32		1.25 [61] 0.31	0.20 [62] 0.01
Methyl methacrylate	0.83 [34] 1.22	0.19 [41] 0.14	0.32 [45] 0.70		0.49 [54] 0.43	3.4 [58] 0.01	0.32 [60] 0.63		28.6 [63] 0.04	1.79 [64] 0.29 [65]	24.02 [64] 0.026
Methyl acrylate		0.87 [42] 1.27	0.07 [46] 1.09	19.40 [49] 0.02	0.17 [55] 0.72	2.79 [59] 0.012		0.04 [63] 28.6			6.38 [66] 0.03
Butyl acrylate		0.83 [42] 1.08	0.07 [46] 1.04	13.94 [50] 0.01	0.119 [56] 0.354		0.31 [61] 1.25	0.29 [64] 1.79 [65]			5.94 [64] 0.026 [67]
Vinyl acetate	0.03 [35] 2.39	10^{-4} [43] 9.32		1.40 [51] 0.79	0.05 [57] 48.0	0.019 [59] −0.06	0.01 [62] 0.20	0.026 [64] 24.02	0.03 [66] 6.38	0.026 [64] 5.94 [67]	

M_A \ M_B	r_{AB} (Reference) r_{BA}

[31, 32]. Equation 6.7 is known as the *copolymerization* or the *Mayo–Lewis equation*. The physical meaning of Equation 6.7 is better appreciated by writing it in terms of mole fractions. If f_i is the mole fraction of unreacted monomer i and F_i is the mole fraction of monomer i in the copolymer formed instantaneously, then

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]}; \; f_2 = 1 - f_1 \tag{6.9}$$

and

$$F_1 = \frac{\dfrac{d[M_1]}{dt}}{\dfrac{d[M_1]}{dt} + \dfrac{d[M_2]}{dt}}; \quad F_2 = 1 - F_1 \tag{6.10}$$

Note that Equation 6.10 defines a molar fraction in the copolymer formed at a given instant, that is, an instantaneous molar fraction. If the composition in the feed changes during the course of the copolymerization (as in a batch reactor), it is necessary to integrate the quantity in Equation 6.10 with respect to time or conversion to calculate a cumulative F_i.

By using the definitions of Equations 6.9 and 6.10 in combination with Equation 6.7 and the chain rule, Equation 6.7 can be written as

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{6.11}$$

Equation 6.11 is another form of the copolymerization equation and in this form it directly provides the instantaneous composition of a copolymer formed when the composition of the feed is given by f_1, f_2.

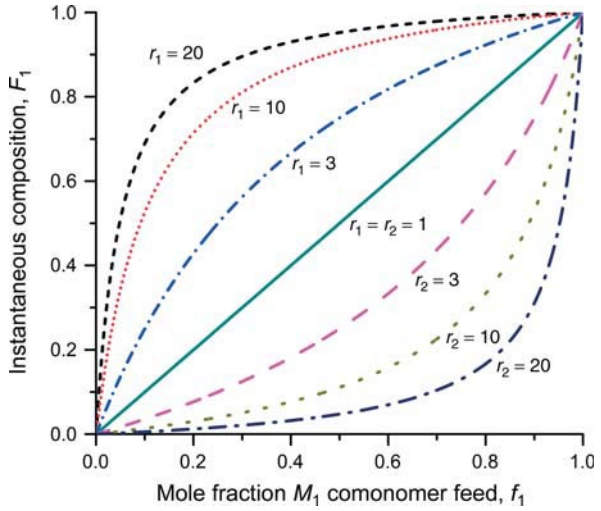

Figure 6.6 Dependence of instantaneous copolymer composition F_1 on initial comonomer feed composition f_1 in an ideal copolymer. The reactivity ratios satisfy $r_1 r_2 = 1$. (*See insert for the color representation of the figure*.)

In the derivation of the copolymerization equation use has been made of the QSSA; however, this is not a necessary but a sufficient condition for its derivation. It is possible to derive the equation based on statistical arguments [67], without resorting to the QSSA, but using instead the "chain continuity" condition as defined by Farina [68]. A possible physical interpretation of this condition is that the environment surrounding the chain during its formation (in particular, the monomer composition) should not change significantly, while the chain grows sufficiently to reach a statistical average composition. From a system dynamics point of view, this condition is a consequence of the dynamic decoupling (widely different time constants) of the phenomena defining the chain composition and the phenomena defining the rate of change of "slow" variables (global kinetics, unreacted monomer composition) [69].

6.3.1.1 Copolymer Composition Behavior Depending on the relative values of the reactivity ratios, copolymerization systems show different composition behavior. It is instructive to analyze some model behaviors.

Ideal Copolymerization This is defined by the condition $r_1 r_2 = 1$ and corresponds to systems in which both types of propagating chains show the same relative preference for propagation with one or the other of the monomers, since in this case

$$\frac{k_{p11}}{k_{p12}} = \frac{k_{p21}}{k_{p22}} \tag{6.12}$$

By using the mathematical condition that defines the ideal copolymerization, the two forms of the copolymer equation, Equations 6.7 and 6.11, adopt simplified forms given by Equations 6.13 and 6.14, respectively:

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \tag{6.13}$$

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2} \tag{6.14}$$

The term *ideal* for this copolymerization was adopted by Wall [70] due to the similitude that plots of Equation 6.14 for this kind of systems have with plots of vapor–liquid equilibrium for ideal binary solutions, but it has no other implication. Figure 6.6 shows a plot of Equation 6.14 for different values of the reactivity ratio r_1. Note that when one of the two ratios is much larger than the other, the copolymer composition of the monomer with the larger ratio will be much higher than the composition of that monomer in the feed. In a batch reaction, this would lead to a fast depletion of that monomer and therefore to a significant drift of composition with the progress of the reaction conversion. This is illustrated in Figure 6.7 and, in particular, in Figure 6.7b for a system in which $r_1 = 28.6$ and the initial monomer feed is $f_1 = 0.2$. Procedures to deal with this problem are discussed in Section 6.4.5.

Alternating Copolymerization This is defined by the condition $r_1 = r_2 = 0$, which indicates that in these systems, cross-propagation is favored over homopropagation. This is clear, since in this case

$$\frac{k_{p11}}{k_{p12}} = \frac{k_{p22}}{k_{p21}} = 0 \tag{6.15}$$

The copolymerization equation in these systems adopts the simple forms

$$\frac{d[M_1]}{d[M_2]} = 1 \tag{6.16}$$

$$F_1 = 0.5 \tag{6.17}$$

This indicates that for any feed composition, the copolymer formed will have an equimolar regularly alternating composition. The chemistry behind these systems has been extensively discussed in the literature, and the charge-transfer complex concept was for a long time the prevailing theory to explain this behavior [73–75]. More recently, Hall and Padias [76, 77] have proposed an alternate explanation based on polar effects when an electron-donor and an electron-acceptor monomer interact. This last theory has the additional virtue of explaining the fact that many

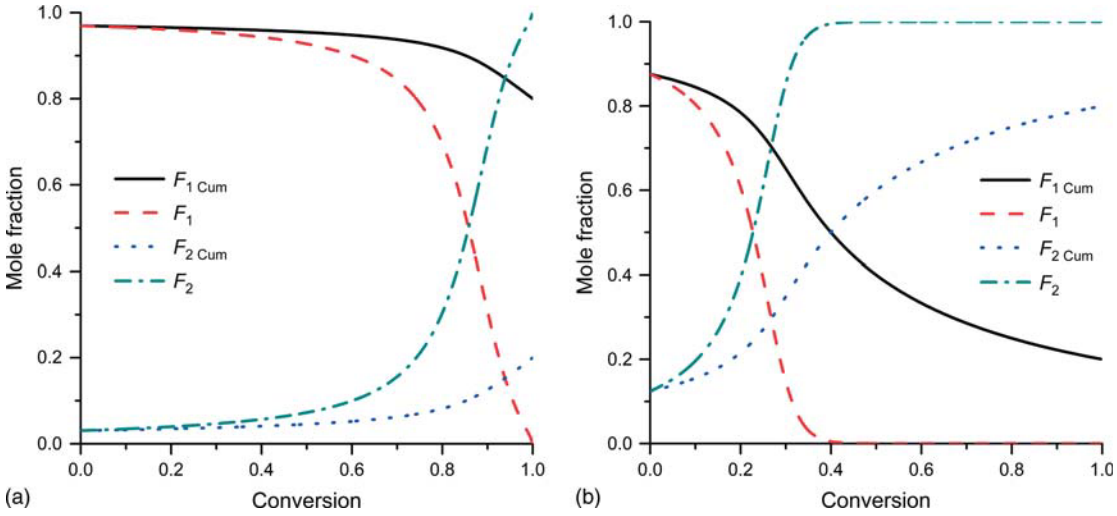

Figure 6.7 Variations in both cumulative ($F_{1\ Cum}$) and instantaneous (F_1) copolymer compositions with conversion for: (a) acrylamide (M_1)–styrene (M_2) system, $f_{1,0} = 0.8$, $f_{2,0} = 0.2$, $r_1 = 8.97$, $r_2 = 0.65$ [71]; (b) MMA (M_1)–vinyl acetate (M_2) system, $f_{1,0} = 0.2$, $f_{2,0} = 0.8$, $r_1 = 28.6$, $r_2 = 0.04$ [72].

systems that behave as alternating copolymerizations also show spontaneous initiation [78].

Some copolymerization systems are not strictly alternating, but still they show a tendency toward alternation. This occurs when both r_1 and $r_2 < 1$. The alternating trend increases as the reactivity ratios approach zero. An interesting feature of these systems is that they present the so-called azeotropic composition, at which $F_1 = f_1$. At this composition, the copolymer formed has the same composition as the monomers in the feed and, therefore, systems copolymerizing at this condition do not show compositional drift. It can be shown that a necessary condition that the reactivity ratios have to satisfy in order for a copolymerization system to show an azeotropic point is that either both r_1 and $r_2 < 1$ or both r_1 and $r_2 > 1$.

To obtain an equation for calculating the azeotropic composition, one can start by using the equivalent azeotropic condition $\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$ in Equation 6.7, then writing the result in terms of mole fractions, as in the derivation of Equation 6.11, and finally solving for f_1. The result is

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \tag{6.18}$$

Figure 6.8 shows several plots of Equation 6.11 for different values of r_1 at a fixed value of $r_2 = 0.1$. As the value of r_1 increases from 0.1 to 20, the behavior of the system changes from that of a nearly alternating copolymerization system to an ideal one (and even beyond when, e.g., $r_1 = 20$). Note that all the curves corresponding to values of $r_2 < 1$ cross the line of $F_1 = f_1$ at their azeotropic compositions. Figure 6.9 shows the change of

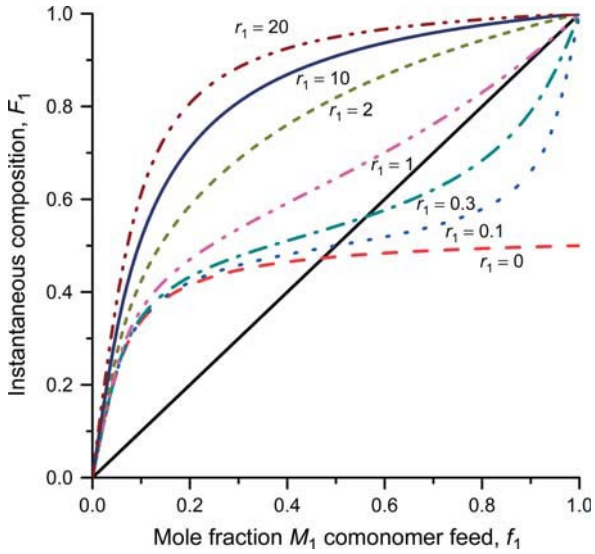

Figure 6.8 Dependence of instantaneous copolymer composition F_1 on initial comonomer feed composition f_1 for different values of r_1; $r_2 = 0.1$. (*See insert for the color representation of the figure.*)

composition with conversion for two different systems in which the composition drift is relatively small. One of them belongs to a system approaching ideal behavior, but in which both reactivity ratios are near 1. This is typical of copolymerizations involving two monomers of the same chemical family (MMA and benzyl methacrylate (BzMA) in this example). The other case is a system exhibiting an azeotropic point that is initially fed with a monomer composition near that point (styrene, St, and MMA).

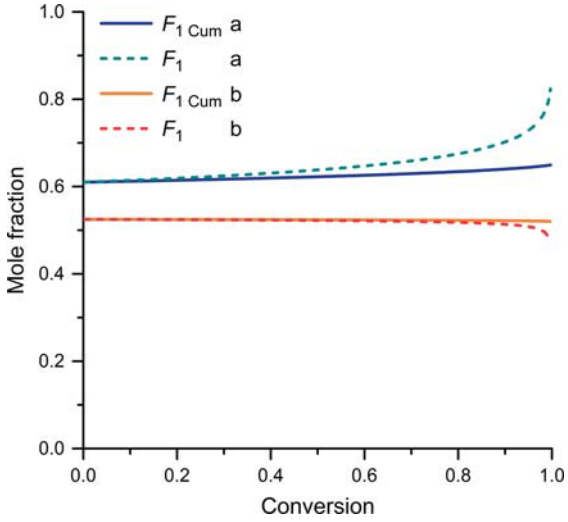

Figure 6.9 Variations in both cumulative ($F_{1\ Cum}$) and instantaneous (F_1) copolymer compositions with conversion for two systems. The initial conditions are as follows: (a) MMA (M_1)–BzMA (M_2) system with $f_{1,0} = 0.65$, $f_{2,0} = 0.35$, $r_1 = 0.808$, $r_2 = 1.112$ [79]; (b) St (M_1), MMA (M_2) system with $f_{1,0} = 0.52$, $f_{2,0} = 0.48$, $r_1 = 0.52$, $r_2 = 0.45$ [80].

6.3.2 Other Copolymerization Models

Although the terminal model is very useful for the correlation of composition data in copolymerization, its predictions deviate from the real behavior for systems that do not satisfy all the assumptions on which it is based. For those systems meeting all the assumptions, the terminal model can predict both the composition and the copolymerization rate. On the other hand, copolymerization systems that are not adequately described by the terminal model can be classified in two categories. In one category, the terminal model explains well the behavior of composition, but it is incapable of adequately predicting the rate of copolymerization; an example of this is the copolymerization of styrene with MMA [81]. Why is this so? The apparent reason for this is the dynamic decoupling of the phenomena determining the chain composition (linked to the rate of exchange of growing chain types) and the polymerization rate (linked to the total population of growing chains). Note that the copolymerization equation, which explains the composition behavior, is independent of the absolute propagation rate coefficients and depends only of the reactivity ratios. The same has been proved for three monomers (Eq. 6.43) [82] and for four monomers [83], and it has been also shown that the composition is independent of absolute propagation rate coefficients for any number of monomers [84, 85]. In the second category, there are some systems in which not even the composition behavior can be explained by the terminal model. In this last case, it is possible that the reactivity of the growing chain depends not only on the last unit but also on the penultimate (or even other) units. In other systems, the reversibility of the propagating reaction can be of importance and this has been neglected in the derivation of the copolymerization equation. In the following, some models that take into account these phenomena are presented.

6.3.2.1 Penultimate Model Some copolymerization systems in which the values for reactivity ratios measured at different compositions are inconsistent can be adequately represented by the penultimate model [86]. In this case, the reactivity of the propagating chain depends on the chemical nature of the last two monomeric units: the one at the active end and the previous one (penultimate) [87, 88]. This is common in systems in which the monomers contain bulky substituents such as the fumaronitrile–styrene copolymerization [89]. In other systems, the penultimate effect has been reported to be limited [90]. The penultimate model can be formulated as follows. Consider the reaction of a growing chain having a penultimate unit j and terminal unit i with a monomer n, M_n:

$$R_{ji} + M_n \xrightarrow{k_{pjin}} R_{jn} \quad \text{for } i = 1, 2; \quad j = 1, 2; \quad n = 1, 2 \tag{6.19}$$

There are eight possible reactions of this type obtained by combining the possible values of i, j, and n. Applying the QSSA to the four types of growing chains (four combinations of i, j values), it is possible to write the relationship between F_1 and f_1 in a form similar to the copolymerization equation, but using pseudoreactivity ratios, r_i^*, as follows [91]:

$$F_1 = \frac{r_1^* f_1^2 + f_1 f_2}{r_1^* f_1^2 + 2 f_1 f_2 + r_2^* f_2^2} \tag{6.20}$$

The pseudoreactivity ratios are defined as

$$r_1^* = r_{21} \frac{r_{11} f_1 + f_2}{r_{21} f_1 + f_2} \tag{6.21}$$

$$r_2^* = r_{12} \frac{f_1 + r_{22} f_2}{f_1 + r_{12} f_2} \tag{6.22}$$

Additionally, four reactivity ratios must be defined:

$$r_{11} = \frac{k_{p111}}{k_{p112}} \tag{6.23}$$

$$r_{12} = \frac{k_{p122}}{k_{p121}} \tag{6.24}$$

$$r_{21} = \frac{k_{p211}}{k_{p212}} \tag{6.25}$$

$$r_{22} = \frac{k_{p222}}{k_{p221}} \tag{6.26}$$

6.3.2.2 Depropagation Models In some copolymerizations, one or both monomers can present a tendency toward depropagation because they are near their ceiling temperature. This trend is increased with higher reaction temperatures and lower monomer concentrations, and these systems will show composition behavior that deviates from terminal model predictions. Several systems fall in this category: styrene-α-methyl styrene [92], MMA–α-methyl styrene [93], *N*-phenylmaleimide-styrene [94] among others. One of the most relevant models for these systems was developed by Lowry [95]. In his development, Lowry considers two cases in which monomer 1 does not show any tendency to depropagation, but monomer 2 depropagates depending on the nature of the 1 or 2 units preceding the chain end. In the first case analyzed by Lowry, monomer 2 (M_2) depropagates if the penultimate unit is also M_2. In the second case, monomer 2 depropagates if it is preceded by a sequence of at least two monomer 2 units. These cases are shown schematically in Figure 6.10.

For the first case of Lowry, the copolymer composition can be represented as follows:

$$F_1 = \frac{\left(r_1\left[M_1\right] + \left[M_2\right]\right)(1-\alpha)}{r_1\left[M_1\right](1-\alpha) + \left[M_2\right](2-\alpha)} \tag{6.27}$$

where

$$\alpha = 0.5\left\{\left[1 + K\left[M_2\right] + \left(\frac{K\left[M_1\right]}{r_2}\right)\right] - \left[\left(1 + K\left[M_2\right] + \left(\frac{K\left[M_1\right]}{r_2}\right)\right) - 4K\left[M_2\right]\right]^{1/2}\right\} \tag{6.28}$$

and K is the equilibrium constant for the first case reaction in Figure 6.10.

For the second case, the expression for the copolymer composition is

$$F_1 = \frac{\left\{\frac{\left[r_1 M_1\right]}{\left[M_2\right]} + 1\right\}\left\{\alpha\gamma + \frac{\alpha}{1-\alpha}\right\}}{\left\{\frac{\left[r_1 M_1\right]}{\left[M_2\right]} + 1\right\}\left\{\alpha\gamma + \frac{\alpha}{1-\alpha}\right\} + \alpha\gamma - 1 + \frac{1}{(1-\alpha)^2}} \tag{6.29}$$

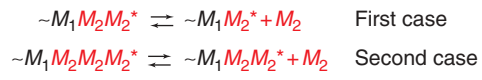

Figure 6.10 Schematic representation of depropagation first and second cases defined by Lowry.

where

$$\gamma = \frac{\left[K\left[M_2\right] + \left(K[M_1]/r_2\right) - \alpha\right]}{K\left[M_2\right]} \tag{6.30}$$

where α is also given by Equation 6.28 but the equilibrium constant K, there and in Equation 6.30, is that of the second case reaction in Figure 6.10.

There is the third case in the Lowry theory corresponding to systems in which both monomers can depropagate as long as they are preceded by a sequence of two M_2 units; however, the mathematical expressions are rather intricate and they are not reproduced here. In general, more recent work analyzes the general case of depropagation including the important topic of cross-depropagation. Kruger studied a copolymerization system starting from the terminal model [96] and Szymanski developed an equilibrium theory for depropagating systems having any number of comonomers [97]; this treatment includes the terminal and penultimate models. Recently, several systems (co- and terpolymerizations) have been analyzed experimentally and by mathematical modeling by Penlidis et al. [93, 98, 99].

This work also includes the mathematical analysis for up to six monomers [100]. The trend in these more general treatments is oriented toward the use of numerical methods for the solution of the mathematical problems associated, since closed, analytical expressions are difficult to handle and are of little practical use.

6.3.2.3 Models Involving the Participation of Complexes As mentioned in Section 3.1, several copolymerizations that lead to alternating copolymers have been analyzed by the use of the concept of chain transfer complexes. Some of these systems are styrene–maleic anhydride [101–103], allyl acetate–maleic anhydride [104], and norbornene–maleic anhydride [105].

In these models, the complex formed by the monomer pair competes with the individual monomer molecules for the propagation reaction with the radicals. There are two variations of this approach: in the complex participation model, the pair of monomers form a complex and are added to the chain radical [106–109]. On the other hand, in the complex dissociation model, the complex participates in the propagation process, but dissociates upon reaction and only one of the monomers is added to the chain [101, 103]. Although there is ample experimental evidence for the existence of such complexes in these copolymerizations (such as the bright colors associated with them) [76], it is questionable whether the complexes actually participate in the propagation step [76]. Additionally, for several years, Hall and Padias have accumulated experimental and theoretical evidence that refutes the validity of the models based on complex participation [76, 77]. Both the complex participation and the penultimate models were combined in the so-called comppen model [110].

6.3.2.4 Model Discrimination This is an extensive and difficult topic, and therefore, no detailed treatment of the subject is provided here; it involves elements not only of polymer science but also of statistics. Instead, some general considerations are provided. Generally, caution must be exerted when a model is applied to a particular copolymerization. The kinetics of copolymerization are complex for several reasons: (i) it involves at least four propagation constants; (ii) it is not clear yet if a chemical or a diffusion-controlled termination occurs; (iii) for systems with diffusion-controlled termination, the value of the termination constant may depend on the chain length; etc. In many copolymerizations, several of the kinetic constants are unknown, let alone the parameter values for multicomponent (three or more monomer) systems. In addition, it has been reported that the propagation step can often influence the determination of the termination constant or, in copolymerization systems exhibiting self-initiation, propagation, and initiation phenomena can be difficult to separate [78].

For all these reasons, careful assessment of the model adequacy, aided by statistical techniques, must be used to discriminate among competing models aimed at explaining copolymerization data. Statistical experimental design should also be used whenever possible.

The need of using experimental data on sequence distribution to discriminate among models has been mentioned [101, 111]. Burke et al. [112, 113] compared several statistical techniques for model discrimination and applied them to discriminate among the terminal and the penultimate model. They conclude that the Buzzi–Ferraris technique [114–116], which is based on sequential experimental designs that maximize the information needed at each stage (either for parameter refinement or for emphasizing model differences), is capable of model discrimination in relatively few experiments and can detect even small penultimate effects. Most authors agree that the error associated with measurements also contributes to the difficulty of discerning among competing models [32]; therefore, statistical techniques are strongly recommended for this type of analysis.

6.3.3 Reactivity Ratio Estimation

Having established the importance of reactivity ratios, it falls to the researcher to have to estimate their values. Given the number of statistical tools and computational devices available over the past several decades, one would expect this to be straightforward. However, there has been resistance to using proper parameter estimation techniques and the reader is advised to exercise caution when using reactivity ratios found in the literature [117]. A good practice is to consider reevaluating these from their raw data if at all possible. In any case, the objective in this section is to outline a methodology to estimate reactivity ratios of the highest precision possible.

A first important question concerns whether the goal is to discriminate between competing models (i.e., terminal vs penultimate model kinetics) or to seek the best parameter estimates. We first assume that terminal model kinetics are being considered and later discuss implications regarding the assumption of penultimate model kinetics. As seen in the previous section, for terminal model kinetics, reactivity ratios are typically estimated using the instantaneous copolymer composition equation or the Mayo–Lewis equation, expressed in two common forms, Equations 6.7 and 6.11.

When considering the estimation of parameters, a protocol such as suggested by Polic et al. [118] is a wise choice. The general protocol consists of the following: (i) parameter sensitivity analysis, (ii) statistical design of experiments, and estimation of (iii) parameters, and (iv) confidence regions. Parameter sensitivity analysis answers the question about which measured response gives the best parameter estimates. Most reactivity ratio estimates have been derived from polymer composition data measured directly, for example, using spectroscopic techniques such as NMR or IR or indirectly by measuring residual monomer using gas chromatography (GC). Recent work offers a review on the use of triad sequence distribution data with case studies demonstrating improved precision of the reactivity ratio estimates [119].

The statistical design of experiments includes the consideration of reaction conditions (e.g., temperature and feed composition) as well as extent of reaction or conversion, number of experimental points and replicates, and the relative location of the design points (e.g., several equidistant points versus selected points on the feed composition scale). As discussed later, reactivity ratios are generally insensitive to moderate temperature changes (i.e., $\pm 20\,^{\circ}\mathrm{C}$). Evidently, one would prefer to design experiments within the application range. The use of Equation 6.7, a differential equation, implies only small changes in copolymer composition can be used, and thus, the use of low conversion experiments ($<5\%$) for data collection is necessary. Depending on the copolymer system, this constraint can either be relaxed to say 10% conversion or may even necessitate ultralow conversions near 1% [120]. If higher conversion data are unavoidable, integration of Equation 6.7 or 6.11 is necessary [121]. A methodology dictating the feed composition, number of experimental points, and number of replicate experiments for unconstrained cases is given by Tidwell and Mortimer [122]. Their recommendation is to perform several replicates, say four, at two unique monomer feed compositions f_1' and f_1'' [117, 120]:

$$f_1' = \frac{2}{2 + r_1^*} \tag{6.31}$$

$$f_1'' = \frac{r_2^*}{2 + r_2^*} \tag{6.32}$$

where r_1^* and r_2^* are initial estimates of the reactivity ratios that can be estimated using the well-known, yet highly approximate, Q-e scheme [123]. Alternatively, screening experiments (e.g., a set of equidistant points along the feed composition axis) can be used. The use of several equidistant points is more practical for model discrimination [112, 124]. In the event of comonomer feed composition constraints, the methodology described by Burke et al. can be used [125].

The next step in the protocol answers the question about what is the best method to estimate the reactivity ratios. Historically, because of its simplicity, linearization techniques such as the Fineman–Ross, Kelen–Tudos, and extended Kelen–Tudos methods have been used. Easily performed on a simple calculator, these techniques suffer from inaccuracies due to the linearization of the inherently nonlinear Mayo–Lewis model. Such techniques violate basic assumptions of linear regression and have been repeatedly shown to be invalid [117, 119, 126]. Nonlinear least squares (NLLS) techniques and other more advanced nonlinear techniques such as the error-in-variables-model (EVM) method have been readily available for several decades [119, 120, 126, 127].

Finally, we are concerned with the precision of the reactivity ratios or, in other words, the joint confidence regions of the parameter estimates. We have stated at the beginning of this section that our objective is to estimate reactivity ratios of maximum precision. This is equivalent to minimizing the joint confidence region of the parameters. The joint confidence regions can be generated using methods such as shown by Polic et al. [117].

Regarding the question of alternative copolymerization kinetic models, as mentioned earlier, in the event of discriminating between competing models (e.g., terminal model kinetics vs penultimate model kinetics), a set of equidistant monomer feed compositions along the entire composition range can serve as an appropriate design of experiments. Once one has determined that an alternative model is operative, the same four questions noted for the terminal model above should be revisited. There are several examples of the estimation of penultimate unit kinetic parameters in the literature [125, 112].

6.3.4 Sequence Length Distribution

Apart from considering the effect of the macroscopic copolymer composition on polymer properties, the exact arrangement or sequence of individual monomers bound in the copolymer chains can also have a significant effect. While copolymers are often referred to as *random*, for most cases (i.e., other than the truly random case of $r_1 = r_2 = 1$) there is a definite trend toward a regular microstructure. For example, if $r_2 > 1$, sequences of M_2 will tend to be formed. The copolymer microstructure is defined by the distribution of the various lengths of M_1 and M_2 sequences, that is, the *sequence length distribution*.

The probability (P_{11}) of forming a M_1M_1 sequence (or dyad) in the copolymer chain is given by the ratio of the rate of adding M_1 to M_1^* to the sum of the rates of adding M_1 and M_2 to M_1^*:

$$P_{11} = \frac{k_{p11}\left[M_1^*\right]\left[M_1\right]}{k_{p11}\left[M_1^*\right]\left[M_1\right] + k_{p12}\left[M_1^*\right]\left[M_2\right]} = \frac{r_1\left[M_1\right]}{r_1\left[M_1\right] + \left[M_2\right]} \tag{6.33}$$

Similarly, the probabilities P_{12}, P_{21}, and P_{22} for forming the dyads, M_1M_2, M_2M_1, and M_2M_2, respectively, are given by

$$P_{12} = \frac{\left[M_2\right]}{r_1\left[M_1\right] + \left[M_2\right]} \tag{6.34}$$

$$P_{21} = \frac{\left[M_1\right]}{r_2\left[M_2\right] + \left[M_1\right]} \tag{6.35}$$

$$P_{22} = \frac{r_2\left[M_2\right]}{r_2\left[M_2\right] + \left[M_1\right]} \tag{6.36}$$

The number-average sequence length of monomer M_1, in a way that is completely analogous to the definition of number-average molecular weight, is

$$\bar{n}_1 = \sum_{x=1}^{\infty} x\left(N_1\right)_x = \left(N_1\right)_1 + 2\left(N_1\right)_2 + 3\left(N_1\right)_3 + \mathrm{L} \tag{6.37}$$

where $\left(N_1\right)_x$ is the mole fraction of a sequence of monomer 1 units of length x. $\left(N_1\right)_x$ is the probability of forming such a sequence and is defined as

$$\left(N_1\right)_x = \left(P_{11}\right)^{(x-1)} P_{12} \tag{6.38}$$

Similarly, for sequences of monomer 2, we have

$$\left(N_2\right)_x = \left(P_{22}\right)^{(x-1)} P_{21} \tag{6.39}$$

Equations 6.38 and 6.39 enable one to calculate the distribution of different sequence lengths for each monomer.

The fractions of triad sequences, A_{ijk}, are related by the probability functions, P_{ij}, as shown below [128]:

$$A_{iii} = \left(P_{ii}\right)^2 = \left(\frac{r_{ij} f_i}{f_i + r_{ij} f_i}\right)^2 \tag{6.40}$$

$$A_{jij} = \left(P_{ij}\right)^2 = \left(\frac{f_j}{f_j + r_{ij} f_i}\right)^2 \neq P_{ji} P_{ij} \tag{6.41}$$

$$A_{iij} = A_{jii} = P_{ii} P_{ij} = \frac{r_{ji} f_i f_j}{\left(f_i + r_{ij} f_i\right)^2} \tag{6.42}$$

As mentioned earlier, these sequence distributions can be used to derive the copolymer composition equation. Furthermore, employing experimental triad distribution data, one can also calculate the reactivity ratios [119]. The measurement of triad and dyad sequences is largely accomplished via ^{1}H and ^{13}C NMR spectroscopy.

6.3.5 Composition Measurement Methods

As alluded to earlier, copolymer composition measurement can be achieved by direct and indirect measurements. In some cases, one can infer the copolymer composition by measuring the amounts of monomers consumed in the process. Alternatively, one can directly measure the composition by sensing the characteristic moieties of the individual monomers bound in the copolymer chains. Several techniques are available for each of the direct or indirect measurement of the copolymer composition.

As an example of an indirect measure, we can consider chromatography, which is a technique for separating a mixture into its individual components for identification and quantification. For copolymer composition, GC is often used due to the volatility of most monomers. The unreacted monomers are thus vaporized at a temperature below 400 °C, detected in the chromatograph, and the polymer composition is thus inferred from the disappearance of the monomers.

Nuclear magnetic resonance (NMR) spectroscopy is a popular direct measurement technique that provides quantitative information about the chemical structure of copolymers. ^{1}H and ^{13}C isotopes are the two commonly employed nuclei, but other isotopes (^{15}N, ^{19}F, ^{19}F, ^{29}Si, and ^{31}P) can be used depending on the comonomers. Other spectroscopic techniques (e.g., infrared, ultraviolet, and Raman spectroscopy) are also used [129–132].

It is worth noting the emergence of several online or in-line composition measurement techniques such as ATR-FTIR and Raman spectroscopy as well as the application of GC and NMR in an online manner [133].

6.3.6 Extensions to Multicomponent Copolymerization

The terminal model for copolymerization can be naturally extended to multicomponent systems involving three or more monomers. Multicomponent copolymerizations find practical application in many commercial processes that involve three to five monomers to impart different properties to the final polymer (e.g., chemical resistance or a certain degree of crosslinking) [134]. There is a classical mathematical development for the terpolymerization or three-monomer case, the Alfrey–Goldfinger equation (Eq. 6.43) [82], and for special cases of this equation when restrictions are imposed on the reactivity ratios of some of the monomer pairs [135–137]; also in addition, the tetrapolymer case has been mathematically analyzed in the literature [83a]. However, as one introduces more monomers, the mathematical manipulation becomes more and more complex and cumbersome. The N-monomer case has been treated using determinants by Walling and Briggs [84] and has been recently reformulated in matrix form [85], more amenable for computational work; this is discussed below.

$$\begin{aligned} F_1 : F_2 : F_3 = {} & \left[M_1\right]\left(\frac{\left[M_1\right]}{r_{31}r_{21}} + \frac{\left[M_2\right]}{r_{21}r_{32}} + \frac{\left[M_3\right]}{r_{31}r_{23}}\right) \\ & \times \left(\left[M_1\right] + \frac{\left[M_2\right]}{r_{12}} + \frac{\left[M_3\right]}{r_{13}}\right) : \\ & \left[M_2\right]\left(\frac{\left[M_1\right]}{r_{12}r_{31}} + \frac{\left[M_2\right]}{r_{12}r_{13}} + \frac{\left[M_3\right]}{r_{32}r_{13}}\right) \\ & \times \left(\frac{\left[M_1\right]}{r_{21}} + \left[M_2\right] + \frac{\left[M_3\right]}{r_{23}}\right) : \\ & \left[M_3\right]\left(\frac{\left[M_1\right]}{r_{31}r_{21}} + \frac{\left[M_2\right]}{r_{23}r_{12}} + \frac{\left[M_3\right]}{r_{13}r_{23}}\right) \\ & \times \left(\frac{\left[M_1\right]}{r_{31}} + \frac{\left[M_2\right]}{r_{32}} + \left[M_3\right]\right) \end{aligned} \tag{6.43}$$

The general mathematical multicomponent approach, based on matrix notation, can be advantageous from the practical point of view for the modeling of this kind of systems [138, 139]. Consider the application of the terminal model to a general multicomponent copolymerization of c comonomers. A general propagation step can be written as follows:

$$R_i + M_j \xrightarrow{k_{pij}} R_j \quad \text{for } i = 1, c; \quad j = 1, c \tag{6.44}$$

Material balances on the propagating chains of type i result in

$$\frac{\mathrm{d}\left[R_i\right]}{\mathrm{d}t} = \sum_{j=1}^{c} k_{\mathrm{p}ji}\left[R_j\right]\left[M_i\right] - \sum_{j=1}^{c} k_{\mathrm{p}ij}\left[R_i\right]\left[M_j\right] \quad i = 1, c \tag{6.45}$$

which by virtue of the application of the QSSA yields:

$$\sum_{j=1}^{c} k_{\mathrm{p}ji}\left[R_j\right]\left[M_i\right] - \sum_{j=1}^{c} k_{\mathrm{p}ij}\left[R_i\right]\left[M_j\right] \quad i = 1, c \tag{6.46}$$

Defining the fraction, p_i, of a type i propagating chain as

$$p_i = \frac{\left[R_i\right]}{\sum_{j=1}^{c}\left[R_j\right]} \quad i = 1, c \tag{6.47}$$

and dividing Equation 6.46 by the product $\sum_{j=1}^{c}\left[R_j\right]\ \sum_{j=1}^{c}\left[M_j\right]$, Equation 6.46 can be written in terms of the dimensionless variables p_i and f_i, yielding

$$\sum_{j=1}^{c} k_{\mathrm{p}ji}\, p_j\, f_i = \sum_{j=1}^{c} k_{\mathrm{p}ij}\, p_i\, f_j \tag{6.48}$$

Considerable simplification of the mathematical treatment is achieved by noting that Equation 6.48 is linear on the p_i, $i = 1, c$ (probabilities of propagating chain types). Out of the c equations in Equation 6.48, only $c-1$ are linearly independent, and so, to solve for the p_i, $i = 1, c$, in terms of the f_i, $i = 1, c$, an additional consistency equation, which can be seen as a dimensionless expression of the mass balance of the propagating chain types directly arising from the definition 6.47, is necessary:

$$\sum_{j=1}^{c} p_j = 1 \tag{6.49}$$

Taking $c - 1$ equations of Equation 6.48, together with Equation 6.49, a linear system of equations can be written in matrix form as follows:

$$\mathbf{Xp} = \mathbf{b} \tag{6.50}$$

where $\mathbf{p}$ is the $c \times 1$ vector of the p_i (distribution of propagating chain types); $\mathbf{b}$ is a $c \times 1$ vector with all terms equal to zero, except for the last one (c-th term), which is unity; and $\mathbf{X}$ is a $c \times c$ matrix having as elements:

$$\begin{aligned} X_{ij} &= k_{\mathrm{p}ji}\, p_i, \quad i = 1, \ldots, c-1; \\ &\quad j = 1, \ldots, c \; i \neq j \\ X_{ii} &= -\sum_{\substack{j=1 \\ j\neq i}}^{c} k_{\mathrm{p}ij}\, f_j, \quad i = 1, \ldots, c-1; \\ X_{cj} &= 1, \quad j = 1, \ldots, c \end{aligned} \tag{6.51}$$

Equation 6.50 is easily solved for $\mathbf{p}$ by matrix inversion as

$$\mathbf{p} = \mathbf{X}^{-1}\mathbf{b} \tag{6.52}$$

Once the distribution of propagating chain types is known, the instantaneous composition of the copolymer is given by

$$F_i = \frac{\dfrac{\mathrm{d}\left[M_i\right]}{\mathrm{d}t}}{\sum_{k=1}^{c}\dfrac{\mathrm{d}\left[M_k\right]}{\mathrm{d}t}} \tag{6.53}$$

which from the mass balances of the monomers can be written as

$$F_i = \frac{\sum_{j=1}^{c} k_{\mathrm{p}ji}\left[R_j\right]\left[M_i\right]}{\sum_{k=1}^{c}\sum_{j=1}^{c} k_{\mathrm{p}jk}\left[R_j\right]\left[M_k\right]} \tag{6.54}$$

or dividing the numerator and the denominator by the product of the total radical and the total monomer concentrations, the result is

$$F_i = \frac{\sum_{j=1}^{c} k_{\mathrm{p}ji}\, p_j\, f_i}{\sum_{k=1}^{c}\sum_{j=1}^{c} k_{\mathrm{p}jk}\, p_j\, f_k} \tag{6.55}$$

The application of Equation 6.52, followed by Equation 6.55, provides the instantaneous multicomponent copolymer composition under the terminal model and it is especially useful in the framework of mathematical modeling involving kinetic calculations (conversion − time) since, in this case, explicit p_i values are required (see the pseudokinetic [140] or pseudo-homopolymer approach [138] for kinetic calculations in Chapter 12). A drawback of this approach with respect, for example, to the copolymerization (two monomers) or the Alfrey–Goldfinger (three monomers) equations, is that in this case explicit values for all the homopropagation and cross-propagation kinetic constants are required, instead of reactivity ratios only. Often, however, only the composition behavior of a system in terms of reactivity ratios is required, since the values of the homopropagation kinetic constants is unknown or unreliable. Recently, a matrix approach, similar to that used in Equations 6.50–6.52, has been proposed that provides the composition behavior for N-monomers based only on reactivity ratios [85]; this represents a more efficient formulation than the original work of Walling and Briggs [84], which is of little practical use.

In another extension for copolymerizations involving several monomers, Tobita has studied the full multivariate distribution of chain length and compositions for multicomponent free radical polymerization by using generating functions [141, 142].

6.4 REACTION CONDITIONS: CONSIDERATIONS

These effects are dependent on the type of mechanism: radical, anionic, and cationic. The treatment here is restricted to radical copolymerizations; see Chapters 7 and 8 for a discussion of the anionic and cationic polymerization cases.

6.4.1 Copolymerization Rate

Unlike the copolymer composition, the rate of copolymerization depends on initiation and termination, as well as on propagation. In a way similar to the modeling of homopolymerizations, one must take into account that the termination and, at higher conversions, initiation and propagation are diffusion controlled to properly model the gel effect. In addition, one must consider the various alternative models for propagation and termination (e.g., terminal vs penultimate; inclusion of depropagation). For multicomponent polymerizations, the use of the pseudokinetic rate constant method for modeling the rate is highly effective [143–145].

Using terminal model kinetics as an example, the propagation equations for copolymerization are as follows:

$$R^g_{r,i} + M_j \xrightarrow{k_{pij}} R^g_{r+1,ij} \tag{6.56}$$

where $R^g_{r,i}$ is a radical of chain length r ending in monomer i, and k_{pij} is the rate parameter for the addition of monomer j to a radical ending in monomer i. In other words, the forward rate of reaction of a growing polymer chain is assumed to depend only on the type of monomer on the chain that bears a free radical. According to the pseudokinetic rate constant method, it is useful to define overall rate parameters. The overall propagation pseudokinetic rate parameter for an N-component polymerization can be defined as [143]

$$k_{po} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{pij}\varphi_i f_j \tag{6.57}$$

For a copolymerization reaction, the φ_i values are as follows:

$$\varphi_1 = \frac{k_{p21} f_1}{k_{p21} f_1 + k_{p12} f_2} \tag{6.58}$$

$$\varphi_2 = 1 - \varphi_1 = \frac{k_{p12} f_2}{k_{p21} f_1 + k_{p12} f_2} \tag{6.59}$$

The overall termination pseudokinetic rate parameter may be defined as

$$k_{to} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{toij}\varphi_i\varphi_j \tag{6.60}$$

The cross-termination rate constant can be defined, for example, as a function of the instantaneous copolymer composition, F_i, or other alternative models can be invoked [144]:

$$k_{toij} = k_{toi} F_i + k_{toj} F_j \tag{6.61}$$

Diffusion-control models can be invoked for the individual rate parameters using, for example, the free volume theory [144, 145].

Similarly, all other rate parameters may be defined using the pseudokinetic approach. For example, the overall chain transfer to CTA (Chain Transfer Agent) pseudokinetic rate parameter is calculated as

$$k_{fcta} = \sum_{j=1}^{N} k_{fctaj}\varphi_j \tag{6.62}$$

where k_{fctaj} is the rate parameter for the transfer of a growing radical to chain transfer agent j. An overall pseudokinetic rate parameter for transfer to monomer is calculated as

$$k_{fm} = \sum_{i=1}^{N}\sum_{j=1}^{N} k_{fmij}\varphi_i f_j \tag{6.63}$$

where k_{fmij} is the rate parameter for the transfer of a radical to monomer i from a radical ending in monomer j.

When depropagation effects are ignored, polymerization rates for individual monomer species are defined as

$$R_{pj} = \left(\frac{R_I}{2\bar{k}_t}\right)^{1/2} [M]\, f_j \sum_{j=1}^{N} k_{pij}\varphi_i \tag{6.64}$$

where R_I is the rate of initiation. The overall rate of polymerization, R_{po}, can be obtained as the sum of the rates of polymerization of the individual species, or as

$$R_{po} = \left(\frac{R_I}{2\bar{k}_t}\right)^{1/2} [M]\, k_{po} \tag{6.65}$$

6.4.2 Effect of Temperature

Many industrial scale polymerization reactions are carried out at relatively low temperatures (20–80 °C). Not surprisingly, most of the published research has focused on studying copolymerization reactions in this lower temperature

range. However, there is significant interest in copolymerization at elevated temperatures (80–160 °C). This interest relates to frequent excursions into higher temperature ranges that often occur during industrial scale polymerizations due to poor heat transfer [146, 147], and since higher temperature stages at the end of the polymerization are often used to consume any residual monomers or initiators [148]. The higher temperature operation can provide benefits such as higher reaction rates and lower viscosity (and thus better mixing and heat transfer). There are some drawbacks including the presence of unwanted side reactions and perhaps, significant depropagation.

Copolymerization reactivity ratios are often considered to be more or less temperature invariant, but this is strictly true only over moderate temperature ranges. Considering the reactivity ratios in terms of their homopropagation and cross-propagation rate constants, one can express their temperature dependence using an Arrhenius-type equation:

$$r_1 = \frac{k_{p11}}{k_{p12}} = \frac{A_{11}}{A_{12}} \exp\left(-\frac{E_{11} - E_{12}}{RT}\right) \tag{6.66}$$

$$r_2 = \frac{k_{p22}}{k_{p21}} = \frac{A_{22}}{A_{21}} \exp\left(-\frac{E_{22} - E_{21}}{RT}\right) \tag{6.67}$$

k_{pij} is the rate constant for the addition of monomer j to a growing polymer chain on which the active radical center is located on a monomer i unit. A_{ij} and E_{ij} are the frequency factors and activation energies for the propagation reactions, respectively. Normally, the activation energies for the homopropagation and corresponding cross-propagations are similar (the difference has been reported to be less than 10 kJ/mol for several monomer pairs [32]); thus, the reactivity ratios depend only weakly on temperature. However, if the reaction temperature differs greatly from the conditions used to estimate the reactivity ratios, say, by 20 °C or more, significant changes to the reactivity ratios can result. Thus, any attempts to rely on these parameters in a model may seriously compromise the predictions unless their temperature dependence is accounted for.

As mentioned above, when operating at elevated temperatures, depropagation or depolymerization may become significant. This will occur when the reaction temperature is in the vicinity of the ceiling temperature of the system [149]. Fortunately, for most systems, the ceiling temperatures are far beyond the range of conventional polymerization temperatures and, thus, have little or no effect on the reaction kinetics. However, in light of the interest in higher temperature reactions for the reasons noted above, the depropagation reaction may be of significance and may affect the reaction kinetics. For example, poly(MMA) has a ceiling temperature near 220 °C and its reaction kinetics may begin to exhibit depropagation effects at elevated temperatures. This has been demonstrated even in the copolymerization of butyl acrylate and MMA [150].

Should depropagation become significant, the Mayo–Lewis equation would fail to adequately describe the copolymerization kinetics and one could detect the importance of depropagation by verifying the adequacy of the Arrhenius equations (Eqs. 6.66 and 6.67) to represent the reactivity ratio data. In other words, a plot of the reactivity ratios versus temperature should result in a straight line fit and failure to do so would constitute evidence of significant depropagation effects. The models proposed by Wittmer [151], and later modified by Kruger et al. [96], have been shown useful in modeling copolymerizations with a depropagating monomer. Examples with the copolymerization of α-methylstyrene, a monomer with a low ceiling temperature, and MMA have been published (93a, 150, 152).

6.4.3 Reaction Medium

Several reviews have been published on the effect of solvent in copolymerization [153–156]. Given the radical-mediated mechanism involved, in early studies on radical copolymerization the solvent was expected to have little effect on the reactivity ratios in these systems [157]; however, there are many instances in which this is not true. This early concept may have been supported by the difficulty of distinguishing variations in reactivity ratios due to experimental uncertainties of the associated measurements. Actually, this matter is still a factor to take into account when analyzing differences in reactivity ratios.

Despite the experimental difficulties, it has been established that for systems in which one of the comonomers is ionizable or forms hydrogen bonds, for example, methacrylic acid–MMA, the solvent has a decisive effect that can even change the nature of the copolymerization (alternating or ideal) [24]. Reactivity ratios of nonprotic monomers, such as styrene, MMA, or vinyl acetate, show only a slight solvent effect, but the cause is still unknown [24].

Harwood [158] has proposed that the solvent may influence the way the polymer chains are solvated with monomers, suggesting that the relative concentration of monomers surrounding the active chain end may be different than their global relative concentrations (bootstrap effect). This can be expressed in terms of a partition coefficient:

$$K = \frac{[M_1]_v/[M_2]_v}{[M_1]/[M_2]} \tag{6.68}$$

where $[M_i]_v$ are the monomer concentrations in the vicinity of the reactive chain end and $[M_i]$ are the global monomer concentrations. This may explain the observed effects of

solvents on the reactivity ratios. Mounting experimental evidence consistent with this theory is being accumulated [159–161].

On the other hand, when dealing with heterogeneous systems (e.g., suspension or emulsion polymerizations), it is important not to confuse thermodynamic effects of monomer partitioning among phases with variations in reactivity ratios. For the calculation of these, the concentrations of the monomers at the reaction site should be considered (at the particles) instead of global concentrations in the system.

6.4.4 Effect of Pressure

The analysis for the effect of pressure is similar to that for the temperature effect. When the pressure is taken into account, Equation 6.69 becomes

$$r_1 = \frac{k_{p11}}{k_{p12}} = \frac{A_{11}}{A_{12}} \exp \times \left[-\frac{(E_{11} - E_{12}) + (\Delta V_{11} - \Delta V_{12}) P}{RT} \right] \tag{6.69}$$

where ΔV_{ij} are the activation volumes for the propagation of a radical type i with monomer j. Activation volumes are usually low, but their effect is magnified at high pressures. On the other hand, the pressure effect will be somehow attenuated for the reactivity ratio since it will be proportional to the difference $(\Delta V_{11} - \Delta V_{12})$ only.

The influence of pressure and temperature on activity, monomer content, molar masses, and glass-transition temperatures of copolymers has been assessed [162].

6.4.5 Achieving Uniform Copolymer Composition

More often than not, reactivity differs from monomer to monomer. This is evident when the reactivity ratios differ from a value of one. Thus, if one is operating at concentrations other than the azeotropic composition, batch copolymerization will result in a changing copolymer composition throughout the reaction. For example, a copolymerization with $r_1 > 1$ and $r_2 < 1$ would result in the instantaneous copolymer composition decreasing in monomer 1 as monomer conversion increases. The degree of compositional drift that leads to a heterogeneous copolymer composition depends on the ratio of reactivity ratios (r_1/r_2), where heterogeneity increases with r_1/r_2, the initial monomer composition (f_{10}) and monomer conversion (x). Compositional heterogeneity usually leads to inferior properties, especially optical, rheological, and strength properties. As a result, industrial semibatch processes have been developed to reduce composition drift [163]. One should keep in mind, however, that in certain instances heterogeneous compositions may be desired [164–166]. In the latter case, one may still wish to control the composition to achieve the desired heterogeneity.

Two basic monomer feed policies employed in a semibatch copolymerization can be used to minimize composition drift [163]. Many highly effective commercial processes are based on one or a combination of these policies. Additional promising derivations of these policies have also been presented [167–173]. Henceforth, we refer to the two basic feed policies as Policy I and Policy II, as described in following sections.

6.4.5.1 Policy I Using the copolymer composition equation (Eq. 6.11), we first calculate the desired monomer feed composition (F_1) to achieve the desired copolymer composition (F_1). All of the less reactive monomer and sufficient of the more reactive monomer to achieve the desired F_1 are added to the reactor initially. Thereafter, the more reactive monomer is fed to the reactor at a time-varying feed rate to maintain the molar ratio of monomer 1 to monomer 2 (N_1/N_2 where N_i is the number of moles of monomer i) in the reactor constant. Thus, F_1 remains constant and, consequently, F_1 also remains unchanged.

6.4.5.2 Policy II As for Policy I, we use the desired F_1 in Equation 6.11 to calculate the desired F_1. A "heel" or an initial reactor charge of monomers 1 and 2 at a concentration level equivalent to the desired F_1 is added to the reactor initially. Thereafter, monomers 1 and 2 are fed to the reactor with time-varying feed rates to maintain the monomer concentrations ($[M_1]$ and $[M_2]$) and F_1 constant with time. With feed Policy II, a batch finishing step is required if the residual monomer is beyond acceptable levels. During this final step, some composition drift is likely to occur but will typically be small and probably tolerable from a quality point of view given that it will occur during the final stages of polymerization.

To produce a copolymer with a homogeneous composition in a semibatch process, the following equations should be solved:

$$\frac{dN_1}{dt} = -N_1 \left(k_{p11}\phi_1 + k_{p21}\phi_2\right)\left[P^g\right] + F_{1,in} \tag{6.70}$$

$$\frac{dN_2}{dt} = -N_2 \left(k_{p12}\phi_1 + k_{p22}\phi_2\right)\left[P^g\right] + F_{2,in} \tag{6.71}$$

$$\frac{dV}{dt} = \frac{F_{1,in}MW_1}{\rho_{m1}} + \frac{F_{2,in}MW_2}{\rho_{m2}} - \left[R_{p1}MW_1\left(\frac{1}{\rho_{m1}} - \frac{1}{\rho_p}\right) + R_{p2}MW_2\left(\frac{1}{\rho_{m2}} - \frac{1}{\rho_p}\right)\right] V \tag{6.72}$$

with initial conditions

$$t = 0, \quad N_1 = N_{10}, \quad N_2 = N_{20}, \quad V = V_0 \tag{6.73}$$

For a binary copolymerization,

$$\phi_1 = \frac{\left[P_1^g\right]}{\left[P^g\right]} = \frac{k_{\mathrm{p}21} f_1}{k_{21} f_1 + k_{\mathrm{p}12} f_2} \tag{6.74}$$

In Equations 6.70–6.74, $k_{\mathrm{p}ij}$ is the propagation rate coefficient for the addition of monomer j to a growing polymer radical ending in monomer i, ϕ_i is the mole fraction of radicals ending in monomer i, $[P^g]$ is the total concentration of radicals in the reactor, $F_{i,\mathrm{in}}$ is the time-varying feed rate of monomer i to the semibatch reactor, V is the reactor volume, MW_i is the molecular weight of monomer i, $R_{\mathrm{p}i}$ is the rate of polymerization of monomer i, and $\rho_{\mathrm{m}i}$ and ρ_{p} are the densities of monomer i and the polymer, respectively.

According to the definition of Policy I,

$$F_{2,\mathrm{in}} = 0 \quad \text{and} \quad \frac{\mathrm{d}\left({}^{N_1}/_{N_2}\right)}{\mathrm{d}t} = 0 \tag{6.75}$$

and for Policy II,

$$\frac{\mathrm{d}\left[M_1\right]}{\mathrm{d}t} = \frac{\mathrm{d}\left[M_2\right]}{\mathrm{d}t} = 0 \tag{6.76}$$

Since both F_1 and F_1 are constant, ϕ_1 is also constant. Given that the total polymer radical concentration ($[P^{\cdot}]$) varies during the reaction, one can readily solve for the time-varying monomer feed rates, $F_{1,\mathrm{in}}$ and $F_{2,\mathrm{in}}$, using Equations 6.70–6.76.

The practical implementation of the above policies is not necessarily as straightforward as solving the above equations. As can be deduced from Equations 6.70–6.76, $F_{i,\mathrm{in}}$ is a function of the propagation rate coefficients, the monomer concentrations, and most importantly, the total radical concentration. Hence, to precalculate the optimal monomer feed rates, the radical concentration must be specified in advance and kept constant via an initiator feed policy and/or a heat production policy. This is especially important considering that a constant radical concentration is not a typical polymer production reality. This raises the notion that one could increase the reactor temperature or the initiator concentration over time to manipulate the radical concentration rather than manipulate the monomer feed flowrates, that is, keep $F_{i,\mathrm{in}}$ constant for simpler pump operation. Furthermore, these semibatch policies provide the "open-loop" or "off-line" optimal feed rates required to produce a constant composition product. The "online" or "closed-loop" implementation of these policies necessitates a consideration of online sensors for monomer and polymer composition and polymer reactor control methodologies. The use of process control methodologies would permit adjustment for uncontrolled variations in monomer feed rates, the presence of impurities, and other disturbances to the total radical concentration. Finally, but most importantly, we must give consideration to the potential impact of these semibatch feed policies on important polymer properties other than composition.

For the case of Policy I, given the constant monomer ratio, the reaction would proceed in a way similar to a batch reaction. That is, the reaction would commence at a relatively high monomer concentration and proceed with a decrease in overall monomer concentration akin to a batch process. The molecular weight profile and any long-chain branching would therefore be similar to a batch case and would only be of concern toward the end of the reaction.

When operating under semibatch Policy II, common practice is to maintain the reactor contents at low or "starved" monomer concentrations. This provides for relatively straightforward temperature control and overall reactor operation. However, when such low monomer concentrations are used over the duration of the polymerization, the potential for significant long-chain branching and crosslinking exists. The molecular weight profile would, therefore, be radically different from a batch process.

Another practical consideration relates to the use of the semibatch feed policies in emulsion copolymerization. One would need to account for the partitioning of monomers in the different phases as well as the presence of monomer droplets (desired or not) during the particle nucleation and growth stages.

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