

PART III

POLYMERIZATION PROCESSES AND ENGINEERING

POLYMER REACTION ENGINEERING

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12.1 INTRODUCTION

If a definition of polymer reaction engineering (PRE) was sought, a good approach would be to use the definition of chemical engineering [1], but applied to large macromolecules, instead of small molecules. Therefore, one may state that PRE is the branch of engineering that deals with the technology of large-scale *polymer* production and the manufacture of *polymer* products through *polymerization* processes. PRE is a broad and multidisciplinary area, relatively young and developing fast, which combines polymer science, chemistry, and technology with principles of process engineering [2].

The practical history of PRE started and evolved during the first half of the twentieth century as the everyday effort of the industrial pioneers in charge of polymer production facilities to keep businesses running: polymer chemists with little or no training in chemical engineering, or chemical engineers with little or no training in polymer science. From the scientific/academic perspective, once Staudinger's concept of polymer molecules had been accepted, progress accelerated in all areas of polymer science.

The 1930s were rich with theoretical findings in polymer science and engineering and with the commercial production of several new polymers. These investigations would transform our understanding of polymer manufacture and culminate in the development of several continuous polymerization processes and the establishment of PRE as a new area of research in the 1940s [3]. The period from 1950 to 1990 saw the continued growth and evolution of process technologies, largely stimulated by the combination of PRE principles with the fundamental understanding of polymerization kinetics developed in the earlier years [3].

It is roughly in the last 30–40 years that PRE has become a scientific discipline of its own, thanks to “forerunners” such as Böhm, Hamielec [4], Ray, Reichert, and Sinn [5]. It would take a single book to revisit the history and development of PRE. Instead, the interested reader is referred to a few selective yet representative reviews or editorial papers [2–13]. The importance of this area can also be sensed and monitored by following the contents of the dedicated journals to PRE [*Polymer Reaction Engineering* [14], from 1992 to 2003, the *Macromolecular Reaction Engineering* regular section in *Macromolecular Materials & Engineering* [15], from 2004 to 2006, and *Macromolecular Reaction Engineering* [16], from 2007 to present], and two major international conferences (the *International Workshop on Polymer Reaction Engineering*, usually held in Germany and organized by DECHEMA every three years and the conference series “*Polymer Reaction Engineering*,” organized by Engineering Conferences International (ECI), usually held in North America, also every three years, but one year apart from each other). At present, PRE research can be classified in process-oriented, product-oriented, and enabling research (which comprises kinetics, thermodynamics, process observation and control, modeling, and simulation tools) [5]. However, different classifications can be proposed, the bottom line being that every new key discovery in any area of polymer science (e.g., nanomaterials, biomaterials, green and sustainable processes, etc.) will need the application of PRE principles to turn it into a useful commercial application.

In this chapter, we do not cover all the topics studied in PRE. Instead, we provide some basic background sometimes overlooked in the PRE literature, a very useful collection of tips on PRE and modeling, and some

samples of polymerization schemes and the resulting kinetic equations, which are the bases of much of the research published in PRE. The reader will recognize the relationship and connections between this chapter and other chapters from this handbook (e.g., Chapters 6, 9, 13, and 15).

12.2 MATHEMATICAL MODELING OF POLYMERIZATION PROCESSES

12.2.1 Chemical Reactor Modeling Background

Polymerization reactors are a specific kind of chemical reactors in which polymerization reactions take place; therefore, in principle, they can be analyzed following the same general rules applicable to any other chemical reactor. The basic components of a mathematical model for a chemical reactor are a reactor model and rate expressions for the chemical species that participate in the reactions. If the system is homogeneous (only one phase), these two basic components are pretty much what is needed; on the other hand, for heterogeneous systems formed by several phases (emulsion or suspension polymerizations, systems with gaseous monomers, slurry reactors or fluidized bed reactors with solid catalysts, etc.), additional transport and/or thermodynamic models may be necessary to build a realistic mathematical representation of the system. In this section, to illustrate the basic principles and components needed, we restrict ourselves to the simplest case, that of homogeneous reactors; in other sections, additional components and more complex cases are discussed.

The rate expressions will be ideally derived from our knowledge of the reaction or kinetic mechanism. If this is not available, then empirical expressions obtained from experimentation will have to be used. Several techniques have been developed by statisticians and/or chemical engineers to find adequate rate expressions from experimental data. Fortunately, in the polymerization field, there is a good level of knowledge of the reaction mechanism for the most common polymerization chemistries: polycondensation, free radical, ionic coordination, etc.; therefore, whenever possible, to derive rate expressions, it is recommended to start from the accepted reaction mechanism for the type of polymerization of interest.

Reaction mechanisms consist of a set of so-called elementary reactions that describe the chemical steps that occur at the molecular level. Once a kinetic mechanism is postulated, all the relevant chemical species should be listed: these will be those that participate as reactants and/or products in at least one of the elementary reactions of the mechanism. Note that intermediate species, not appearing as reactants entering the reactor or products leaving it in the global reaction stoichiometry, are often relevant chemical species that must be considered (such as growing radicals or ionic propagating species).

For each of the chemical species participating in the mechanism, a mass balance equation must be written. The appropriate form of the mass balance for the specific type of reactor at hand must be used. Two of the most common types of reactors used in industry are the CSTR (continuous stirred tank reactor) and the tubular reactor. The corresponding mathematical models for their idealized forms, based on transport phenomena equations and available in any standard chemical reactor text [17, 18], are the ideal CSTR and the ideal model for the plug flow tubular reactor (PFR). The ideal CSTR model is given by Equation 12.1:¹

$$\frac{dM_i}{dt} = W_{i,\text{in}} - W_{i,\text{out}} + R_i, \quad i = 1, 2, \dots, n \quad (12.1)$$

where M_i is the instantaneous value of mass of species i in the reactor, expressed in moles; $W_{i,\text{in}}$ and $W_{i,\text{out}}$ are the molar flows of species i at the reactor entrance and exit, respectively; and R_i represents the reaction rate expressions for production of species i by elementary chemical reactions in molar units.

While for a CSTR it is possible to apply a macroscopic mass balance, since the spatial distribution of the species inside the reactor is assumed uniform, for a PFR this is not applicable and it is necessary to resort to a microscopic [19] (or differential) mass balance, in which axial diffusion of the chemical species is neglected. Assuming constant density, the following balance equation is obtained for a species A in the PFR:

$$\frac{\partial[A]}{\partial t} + v \frac{\partial[A]}{\partial z} = R_A \quad (12.2)$$

where $[A]$ is the molar concentration of species A , v is the velocity of the stream throughout the reactor, and z is the axis parallel to the reactor length.

Note that because of the microscopic nature of the balance in Equation 12.2, an intensive variable (concentration) must be used in this case, instead of absolute moles. Equations 12.1 and 12.2 are given for the more general non-steady-state operation (including start-ups or grade changes). The steady-state operation is a particular case of these general equations and can be obtained making the time derivative equal to zero in the corresponding equation.

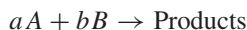
The simplest reactor type, in which only non-steady-state operation is possible, is the batch reactor, for which the mass balance is simply given by

$$\frac{d[A]}{dt} = R_A \quad (12.3)$$

¹In writing the term R_i it has been supposed that the units are mole per unit time. It is customary that the rate expression is given per volume unit; in that case this term must be multiplied by the volume of reaction.

A beaker used at the laboratory level by the synthetic polymer chemist corresponds to this reactor type.

Once the mass balances for each chemical species are written using the corresponding reactor type model, it is necessary to write an explicit expression for the reaction rate (production and consumption) of each chemical species R_i . This is done by the application of the mass action law. This law, in one of its versions, establishes that for an elementary reaction



the reaction rate is given by

$$R_A = k[A]^a[B]^b \quad (12.4)$$

where k is the kinetic rate coefficient or rate constant (temperature and pressure dependent), and $[A]$ and $[B]$ are the molar concentrations of A and B , respectively.

12.2.2 The Method of Moments

To explain this technique, let us consider as an illustration a simple kinetic model for free radical polymerization, which contains only a subset of the possible reactions in these systems (Table 12.1). The application of the technique to a batch reactor, which is the simplest one, will be used to illustrate the method; extension to other reactor types is straightforward.

Mass balances for a batch reactor yield the following equations:

$$\frac{dI}{dt} = -k_d I \quad (12.5)$$

$$\frac{dR}{dt} = 2fk_d I - k_i \frac{RM}{V} \quad (12.6)$$

$$\frac{dM}{dt} = \frac{-\left(k_p M \sum_{n=1}^{\infty} P_n + k_i RM\right)}{V} \quad (12.7)$$

where P , the zeroth moment of the live polymer, is defined as

$$P = \sum_{n=1}^{\infty} P_n \quad (12.8)$$

The equations for indexed variables (live and dead polymer) result in

$$\frac{dP_1}{dt} = \frac{\left(k_i RM - k_t P_1 \sum_{i=1}^{\infty} P_i - k_p P_1 M\right)}{V} \quad (12.9)$$

$$\frac{dP_n}{dt} = \frac{\left(k_p P_{n-1} M - k_t P_n \sum_{i=1}^{\infty} P_i - k_p P_n M\right)}{V}, \quad n > 1 \quad (12.10)$$

$$\frac{dD_n}{dt} = \frac{\left(k_{td} P_n \sum_{i=1}^{\infty} P_i\right)}{V}, \quad n \geq 1 \quad (12.11)$$

To apply the method of moments, the definitions of the K th moments of the chain length distributions (CLDs) for live and dead polymer, respectively, are invoked:

$$\mu_K = \sum_{i=1}^{\infty} i^K P_i, \quad \lambda_K = \sum_{i=1}^{\infty} i^K D_i \quad (12.12)$$

From the first moments of the CLD, it is possible to calculate the number and weight-average molecular weight as follows.

$$\bar{M}_n = \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} W_m \quad (12.13)$$

$$\bar{M}_w = \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1} W_m \quad (12.14)$$

where W_m is the molecular weight of the monomeric unit. The method of moments converts the system of Equations 12.8, 12.9 and 12.10 into a finite dimension system in which, instead of describing the full CLD (equivalent to the molecular weight distribution, MWD, if Equation 12.12 is defined in terms of molar mass M_i , instead of chain length i), equations for the moments (0, 1, 2, ...) are obtained. It is sufficient to calculate the first few moments of these distributions to obtain average molecular weights. To apply the method of moments, the following steps must be performed:

1. Multiplication of the equation for the species “ n ” of each polymer distribution by n^K ($n = 1, 2, \dots, \infty$).
2. For each distribution (live and dead polymer in this case), summation of the equations resulting from the first step, varying n from 1 to infinity.

To illustrate the technique, the method is applied to Equations 12.9 and 12.10 (live polymer CLD) and Equation 12.11 (dead polymer CLD). By applying steps 1 and 2, the result is, for live polymer:

$$\sum_{n=1}^{\infty} n^K \frac{dP_n}{dt} = \frac{d \sum_{n=1}^{\infty} n^K P_n}{dt} = \frac{k_i RM}{V} + k_p M \sum_{n=2}^{\infty} n^K \frac{P_{n-1}}{V} - k_p M \sum_{n=1}^{\infty} n^K \frac{P_n}{V} - k_{td} P \sum_{i=1}^{\infty} n^K \frac{P_n}{V} \quad (12.15)$$

TABLE 12.1 Simple Kinetic Mechanism for Free Radical Polymerization

Reaction Step	Kinetic Expression
Initiator decomposition	$I \xrightarrow{k_d} 2R$
First propagation	$R + M \xrightarrow{k_i} P_1$
Propagation	$P_n + M \xrightarrow{k_p} P_{n+1} \quad n = 1, \dots, \infty$
Termination by disproportionation	$P_n + P_m \xrightarrow{k_{td}} D_n + D_m \quad n, m = 1, \dots, \infty$

I is initiator; M , the monomer; R , the primary radicals; P_n , the living polymer of length n ; and D_m , the dead polymer of length m . (Note that it is also customary in the PRE literature to denote primary radicals as R_{in} or R_0 , living polymer as R_n^\bullet and dead polymer as P_m).

which can subsequently be written as

$$\frac{d\mu_K}{dt} = \frac{k_i RM}{V} + k_p M \sum_{n=2}^{\infty} n^K \frac{P_{n-1}}{V} - k_p \frac{M\mu_K}{V} - k_{td} \frac{\mu_0 \mu_K}{V},$$

$$K = 0, 1, 2, \dots \quad (12.16)$$

where the identity $\mu_0 = P = \sum_{n=1}^{\infty} P_n$ has been used. To write the second term on the right-hand side in terms of moments, a change of variable for the length subscript m is made, by setting: $m \equiv n - 1$, resulting in

$$\sum_{n=2}^{\infty} n^K P_{n-1} = \sum_{m=1}^{\infty} (m+1)^K P_m = \sum_{m=1}^{\infty} (m+1)^K P_m \quad (12.17)$$

Using the binomial theorem $(m+1)^K = \sum_{R=0}^K \binom{K}{R} m^{K-R}$ where the binomial coefficients are defined as

$$\binom{K}{R} = \frac{K!}{R!(K-R)!} \quad (12.18)$$

Equation 12.17 turns into Equation 12.19:

$$\begin{aligned} \sum_{n=1}^{\infty} n^K P_{n-1} &= \sum_{m=1}^{\infty} \sum_{R=0}^K \binom{K}{R} m^{K-R} P_m \\ &= \sum_{R=0}^K \sum_{m=1}^{\infty} \binom{K}{R} m^{K-R} P_m \\ &= \sum_{R=0}^K \mu_{K-R} \end{aligned} \quad (12.19)$$

Substituting this result into Equation 12.16, the final expression becomes

$$\frac{d\mu_K}{dt} = k_i \frac{RM}{V} + k_p M \sum_{R=0}^K \binom{K}{R} \frac{\mu_{K-R}}{V} - k_p M \frac{\mu_K}{V} - k_{td} \frac{\mu_0 \mu_K}{V}, \quad K = 0, 1, 2, \dots \quad (12.20)$$

Applying the technique to Equation 12.11 for the dead polymer CLD, the result is

$$\sum_{n=1}^{\infty} n^K \frac{dD_n}{dt} = \frac{d \sum_{n=1}^{\infty} n^K D_n}{dt} = k_{td} P \sum_{i=1}^{\infty} n^K \frac{P_n}{V} \quad (12.21)$$

which is equivalent to

$$\frac{d\lambda_K}{dt} = k_{td} \frac{\mu_0 \mu_K}{V}, \quad K = 0, 1, 2, \dots \quad (12.22)$$

Expansion of the binomial coefficients in Equation 12 allows the derivation of one equation for each of the K th moments. The integration of Equations 12.20 and 12.22 for as many moments as required (usually the first three) yields information on the evolution of the CLD (or the associated MWD) in terms of its averages.

12.2.3 Bivariate Distributions

In some cases, it is necessary to use more than one subscript for the description of distributions in polymerization systems. One of such cases is the modeling of the bivariate distribution of chain length and number of branches resulting from polymerizations involving branched polymers. The extension of the method of moments to bivariate distributions is straightforward. Let us consider the bivariate distribution of live polymer of length n and number of branches b : $P_{n,b}$, for the sake of illustration of the method of moments, consider only the kinetic steps of propagation and transfer to polymer (see Table 12.2 for the reduced kinetic mechanism).

For a batch reactor, the application of the mass action law considering only these two kinetic steps results in

$$\begin{aligned} \frac{dP_{n,b}}{dt} &= \dots - k_p (P_{n,b} M + P_{n-1,b} M) \\ &\quad - k_{trp} P_{n,b} \left(\sum_{m=1}^{\infty} \sum_{c=0}^{\infty} m D_{m,c} \right) \\ &\quad + k_{trp} n D_{n,b-1} \sum_{h=1}^{\infty} \sum_{e=0}^{\infty} P_{h,c} + \dots, \\ n &= 1, \dots, \infty; \quad b = 0, \dots, \infty \end{aligned} \quad (12.23)$$

TABLE 12.2 Reduced Kinetic Mechanism for Transfer to Polymer

Reaction Step	Kinetic Expression	
Propagation	$P_{n,b} + M \xrightarrow{k_p} P_{n+1,b}$	$n = 1, \dots, \infty \quad b = 0, \dots, \infty$
Transfer to polymer	$P_{n,b} + D_{m,c} \xrightarrow{k_{tp}} D_{n,b} + P_{m,c+1}$	$n, m = 1, \dots, \infty \quad b, c = 0, \dots, \infty$

Note that in the transfer to polymer reaction there are as many possible sites of reaction as monomeric units in the dead polymer chain participating in the reaction.

The bivariate moments for live and dead polymer are defined respectively as follows:

$$\mu_{G,H} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H P_{n,b} \quad (12.24)$$

$$\lambda_{G,H} = \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H D_{n,b} \quad (12.25)$$

From these definitions, the number and weight-average molecular weights, as well as the number average of branches can be written, respectively, as

$$M_n = \frac{\mu_{1,0} + \lambda_{1,0}}{\mu_{0,0} + \lambda_{0,0}} W_m \quad (12.26)$$

$$M_w = \frac{\mu_{2,0} + \lambda_{2,0}}{\mu_{1,0} + \lambda_{1,0}} W_m \quad (12.27)$$

$$B_n = \frac{\mu_{0,1} + \lambda_{0,1}}{\mu_{0,0} + \lambda_{0,0}} \quad (12.28)$$

The application of the method of moments to the live polymer requires the application of the summation operator defined by Equation 12.24 on both sides of Equation 12.23, resulting in

Left-hand side:

$$\sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H \frac{dP_{n,b}}{dt} = \frac{d \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H P_{n,b}}{dt} = \frac{d\mu_{G,H}}{dt} \quad (12.29)$$

Right-hand side:

$$\begin{aligned} \dots - k_p M \mu_{G,H} + k_p M \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H P_{n-1,b} \\ - k_{tp} \mu_{G,H} \lambda_{1,0} + k_{tp} \mu_{0,0} \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^{G+1} b^H D_{n,b-1} + \dots \end{aligned} \quad (12.30)$$

Some of the terms are directly written as a function of moments; for others, some algebraic manipulation is needed. The positive term for propagation can be treated using the change of variable $m \equiv n - 1$, as in the univariate case, resulting in

$$\begin{aligned} \sum_{n=1}^{\infty} \sum_{b=0}^{\infty} n^G b^H P_{n-1,b} &= \sum_{m=1}^{\infty} \sum_{b=0}^{\infty} b^H (m+1)^G P_{m,b} \\ &= \sum_{m=1}^{\infty} \sum_{b=0}^{\infty} \sum_{R=0}^G \binom{G}{R} m^{G-R} b^H P_{m,b} \\ &= \sum_{R=0}^G \binom{G}{R} \mu_{G-R,H} \end{aligned} \quad (12.31)$$

where the binomial theorem has already been applied. A similar change of variable ($r \equiv b - 1$) can be applied to the positive transfer to polymer term. The final result for the moment expression is

$$\begin{aligned} \frac{d\mu_{G,H}}{dt} \dots - k_p M \mu_{G,H} + k_p M \sum_{R=0}^G \binom{G}{R} \mu_{G-R,H} \\ - k_{tp} \mu_{G,H} \lambda_{1,0} + k_{tp} \mu_{0,0} \sum_{K=0}^H \binom{H}{K} \lambda_{G+1,H} + \dots \end{aligned} \quad (12.32)$$

Other kinetic steps can be treated in a similar manner.

12.2.4 Pseudo-Homopolymer Approach or Pseudokinetic Rate Constants Method (PKRCM)

In multimonomer polymerizations, the number of possible reactions increases rapidly with the number of monomers. For example, for the copolymerization of two monomers under the assumption of terminal model kinetics, four propagation steps must be considered (see Eq. 6.1). Similarly, for the termination step (chemically controlled), three reactions are possible:



where D stands for dead polymer and $k_{112} = k_{121}$.

When the MWD is to be modeled, there are two possibilities: (i) One is to use $c + 1$ subscripts for a c comonomer system, one for the radical type, and c for the number of monomer units of each type in the polymer chain. For example, $R_{1,r,m}$ could represent a type 1 radical having “ r ” monomer-1 units and “ m ” monomer-2 units already in the chain. The treatment for any number of monomers using this approach is possible via the method of moments or generating functions [6], but as the number of monomers increases, the algebra becomes more intricate. (ii) The second approach is to use only two subscripts, without regard to the number of monomers involved, one of the subscripts defining the monomer type and the second one defining the total number of units in the chain, regardless of their chemical nature. In this second case, and following the example given before, the quantity to be modeled would be $R_{1,q}$ ($q = r + m$). Although some information on the composition is lost using this approach, simple mass balances on each monomer (which are necessary anyways) can provide the evolution of the average composition with reaction time; the only information lost is the (stochastic) broadening of the composition distribution. Besides, if the chains are long, all the chains formed instantaneously will have similar composition.

The second approach implies that the MWD equations for a multicomponent monomer system are treated as those of a homopolymer. These ideas appeared in the literature under slightly different names but around the same period, when more researchers started studying copolymerization systems (e.g., Ballard et al. [20]). Hamielec’s group formalized this approach under the name of *pseudokinetic rate constants method* (PKRCM) and illustrated its use for linear, branched, and crosslinked copolymerization systems [21], as well as for batch, semibatch, and continuous reactors [22]. Ray’s group also made use of what they referred to as *apparent rate constants* [23]. The group of Morbidelli used a similar idea that they termed as *pseudo-homopolymer* approach [24].

Li et al. [25] validated the use of the PKRCM for the case of MMA/EGDMA (methyl methacrylate) with gelation. Tobita and Hamielec used this method to model gelling systems, at both the pre- and postgelation regimes [26]; they also showed that this method could be used equally well for copolymerization systems described by higher order Markov chain statistics such as the penultimate model [27]. Zabisky et al. used it to model olefin copolymerization in high pressure tubular reactors [28]. Finally, Xie and Hamielec further extensively evaluated the use of the PKRCM for the calculation of molecular weight development in linear [29] and nonlinear (with long-chain branching (LCB) [30]) copolymerization systems. Ever since the PKRCM has become a standard tool in PRE.

In any of the forms mentioned above, the approach requires the use of the long-chain hypothesis (LCH), which assumes that the monomer consumption is essentially due to propagation reactions and the quasisteady-state approximation (QSSA) for radicals, by virtue of which the rates of radical generation and consumption are instantaneously equated. The basis of the pseudo-homopolymer approach is introduced here using as an example of the modeling of the MWD for a multicomponent (c monomers) system, following the terminal model. Table 12.3 lists the kinetic mechanism for this system. In this table, P_i^n stands for polymeric radicals of type i and length n , and D^n is dead polymer of length n .

To describe the MWD for live polymer, mass balances for polymeric radicals are written:

$$\frac{dP_i^1}{dt} = k_i R M_i - P_i^1 \sum_{j=1}^c k_{pji} M_j - P_i^1 \sum_{m=1}^{\infty} \sum_{j=1}^c k_{ij} P_j^m, \quad i = 1, \dots, c \quad (12.34)$$

$$\begin{aligned} \frac{dP_i^n}{dt} &= \sum_{j=1}^c k_{pji} P_j^{n-1} M_i - P_i^n \sum_{j=1}^c k_{pij} M_j \\ &\quad - P_i^n \sum_{m=1}^{\infty} \sum_{j=1}^c k_{ij} P_j^m, \quad i = 1, \dots, c; \\ n &= 2, \dots, \infty \end{aligned} \quad (12.35)$$

Note that in this representation an equation is needed for each type of polymeric radical of a given length. By taking the summation of Equations 12.34 and 12.35 from $n = 1$ to ∞ , using the LCH and the QSSA (the time derivative is set to zero), and the definition $P_i = \sum_{n=1}^{\infty} P_i^n$, the result is

$$\sum_{j=1}^c k_{pji} P_j M_i = \sum_{j=1}^c k_{pij} P_i M_j, \quad i = 1, \dots, c \quad (12.36)$$

TABLE 12.3 Kinetic Mechanism for Molecular Weight Distribution in Multicomponent Copolymerization

Reaction Step	Kinetic Expression	
Initiation	$I \xrightarrow{k_d} 2R$	$i = 1, \dots, c$
	$R + M_i \xrightarrow{k_i} P_i^1$	
Propagation	$P_i^n + M_j \xrightarrow{k_{pij}} P_i^{n+1}$	$i = 1, \dots, c$
		$j = 1, \dots, c$
		$n = 1, \dots, \infty$
Termination	$P_i^n + P_j^m \xrightarrow{k_{ij}} D^{n+m}$	$i = 1, \dots, c$
		$n, m = 1, \dots, \infty$

Using the definition for the fraction of radical types,

$$P_i = \frac{[P_i]}{\sum_{j=1}^c [P_j]} \quad (12.37)$$

dividing Eq. 12.36 by the product $\sum_{j=1}^c [P_j] \sum_{j=1}^c [M_j]$, and expressing it in terms of p_i and f_i (mole fraction of monomer i), Equation 12.38 is finally obtained:

$$\sum_{j=1}^c k_{pji} p_j f_i = \sum_{j=1}^c k_{pij} p_i f_j \quad (12.38)$$

As discussed in Chapter 6 (see discussion of Equation 6.48, Section 6.3.6), only $c - 1$ out of the c equations represented by Equation 12.38 are linearly independent. An additional independent equation for the p_i terms is

$$\sum_{i=1}^c p_i = 1 \quad (12.39)$$

The solution of Equations 12.38 and 12.39 (which is a linear algebraic system for the p_i 's) provides the instantaneous radical-type distribution. Once a procedure to explicitly calculate this distribution has been made available, it is possible to apply the pseudo-homopolymer approach by performing the following steps:

1. By application of the ergodic hypothesis, by which the average radical type over the whole population of growing chains at a given instant is the same as the time average of the radical type of each growing chain, every instance of P_i^n (in Equations 12.34 and 12.35) is replaced by $P^n p_i$ ($n = 1, \dots, \infty$) where $P^n = \sum_{i=1}^c P_i^n$.
2. For each one of Equations 12.34 and 12.35, a summation over $i = 1, \dots, c$ is calculated.

The result on Equations 12.34 and 12.35 is, respectively,

$$\begin{aligned} \frac{dP^1}{dt} &= R \sum_{i=1}^c k_i M_i - P^1 \sum_{j=1}^c \sum_{i=1}^c k_{pij} p_i M_j \\ &\quad - P^1 \sum_{m=1}^{\infty} \sum_{i=1}^c \sum_{j=1}^c k_{ij} p_i p_j P^m \end{aligned} \quad (12.40)$$

$$\begin{aligned} \frac{dP^n}{dt} &= \sum_{i=1}^c \sum_{j=1}^c k_{pji} P^{n-1} p_j M_i - P^n \sum_{i=1}^c \sum_{j=1}^c k_{pij} p_i M_j \\ &\quad - P^n \sum_{m=1}^{\infty} \sum_{i=1}^c \sum_{j=1}^c k_{ij} p_i p_j P^m \end{aligned} \quad (12.41)$$

TABLE 12.4 Pseudokinetic or Apparent Rate Constants

Reaction	Apparent Rate Constant
Initiation	$\bar{k}_i = \sum_{i=1}^c f_i k_i$
Propagation	$\bar{k}_p = \sum_{i=1}^c \sum_{j=1}^c p_i f_j k_{pij}$
Termination	$\bar{k}_t = \sum_{i=1}^c \sum_{j=1}^c p_i p_j k_{ij}$

Finally, replacing M_i by $f_i M$, Equations 12.40 and 12.41 can be written as:

$$\begin{aligned} \frac{dP^1}{dt} &= RM \sum_{i=1}^c k_i f_i - \left(\sum_{j=1}^c \sum_{i=1}^c p_i f_j k_{pij} \right) P^1 M \\ &\quad - \left(\sum_{i=1}^c \sum_{j=1}^c p_i p_j k_{ij} \right) P^1 \sum_{m=1}^{\infty} P^m \end{aligned} \quad (12.42)$$

$$\begin{aligned} \frac{dP^n}{dt} &= \left(\sum_{i=1}^c \sum_{j=1}^c p_j f_i k_{pji} \right) P^{n-1} M \\ &\quad - \left(\sum_{i=1}^c \sum_{j=1}^c p_i f_j k_{pij} \right) P^n M \\ &\quad - \left(\sum_{i=1}^c \sum_{j=1}^c p_i p_j k_{ij} \right) P^n \sum_{m=1}^{\infty} P^m \end{aligned} \quad (12.43)$$

Note that by defining the terms in parenthesis as pseudokinetic or apparent rate constants (Table 12.4) Equations 12.42 and 12.43 are identical to those describing the MWD of the live polymer in a homopolymerization.

12.3 USEFUL TIPS ON POLYMER REACTION ENGINEERING (PRE) AND MODELING

These tips are useful so that one does not use mathematical equations (models) blindly. Almost anybody can write equations for reaction systems, especially these days with the proliferation of computer modeling and other numerical packages and tools. These practical tips will help make the input to and output from these equations more meaningful. Each tip can be considered independently of the others. However, put all of them together and one will see a beautiful "PRE painting." Several hints and food-for-thought questions/points will add more color to the picture. Instead of a title, each tip is related to several key words that provide an overview of the topic(s) covered under the specific tip.

Tip 1: Initiators, initiator data, and initiator decomposition. Several books on polymer science and engineering cite information about commercial initiators (decomposition rate constants, activation energies, and half-lives). It should be noted that these initiator data may not be accurate for a particular monomer–polymer system. Commercial manufacturers usually report initiator decomposition data determined in organic solvents (toluene or benzene). These values are, at best, starting values for certain kinetic parameters. Published initiator decomposition data measured in the specific monomer–polymer environment are very rare, if at all available.

Tip 2: Chain stereoregularity and active sites. In free radical polymerization, polymer chain configuration and MWD are often independent of initiator type and initiation mechanism, depending strongly on reaction temperature, initiation rate, and monomer concentration. One can, therefore, often predict chain stereoregularity and MWD without a detailed knowledge of the initiation mechanism.

This is usually not possible with ionic polymerization. Here, the modes of propagation, transfer, and termination reactions are influenced significantly by the initiation stage. For example, a heterogeneous coordination catalyst has reactive sites with a distribution of activities for propagation and produces a polymer with a very broad MWD. For polymer reactor calculations, it is sufficient to realize that there is a small but finite time for the development of active sites on addition of the ionic catalyst system to the monomer solution. The number of active sites remains relatively constant thereafter, with a slow reduction in number due to some site decay or poisoning. During calculations of polymer production rate (productivity) and molecular weights (quality), the number of active sites is usually introduced as an adjustable parameter in the reactor model.

Tip 3: Radical lifetime. The lifetime of a radical is of the order of 0.1–1 s. How can one calculate/verify this quickly? The number of monomer units added to a radical center per second is simply equal to the product ($k_p[M]$). Consider a typical value for k_p of 500 l/mol/s and a typical $[M]$ of 10 mol/l, yielding 5000 monomer units added to a radical in one second. Hence, a polymer chain with a molecular weight of 500,000 was a polymer radical for about one second, considering a typical molecular weight for a monomer to be 100 g/mol.

Tip 4: Chain microstructure and propagation reactions. Propagation reactions are mainly responsible for the development of polymer chain microstructure (and control chain composition and sequence length distribution in copolymerizations). In free radical polymerization, the stereoregularity of a high molecular weight homopolymer chain depends on polymerization temperature almost exclusively. It is usually independent of initiator type and monomer concentration. Calculations on stereoregularity

are not usually done for reactors producing polymers via radical polymerization. To achieve high degrees of regularity in chain microstructure, one must resort to ionic polymerizations.

Tip 5: Transfer reactions, branching, effects on molecular weight averages, and effects on polymerization rate. During free radical polymerization (in fact, with some slight changes in the mechanism, accordingly, in any chain growth polymerization), transfer reactions may take place between the growing radical and initiator (not often nowadays due to better understanding of the initiator molecule chemistry), monomer (an important reaction), solvent (if the solvent has labile hydrogens or halogens), impurity (often, but equally often neglected), chain transfer agent (CTA, usually the preferred transfer reaction for molecular weight reduction and control), any small molecule present in the polymerizing mixture and polymer (a large molecule). The last reaction essentially “resurrects” the usually “dead” polymer molecules and makes them behave as reactants again. The transfer radical usually reacts rapidly with monomer to generate a new radical.

These transfer reactions, with the exception of transfer to polymer, cause a shift in the MWD of the polymer to lower molecular weights. Transfer to (dead) polymer leads to (trifunctional) branching, causing a shift to higher molecular weights. Transfer to polymer does not change the total number of polymer molecules and hence the number-average molecular weight is unaffected. In contrast, the weight-average molecular weight increases appreciably, thus increasing molecular weight dispersity (polydispersity) as well. The number of labile atoms (hydrogens or chlorines) in a polymer chain is usually equal to the number of monomer units in the chain; therefore, the rate of transfer to polymer will be proportional to the mass of polymer (weight fraction of polymer in the polymerizing mixture) rather than to the number of polymer molecules. Transfer to polymer will be promoted at high conversion levels and will increase with temperature.

Transfer reactions do not change the total number of radicals in the mixture and therefore usually (ideally) do not influence the rate of polymerization (nor copolymer composition). However, there might be indirect effects on the rate (especially in systems with strong diffusional limitations, where a lowering of the rate may be observed with increased concentrations of CTA or solvent). If the transfer radicals have low activity, then retardation may be observed.

Tip 6 (related to Tip 5): Impurities, transfer to monomer, and terminal double bonds. The role of impurities should not be neglected, especially in emulsion/dispersion systems. See the case studies described in Penlidis et al. [31], Chien and Penlidis [32], and Dubé and Penlidis [33], for both homopolymerization and multicomponent polymerization systems, in both bulk/solution and emulsion. Transfer to

monomer is important in controlling the molecular weights of the polymer produced in many commercial polymerizations. The characteristic here is that the monomer radicals obtained from transfer to monomer, on propagation and, eventually, termination, will yield dead polymer chains having a terminal double bond (TDB) (this will have interesting repercussions to be discussed shortly; see Tips 8, 10, and 14).

Tip 7: Glass transition temperature, limiting conversion, methyl methacrylate polymerization, and depropagation. Special conditions are satisfied when the polymerization temperature is below the glass transition point of the polymer being synthesized. With increasing conversion of monomer, a point will be reached where the polymer-in-monomer mixture will become a “glass.” In a glass, even small molecules have low mobility and, for all practical purposes, polymerization rate will tend to zero (for typical polymerization time scales).

Hint 1. Observe conversion versus time data for the bulk polymerization of MMA at 70 °C. At a conversion level of about 90% the polymerization rate will be zero. The conversion versus time curve will “level off.” This will give the “limiting conversion.” The glass transition point (or temperature) of poly(MMA) is in the range of 105–110 °C and apparently a mixture of MMA with poly(MMA) containing 10% monomer has a glass transition point of 70 °C. A mixture containing about 80% poly(MMA) and 20% MMA exhibits a glass transition temperature of about 22.5 °C. One can thus construct a plot of polymerization temperature versus limiting conversion.

Hint 2. An increase in temperature will increase the limiting conversion. Following the MMA polymerization example, polymerizing isothermally at 80 °C will give a limiting conversion about 93%. At 100 °C, the limiting conversion will go up to about 97–98%. If the temperature is 120 °C, the polymerization will almost go to completion, that is, there is no limiting conversion (within experimental error).

Hint 3. We stated in Hint 2, following the MMA polymerization case, that if the polymerization temperature is 120 °C, conversion will “almost” go to completion (no limiting conversion). If temperature keeps on increasing, conversion will become lower. This is not a limiting conversion, but rather an upper “conversion limit” (a thermodynamic equilibrium limit, at that). This conversion limit is related to depropagation reactions (depolymerization). For case studies with depropagation, both in copolymerization and terpolymerization, and with experimental confirmations of mathematical modeling results, see Palmer et al. [34, 35], McManus et al. [36], and Leamen et al. [37, 38].

Food for thought. What temperature does one obtain from a plot of polymerization temperature versus limiting conversion (see Hint 1, Tip 7), if one extrapolate the curve to 100% conversion? In fact, the temperature estimate will

compete in accuracy with any such temperature determination from DSC (differential scanning calorimetry).

Tip 8: Terminal double bond polymerization. Transfer to monomer and termination by disproportionation lead to dead polymer molecules with a TDB. This TDB may react with a polymer radical, thus forming a radical center somewhere along the chain of the combined molecules. This radical center, on propagation with monomer, will eventually form a trifunctionally branched chain.

TDB polymerization reduces the number of dead polymer molecules. Therefore, it causes an increase in both number- and weight-average molecular weights. A practical corollary is that an isothermal batch polymerization yielding a number-average molecular weight that does not change with conversion would rule out the importance of TDB polymerization.

Tip 9: Radical stationary state hypothesis. A few practical steps to check for the validity of the (quasi-) stationary (steady-) state hypothesis (QSSH or simply SSH) for radicals are as follows: (i) determine the rate of change (with time) of the total radical concentration; (ii) find the maximum rate in (i); (c) divide (ii) by the rate of initiation; and (iv) if the ratio is much less than unity, the QSSH (or QSSA, A here stands for assumption) is valid.

Hint 1. One can plot the ratio versus conversion or crosslinker concentration or mole fraction of a comonomer or weight fraction of polymer, and observe how it behaves with respect to unity.

Hint 2. One can also check the ratio of the propagation rate constant over the termination rate constant, evaluated at different times (conversion levels). If this ratio is less than 0.001, then the QSSH is valid.

Food for thought. Does it make sense that we scrutinize the (k_p/k_t) ratio? Where else does this ratio appear (slightly modified) and why is it important for a polymerization?

Tip 10: Troubleshooting with molecular weight data and detection of branching. For an isothermal polymerization, a significant increase in (cumulative) weight-average molecular weight (\bar{M}_w) with conversion (and usually, a corresponding broadening of the MWD) can be the result of diffusion-controlled termination (with most of the chains produced by termination reactions; for an additional discussion on diffusion-control or “gel effect” issues, see Section 4.4.1), LCB reactions (transfer to polymer and/or TDB polymerization), or due to both classes of reactions occurring simultaneously as polymerization proceeds. How do you differentiate among these events?

One experimental approach that has proven to be effective is to measure \bar{M}_w (and plot it vs conversion) by size exclusion chromatography (SEC) or gel permeation chromatography (GPC) and light scattering (LS, usually, low angle laser light scattering, these days). For linear or branched polymer chains, LS gives the correct \bar{M}_w , while SEC/GPC

would underestimate \overline{M}_w , if the polymer chains were branched. Another fact to note is that diffusion-controlled termination and TDB polymerization cause the (cumulative) number-average molecular weight (\overline{M}_n) to increase with conversion, while transfer to polymer has no effect on \overline{M}_n .

Hint 1. Another way to check for the presence of LCB (and hence, reactions in the mechanism that give rise to LCB) is to add a previously synthesized relatively narrow MWD polymer sample (say, from low conversion levels) to its monomer and then initiate polymerization. The previously synthesized polymer will hopefully be clearly separated from the new polymer by SEC/GPC. If the previously synthesized polymer mode (GPC response) has shifted toward larger hydrodynamic volumes, then this is an indication for LCB (say, due to reactions with the backbone polymer molecules via transfer to polymer).

Hint 2. For a detailed discussion on the important topic of branching detection and determination, see Scorah et al. [39, 40].

Hint 3. Check also Tip 14.

Tip 11: Long-chain approximation, density/volume of polymerizing mixture, ideal vs diffusionally limited kinetics. The long-chain approximation (LCA) is valid in polymerizations producing high molecular weight chains. In other words, monomer consumed in reaction steps other than propagation reactions is negligible in the calculation of total monomer consumption and polymer production rate.

The density of the polymerizing mixture increases with monomer conversion and hence the volume of the polymerizing mixture undergoes shrinkage. These form the bases of determining conversion via densitometry and dilatometry.

For isothermal cases, an “ideal” polymerization would show a decrease in polymerization rate with increasing conversion. This is hardly the picture in typical polymerizations due to diffusional limitations. A solution polymerization with a large volume fraction of solvent would tend to exhibit “ideal” polymerization kinetics.

Tip 12: Copolymerization, reactivity ratios, and estimation of reactivity ratios. In a binary copolymerization of monomers M_1 and M_2 , reactivity ratios r_1 and r_2 are important parameters for calculating polymerization rate, copolymer composition, and comonomer sequence length indicators (see Chapter 6 for basic equations and further information).

The tendency of two monomers to copolymerize is noted by the relative values of r_1 and r_2 . If r_1 is greater than 1, then the M_1 radical (i.e., radical ending in M_1 unit) preferentially adds M_1 over M_2 . If r_1 is less than 1, then the M_1 radical preferentially adds M_2 . An r_1 value very close to zero would indicate that M_1 is incapable of homopolymerizing.

The literature is full of values for reactivity ratios fraught with inconsistencies of varying degrees. When dealing with

reactivity ratio estimates, pay attention to the following points: (i) reactivity ratios are rather weak functions of temperature over typical polymerization temperature ranges and changes (emphasis on typical); (ii) use nonlinear regression techniques to estimate reactivity ratios (even better, use the error-in-variables model (EVM) nonlinear regression technique); (iii) reactivity ratios coming from linear regression (based on linearized models) are highly suspect (linear regression is simply incorrect to employ); they can, at best, be used as starting parameter values for the class of nonlinear regression techniques described, for example, in Polic et al. [41]; (iv) it is not only important to obtain point estimates for reactivity ratios but also estimates of their uncertainty in the form of joint confidence regions (contours); see again Polic et al. [41]; (v) the larger the difference between reactivity ratios (i.e., two widely differing reactivity ratio values would be 10 and 0.03, for example), the more interesting the comonomer system behavior will be (in terms of polymerization rate, copolymer composition, and molecular weights) and the trickier the reactivity ratio estimation problem is (from both perspectives of reliable experimental data collection and numerical estimation); see, for instance, Dubé et al. [42].

Tip 13 (related to Tip 12): Copolymerization, copolymer composition, composition drift, azeotropy, semibatch reactor, and copolymer composition control. Most batch copolymerizations exhibit considerable drift in monomer composition because of different reactivities (reactivity ratios) of the two monomers (same ideas apply to terpolymerizations and multicomponent cases). This leads to copolymers with broad chemical composition distribution. The magnitude of the composition drift can be appreciated by the vertical distance between two items on the plot of the instantaneous copolymer composition (ICC) or Mayo–Lewis (model) equation: item 1, the ICC curve (ICC or mole fraction of M_1 incorporated in the copolymer chains, F_1 , vs mole fraction of unreacted M_1 , f_1) and item 2, the 45° line in the plot of F_1 versus f_1 .

For example, in the absence of an azeotrope (the 45° line is the azeotropic line for which $F_1 = f_1$), and when M_1 is more reactive than M_2 (i.e., r_1 greater than 1 and r_2 less than 1), the ICC will decrease in M_1 with an increase in conversion. The extent of composition drift depends on the ratio (r_1/r_2), the initial monomer composition, and the monomer conversion level.

Hint 1. Plot F_1 versus f_1 in a batch copolymerization for different combinations of r_1 and r_2 and observe the composition drift. Is the direction of composition drift always the same? Are azeotropic points stable or unstable to small perturbations in monomer concentration?

Hint 2. One can also appreciate the composition drift picture by plotting the cumulative mole fraction of M_1 in the copolymer chains, \overline{F}_1 , versus conversion.

Food for thought. Another, yet equivalent, way of representing composition drift is to plot the mole fraction of copolymer chains (i.e., mole fraction of monomer incorporated (bound) into the copolymer) with composition in the range between F_{10} and F_{1x} versus F_1 . F_{10} is the initial mole fraction of M_1 in the copolymer, corresponding to f_{10} (the initial mole fraction of M_1 in the comonomer feed at time or conversion zero). F_{1x} is the copolymer composition at some conversion level x corresponding to f_1 . With some algebra and using the definition of conversion, what one is essentially plotting on the y -axis is the ratio (x/x_f) , where x_f is some final conversion level that one would like to achieve in the polymerization. The x -axis of the plot is F_1 . This plot is the cumulative copolymer composition distribution (CCD) and requires a combination of the ICC equation (relating F_1 to f_1) with the Meyer–Lowry equation (relating conversion x to f_1).

(Additional food for thought. What does the plot indicate if the curve one obtains is almost a vertical line?)

Hint 3. Semibatch or continuous reactors involve the continuous (over a certain period or periods of time) or intermittent flow of monomer (or other ingredients, like components of an initiator system, solvent or CTA) into the polymerizing mixture. This flow may in general have several beneficial effects, ranging from extra cooling to more flexibility for molecular weight and branching control, all the way to polymerization rate and composition control.

There are two basic monomer feed policies (and several modifications of the basic ones) that may be used in semibatch polymerization to minimize compositional drift (or optimize other properties). See Hamielec et al. [22] and Fujisawa and Penlidis [43] for more details.

Tip 14: Instantaneous vs cumulative properties, troubleshooting with molecular weight data. What differentiates polymerizations from conventional petrochemical processes (small molecules of the same molecular weight) is the existence of many distributional properties for the polymer product (copolymer composition or sequence length or molecular weight or branching or other property distribution). When a distributional property exists, we can make a distinction between an instantaneous (differential) property and a final, accumulated (or cumulative) property. The cumulative property is the accumulation (integration or sum) of instantaneous properties over a finite period of time or interval of conversion using as appropriate weights how many of the (chains) molecules (with the property in question) have been produced.

In batch polymerizations, we often find that the instantaneous molecular weights vary with time or conversion, and that the cumulative polymer product is made up of chains produced under a variety of conditions. This might be due to local variations or changes in temperature, monomer concentration, initiator concentration, or other recipe ingredient concentration.

Hint 1. If what controls the instantaneous MWD is independent of reaction time or conversion, then the final product will have the most probable (or Flory–Schulz) distribution with a molecular weight dispersity (polydispersity) of 2 (for isothermal operation).

Hint 2. Should transfer to monomer control the molecular weight development, then polymer (cumulative) molecular weight averages would be independent of monomer conversion for isothermal polymerizations. Poly(vinyl chloride) polymerization is an example of this case. Large variations in initiation rate will have little (or no detectable) influence on cumulative molecular weights. The product molecular weight dispersity (polydispersity) will be close to 2. In such a case, to produce a higher molecular weight polymer, we must lower the polymerization temperature (there is no other effective alternative). In fact, in the absence of a CTA, \overline{M}_n and \overline{M}_w depend only on temperature and will be the same in all process types (e.g., bulk, suspension, etc.) and reactor types (e.g., batch, continuous, etc.) operating at the same temperature level.

Hint 3. A considerable increase in number-average molecular weight with conversion is mainly due to TDB polymerization. It is of great interest to compare the growth of the (cumulative) weight-average molecular weight (\overline{M}_w) due to LCB and its growth due to diffusion-controlled termination reactions. With diffusion control, an explosive growth in \overline{M}_w occurs at lower conversions. \overline{M}_w varies almost linearly with conversion but eventually the change decelerates at high conversions or near complete conversion. With LCB (transfer to polymer and TDB polymerization), on the other hand, the growth in \overline{M}_w is initially rather gradual, but \overline{M}_w continues to grow at an accelerated rate in mid- to high conversions, approaching almost infinite molecular weight values at near complete conversion. These observations are useful and practical in differentiating between different events (see also Tip 10).

Tip 15: Expressions for rate of polymerization. The expression for the rate of chain growth polymerization in homogeneous (single phase) polymerization systems (e.g., regular bulk/solution) is given by (for the free radical case)

$$R_p = k_p[M][R] \quad (12.44)$$

R_p is the rate of polymerization (rate of monomer consumption) in moles per liter per second, k_p is the propagation rate constant in liters per mole per second, $[M]$ is the monomer concentration at the reaction site in moles per liter, and $[R]$ is the total concentration of radicals (indicated as P in Section 12.2.1) in moles per liter.

Duality between processes in general tells us that we can express the rates of many other polymerizations in an analogous way, as long as we evaluate the variables involved properly, based on the polymerization at hand. For instance, for anionic polymerization, the general expression

in Equation 12.44 is the same, with [R] being replaced by [LE], the concentration of living ends.

For regular emulsion polymerization (or often referred to as macroemulsion, a heterogeneous multiphase system), a widely used expression for the rate is

$$R_p = k_p [M_p] \frac{(N_p n)}{N_A} \quad (12.45)$$

[M] in Equation 12.44 has been replaced by $[M_p]$ in Equation 12.45. This makes sense, since the monomer concentration that “feeds” the radicals in emulsion polymerization (at the appropriate reaction site) is indeed the monomer concentration in the polymer (latex) particles. Since [R] in Equation 12.44 represents total radical concentration, it has been replaced by the product $(N_p n)$, which represents the total number of radicals present at the reaction site (the main locus of polymerization, which is inside the monomer-swollen polymer particles). N_p is the total number of particles (usually per lit of water) and n represents the average number of radicals per particle. N_A , Avogadro’s number, appears in the equation simply for unit conversion. Needless to say, Equation 12.45 is completely analogous to Equation 12.44.

Hint. Use Equation 12.44 and try to “fit” other types of polymerizations into the general polymerization rate formula. How about suspension polymerization? How about precipitation-type polymerization? How about Ziegler–Natta polymerizations? How about controlled radical polymerizations (CRPs)?

Food for thought. Consider emulsion polymerization again, but now one is interested in describing the rate of polymerization in the water (aqueous) phase only. Are we going to use Equation 12.44 or 12.45? How are we going to modify the terms involved and where are the different concentrations going to be evaluated at?

Tip 16: Polymerization of methyl methacrylate, styrene, and vinyl acetate. MMA, when polymerized, exhibits termination by both combination and disproportionation (in fact, disproportionation is promoted at higher temperatures). Termination by disproportionation leads to the formation of radicals and, eventually, polymer molecules with a TDB. We also know that TDBs will become competitive with the monomer vinyl bonds for radicals as conversion increases. TDB polymerization (characterized by rate constants close (in value) to propagation rate constants) leads to trifunctional LCB. Yet, upon analysis, poly(MMA) chains are linear. How come? What is the explanation/reasoning for this observation? We also know that styrene terminates predominantly via combination. Styrene also exhibits transfer to monomer, which is enhanced at higher temperature levels. Transfer to monomer generates chains with TDBs. Yet, polystyrene is linear. What is the explanation?

Vinyl acetate, another common monomer, is known for producing polymer with high levels of LCB. There might be several independent reasons for this outcome. What are these reasons? Which event contributes more to branching formation?

Tip 17: Termination in homopolymerization and copolymerization, initiation rate in homopolymerization, and copolymerization. Cope with the statement: “Termination reactions are almost always diffusion-controlled right from the outset of polymerization.” *Food for thought (and additional investigation).* How important is the chain length dependence of the termination rate constant in polymer reactor modeling?

Cope with the statement: “In copolymerization, the chemically controlled termination rate constant (i.e., the termination rate constant at time or conversion zero; in essence, the value at very low conversion levels) is a function of both temperature (albeit, weak) and comonomer composition.”

Food for thought. Can one show that in copolymerization (two types of radicals) the initiation rate is given by the exact same expression as in homopolymerization, that is,

$$R_I = 2 f k_d [I] \quad (12.46)$$

R_I represents initiation rate (units of any rate expression), f is the initiator efficiency factor, k_d is the initiator decomposition rate constant (per second), and $[I]$ is the initiator concentration in moles per liter.

Therefore, the expression for the total radical concentration is exactly the same as in homopolymerization.

Tip 18: Internal double bond polymerization. We know that transfer to polymer and TDB polymerization produce trifunctional (long) branches, in addition to increasing the weight-average molecular weight and broadening the MWD (see also Tips 5 and 8). A reaction “similar” to TDB polymerization is the polymerization with internal (pendant) double bonds [double bonds “internal” in dead polymer chains, appearing therein due to (co)polymerization of difunctional (divinyl) monomers (e.g., buta-di-ene)]. Internal double bond (IDB) polymerization produces tetrafunctional (long) branches and leads eventually to the formation of crosslinked polymer (gel). Needless to say, both molecular weight averages increase due to IDB polymerization and the MWD broadens considerably.

In general, monomer addition to a backbone radical center (“internal radical” as opposed to a radical center at the end of a chain) leads to the formation of trifunctional branch points. In addition, b-scission at backbone radical centers can also produce polymer chains with TDBs. IDB polymerization leads to the formation of tetrafunctional branch points. In addition, termination by combination of two backbone radicals also leads to the formation of a tetrafunctional branch point (crosslinking again, leading to

the production of crosslinked gel, i.e., polymer molecules effectively insoluble and hence, of infinite molecular weight due to their interconnected network structure), but swellable by an appropriate solvent (which is a good solvent for the corresponding linear chains or sol).

Tip 19: Intramolecular chain transfer, backbiting, and short-chain branching. Backbiting reactions (intramolecular chain transfer) can account for the high short-chain branching (SCB) frequencies (and often for the excess methyl groups in polymer chains, above and beyond the expected number of end groups). This type of chain transfer is believed to occur by a backbiting reaction between the radical on the terminal carbon atom and a hydrogen atom located on the same chain but five or six carbon atoms away from the radical center (i.e., the radical end “curls” backward and abstracts a hydrogen, thus forming a SCB). This SCB formation is important when studying the kinetics of high pressure low density poly(ethylene), poly(vinyl chloride), and poly(butyl acrylate) at high temperatures.

Tip 20: Polymerization heat effects and energy balances. Polymerizations are highly exothermic reactions. The higher the rate of polymerization, the higher the instantaneous heat generation rate (heat release), and, in principle, the higher the productivity. The main limitation in productivity will be the heat removal rate (i.e., limitations in reactor cooling capabilities). Permitting a temperature increase during polymerization gives higher productivity. The highest productivity could be obtained using adiabatic polymerization (no heat removal from the reactor). However, adiabatic temperature rises are excessive (hence, a very broad MWD with a low molecular weight tail would be obtained) and, hence, the need for good temperature control and/or optimal temperature programming (see also Chapter 13 for more details on energy balances and related model equations). An approximate calculation of the adiabatic temperature rise for bulk (mass) polymerization of styrene would give 300–350 °C. This temperature rise would be much smaller in emulsion or suspension or solution, due to the presence (and high heat capacity) of the water or solvent. The high polymerization heat release allows one to monitor monomer conversion (online or offline) by exploiting reliable heat balances around a reactor and its jacket.

To run a batch reactor at its optimum (minimum) batch time, the heat generation rate at any point during polymerization should equal the heat removal rate, with some allowance for a safety factor. This would translate to a monomer conversion profile varying almost linearly with time.

Heat removal is most commonly achieved through jacket cooling, but with large reactors, additional heat removal sources may be employed, such as reflux condensers, internal cooling coils, etc.

Hint 1. The overall heat transfer coefficient can fall significantly during polymerization (viscosity increase of the polymerizing mixture and scale formation (polymer build-up) on the reactor walls).

Hint 2. As a reactor increases in size, the available heat transfer area (via its walls) increases with reactor volume raised to the 0.67 power. On the other hand, the heat generation rate is proportional to reactor volume raised to the first power.

Hint 3. When heat removal is through reactor walls, it is unsafe to polymerize at temperature levels where the derivative of the heat generation rate becomes large (since in such a case, a very small increase in temperature would require a large decrease in heat transfer fluid temperature in order to avoid a reactor thermal runaway).

Hint 4. In many cases, polymer molecular weights are largely independent of polymerization rate because transfer reactions control (or may be made to control, via the use of a CTA) molecular weight averages and/or other polymer quality indicators. Temperature gradients (and/or “hot spots” in the polymerizing mixture) could in general lead to polymer quality deterioration (as manifested by uncontrolled broadening of the MWD).

Hint 5. In general, it is possible to operate a CSTR at a higher production rate than a comparable batch (or tubular) process (the beneficial effect of cold inlet (monomer) feed allows for a higher specific polymerization rate than in batch). Typical calculations with the energy balance equations of Chapter 13 would indicate that for the same operating conditions, one can run a CSTR at about twice the rate of a batch reactor of the same volume (and heat removal capacity).

Hint 6. In polymer reactor design, polymerization temperature is most often dictated by desired specifications on polymer molecular weight and distribution, rather than polymerization rate.

Tip 21: Crosslinking, gelation, gel formation, and sol versus gel. Experimental data clearly show that once gel (insoluble polymer network, crosslinked polymer) is formed, it grows very rapidly at the expense of the soluble polymer chains (soluble part or sol). Gel acts like a “sponge,” “sucking” in the (linear) polymer chains from the sol. Radical centers located on polymer chains in the gel are longer lived, because of their greatly reduced mobility. These radical centers terminate mainly by reaction diffusion. The greatly reduced termination rates of radical centers located on chains in the gel result in a very high concentration of these radical centers, and this in part is the cause of the rapid growth of gel at the expense of the sol. The more active (reactive) the double bonds bound in copolymer chains, and the greater the number of these double bonds, then the onset of gelation occurs at lower monomer conversion levels. At the same time, the more transfer to a small molecule (such as monomer or CTA),

the further in conversion is the onset of gelation (i.e., a more delayed onset of gelation is observed).

Hint 1. The cumulative number-average molecular weight will increase (sometimes only slightly at higher conversions) with increasing monomer conversion, but it will remain finite. The number-average molecular weight increases with increasing reactivity of pendant double bonds because of the decrease in the total number of dead polymer chains due to the crosslinking reactions. On the other hand, higher order molecular weight averages (weight- and z -average) will increase significantly with increasing monomer conversion and will eventually diverge at the gelation point (i.e., go to infinity). Overall, the molecular weight development of crosslinking copolymerizations is very sensitive to the reactivity of pendant double bonds. If the reactivity of pendant double bonds is assumed to be the same as that of the divinyl monomer (crosslinker), then higher order molecular weight averages will likely be overestimated.

Hint 2. More details on crosslinking systems and their mathematical modeling are given in Section 12.4 and also in Chapter 9.

12.4 EXAMPLES OF SEVERAL FREE RADICAL (CO)POLYMERIZATION SCHEMES AND THE RESULTING KINETIC AND MOLECULAR WEIGHT DEVELOPMENT EQUATIONS

12.4.1 Modeling Linear and Nonlinear Homo- and Copolymerizations Assuming Monofunctional Polymer Molecules and Using the PKRCM

The modeling of homopolymerization as well as linear and nonlinear (chain transfer to polymer and crosslinking) copolymerizations can be represented with the same polymerization scheme shown in Figure 12.1. The kinetic

equations obtained from this polymerization scheme are shown in Figures 12.2 and 12.3.

I , M , T , R_{in}^* , P_r , and D_r in Figures 12.1–12.3 are initiator, monomer, small molecule (e.g., a CTA, an inhibitor, etc.), primary free radicals, polymer radicals, and dead polymer, respectively. (Note that P_r , D_r , and p_i (fraction of radicals type “ i ”) as defined in this chapter are usually termed R_r^* , P_r , and ϕ_i^* in most of the papers from Hamielec’s group). k_d , k_i , k_p , k_{tc} , k_{td} , k_{fT} , k_{fP} , and k_p^{*0} are pseudokinetic rate constants for initiator decomposition, first propagation step (part of the initiation reaction), propagation, termination by combination, termination by disproportionation, transfer to a small molecule T , transfer to polymer, and intrinsic crosslinking (propagation through pendant double bonds). The pseudokinetic rate constants are defined below, in Table 12.5. k_{cp} and k_{cs} represent primary and secondary cyclizations, respectively. Y_i and Q_i are i -th-order moments for living and dead polymer populations, respectively (denoted by μ_K and λ_K in the nomenclature of Section 12.2).

By proper selection of initial conditions or parameter values, the equations of Figures 12.2 and 12.3 can represent linear homopolymerization, linear copolymerization, or nonlinear copolymerization. Examples for the specific case of conventional (noncontrolled) copolymerization with crosslinking can be found in Vivaldo-Lima et al. [44–46]. As a matter of fact, the simulation profiles for homogeneous linear copolymerization of TFE and VAc in supercritical carbon dioxide (sc-CO₂) shown in Chapter 15 (Fig. 15.6) were obtained with this model by setting $k_p^{*0} = k_{cs} = k_{cp} = 0$. So was the case of the heterogeneous linear homopolymerization of MMA in sc-CO₂, also addressed in Chapter 15 (Figs 15.7, 15.8, and 15.9), and copolymerization with crosslinking in sc-CO₂ (Fig. 15.10). The only change in those heterogeneous cases was that additional equations

Initiation	$I \xrightarrow{k_d} 2R_{in}^*$ $R_{in}^* + M \xrightarrow{k_i} P_1$
Propagation	$P_r + M \xrightarrow{k_p} P_{r+1}$
Propagation through double pendant bonds (Crosslinking)	$P_r + D_s \xrightarrow{k_p^{*0}} P_{r+s}$
Transfer to small molecule “ T ”	$P_r + T \xrightarrow{k_{fT}} D_r + T^*$
Transfer to polymer	$P_r + D_s \xrightarrow{k_{fP}} D_r + P_s$
Termination by disproportionation	$P_r + P_s \xrightarrow{k_{td}} D_r + D_s$
Termination by combination	$P_r + P_s \xrightarrow{k_{tc}} D_{r+s}$

Figure 12.1 Polymerization scheme for nonlinear copolymerization with crosslinking under PKRCM and monofunctional polymer molecules.

Initiator consumption	$\frac{d[I]}{dt} = -k_d [I]; R_1 = 2fk_d[I]$
Overall monomer consumption	$\frac{d[M]}{dt} = -k_p [M] [P]; \frac{dx}{dt} = k_p [P] (1-x)$
Small molecule consumption	$\frac{d[T]}{dt} = -k_{ft} [T] [P]$
Monomer composition	$\frac{df_i}{dt} = \frac{f_i - F_i}{1-x} \frac{dx}{dt}, i = 1, 2, \dots, N$
Instantaneous copolymer composition	$F_j = \frac{\sum_{i=1}^N k_{ij} p_i f_i}{k_p}, N = \text{number of monomers}$
Accumulated copolymer composition	$\bar{F}_j = \frac{f_{j0} - f_j (1-x)}{x}$
Crosslink density	$\frac{d[x\rho_a]}{dt} = \frac{k_p^* [\bar{F}_2 (1 - k_{cp} - \bar{\rho}_a (1 + k_{cs}))] x}{k_p (1-x)} \frac{dx}{dt}$

Figure 12.2 Kinetic equations for small molecules, copolymer composition, and average additional crosslinking density derived from the polymerization scheme of Figure 12.1.

- Mass balance for polymer radicals:

$$\frac{d[P_r]}{dt} = R_1 - k_{tT}[T][P_r] - (k_{tc} + k_{td})[P_r][P] + k_p [M] \{ [P_{r-1}] - [P_r] \} - (k_{fp} + k_p^*) [P_r] Q_1 + k_{fp} Y_0 r D_r + k_p^* \sum_{s=1}^{r-1} s [D_s] [P_{r-s}]$$

- Mass balance for dead polymer:

$$\frac{d[D_r]}{dt} = k_{td}[P_r][P] + k_{tT}[T][P_r] + \frac{1}{2} k_{tc} \sum_{s=1}^{r-1} [P_s][P_{r-s}] - (k_{fp} + k_p^*) Y_0 r [D_r] + k_{fp} [P_r] Q_1 + k_p^* \sum_{s=1}^{r-1} [P_{r-s}] s [D_s]$$

Figure 12.3 Kinetic equations for living and dead polymer molecules derived from the polymerization scheme of Figure 12.1.

had to be used for partition of components among the phases.

12.4.2 Modeling Linear and Nonlinear Homo- and Copolymerizations Assuming Multifunctional Polymer Molecules and Using the PKRCM

In Section 12.2.4, it was mentioned that one possibility to address the calculation of the MWD in copolymerization systems was to use $c + 1$ subscripts for a c comonomer

TABLE 12.5 Pseudokinetic Rate Constants (Pseudo-Homopolymer Approach)

Propagation	$k_p = \sum_{i=1}^3 \sum_{j=1}^2 k_{ij} \phi_i^* f_j$
Propagation through pendant double bonds (crosslinking)	$k_p^* = \sum_{i=1}^3 k_{i3p}^* \phi_i^* (\bar{F}_2 - \bar{\rho}_a - \bar{\rho}_c)$
Transfer to a small molecule	$k_{tT} = \sum_{i=1}^3 k_{tTi} \phi_i^*$
Transfer to polymer	$k_{fp} = \sum_{i=1}^3 \sum_{j=1}^2 k_{fpij} \phi_i^* \bar{F}_j$
Termination by disproportionation	$k_{td} = \sum_{i=1}^3 \sum_{j=1}^3 k_{tdij} \phi_i^* \phi_j^*$
Termination by combination	$k_{tc} = \sum_{i=1}^3 \sum_{j=1}^3 k_{tcij} \phi_i^* \phi_j^*$

system, one for the radical type, and c for the number of monomer units of each type in the polymer chain. When one deals with bivariate (e.g., MWD and CCD) or multivariate (e.g., MWD, CCD, and distribution of branching and crosslinking points), one approach is to use polymer molecules with several subscripts. In the treatment of copolymerization of vinyl/divinyl monomers in the presence of nitroxide-mediated radical polymerization

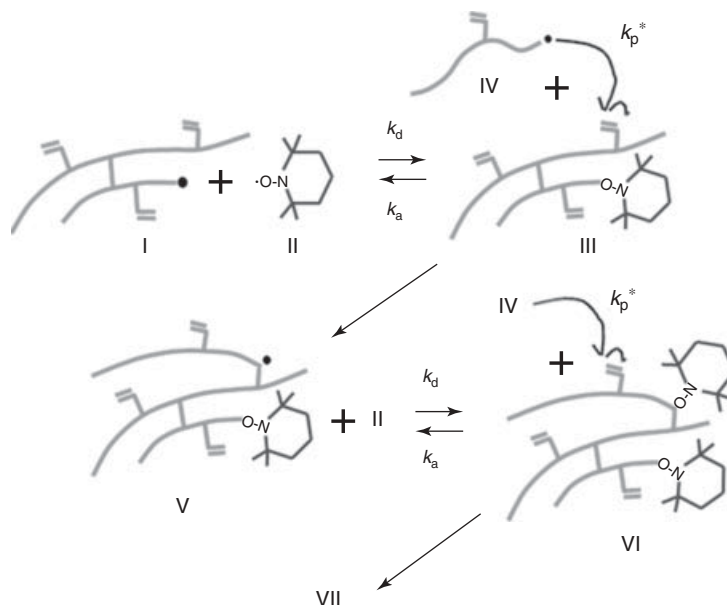


Figure 12.4 Polymer species formed from crosslinking and activation/deactivation reactions in NMRP of vinyl/divinyl monomers. *Source:* Reprinted with permission from Hernández-Ortiz JC, Vivaldo-Lima E, Lona LMF, McManus NT, Penlidis A. *Macromol React Eng* 2009;3:288 [48]. Copyright 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

(NMRP) type of controllers, which is one case of CRP (see Chapter 4 for background on CRP and NMRP), Hernández-Ortiz et al. [47] used a multidimensional type of approach. Instead of using subscripts for every monomer type (multicomponent copolymerization), as mentioned in Section 12.2.4, they used three subscripts to count the number of total monomer units, total number of active (free radical) centers, and total number of dormant centers, namely, they have dealt with a “multifunctional” type of model.

Figure 12.4 shows a schematic representation of the system studied by Hernández-Ortiz et al. [47, 48]. The polymerization scheme for that case is listed in Table 12.6. On the basis of that polymerization scheme, the kinetic equations summarized in Table 12.7 and Equation 12.46 were derived. The pseudokinetic rate constants used are summarized in Table 12.8. The reader is referred to the paper by Hernández-Ortiz et al. [47] for more details. What is interesting here is to point out, as listed in Table 12.9, that simpler cases can be adequately described by simplifying that complex model:

$$\begin{aligned} & \frac{1}{V} \frac{d(V [P_{m,r,d}])}{dt} \\ &= k_p [M] r [P_{m-1,r,d}] - k_p [M] r [P_{m,r,d}] \\ &+ k_{da} (r+1) [P_{m,r+1,d-1}] [\bullet\text{ON}_x] - k_{da} r [P_{m,r,d}] [\bullet\text{ON}_x] \\ &+ k_a (d+1) [P_{m,r-1,d+1}] - k_a d [P_{m,r,d}] \end{aligned}$$

$$\begin{aligned} &+ k_{td} (r+1) [P_{m,r+1,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\ &- k_{td} r [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\ &+ \frac{1}{2} k_{tc} \sum_{n=1}^{m-1} \sum_{s=1}^r \sum_{e=0}^d (s+1) (r-s+1) [P_{n,s+1,e}] \\ &\times [P_{m-n,r-s+1,d-e}] \\ &- k_{tc} r [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\ &+ \frac{1}{2} k_p^* \sum_{n=1}^{m-1} \sum_{s=1}^r \sum_{e=0}^d (s) (m-n) [P_{n,s,e}] [P_{m-n,r-s,d-e}] \\ &- k_p^* r [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} n [P_{n,s,e}] \\ &+ \frac{1}{2} k_p^* \sum_{n=1}^{m-1} \sum_{s=1}^r \sum_{e=0}^d (n) (r-s) [P_{n,s,e}] [P_{m-n,r-s,d-e}] \\ &- k_p^* m [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\ &+ k_{fp} (r+1) [P_{m,r+1,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} n [P_{n,s,e}] \end{aligned}$$

$$\begin{aligned}
 & -k_{fp}r [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\
 & + k_{fp}m [P_{m,r-1,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} n [P_{n,s,e}] \\
 & - k_{fp}m [P_{m,r,d}] \sum_{n=1}^{\infty} \sum_{s=1}^{\infty} \sum_{e=0}^{\infty} s [P_{n,s,e}] \\
 & + k_{fm} (r + 1) [P_{m,r+1,d}] [M] - k_{fm}r [P_{m,r,d}] [M] \\
 & + k_{fd} (r + 1) [P_{m,r+1,d}] [D] - k_{fd}r [P_{m,r,d}] [D] \\
 & + k_{fin} (r + 1) [P_{m,r+1,d}] [I] - k_{fin}r [P_{m,r,d}] [I] \\
 & + k_{fs} (r + 1) [P_{m,r+1,d}] [S] - k_{fs}r [P_{m,r,d}] [S] \\
 & + k_{decomp} (d + 1) [P_{m,r,d+1}] - k_{decomp}d [P_{m,r,d}]
 \end{aligned} \tag{12.47}$$

TABLE 12.6 Elementary Reactions in the Nitroxide-Mediated Radical Copolymerization of Vinyl/Divinyl Monomers

Process	Equation
Initiator decomposition	$I \xrightarrow{k_d} 2R_{in}$
Dimerization	$M + M \xrightarrow{k_{dim}} D$
Thermal initiation	$M + D \xrightarrow{k_{thi}} P_{1,1,0} + D^\bullet$
<i>First Propagation</i>	
Primary radicals	$M + R_{in} \xrightarrow{f k_i} P_{1,1,0}$
Dimeric radicals	$M + D^\bullet \xrightarrow{k_i} P_{1,1,0}$
Solvent radicals	$M + S^\bullet \xrightarrow{k_i} P_{1,1,0}$
Propagation	$P_{m,r,d} + M \xrightarrow{(r)k_p} P_{m+1,r,d}$
<i>Reversible Deactivation of</i>	
Primary radicals	$R_{in} + \bullet ON_x \xrightleftharpoons[k_{a3}]{k_{da3}} R_{in} ON_x$
Dimeric radicals	$D^\bullet + \bullet ON_x \xrightleftharpoons[k_{a3}]{k_{da3}} DON_x$
Solvent radicals	$S^\bullet + \bullet ON_x \xrightleftharpoons[k_{a3}]{k_{da3}} SON_x$
Polymer radicals	$P_{m,r,d} + \bullet ON_x \xrightleftharpoons[(d+1)k_a]{(r)k_{da}} P_{m,r-1,d+1}$
<i>Chain Transfer to</i>	
Initiator	$P_{m,r,d} + I \xrightarrow{(r)k_{fi}} P_{m,r-1,d} + R_{in}$
Monomer	$P_{m,r,d} + M \xrightarrow{(r)k_{fm}} P_{m,r-1,d} + P_{1,1,0}$
Dimer	$P_{m,r,d} + D \xrightarrow{(r)k_{fd}} P_{m,r-1,d} + D^\bullet$
Solvent	$P_{m,r,d} + S \xrightarrow{(r)k_{fs}} P_{m,r-1,d} + S^\bullet$
Polymer	$P_{m,r,d} + P_{n,s,e} \xrightarrow{(rn)k_{fp}} P_{m,r-1,d} + P_{n,s+1,e}$
Propagation with pendant double bound	$P_{m,r,d} + P_{n,s,e} \xrightarrow{(rn)k_{p^*}} P_{m+n,r+s,d+e}$
Termination by disproportionation	$P_{m,r,d} + P_{n,s,e} \xrightarrow{(rs)k_{td}} P_{m,r-1,d} + P_{n,s-1,e}$
Termination by combination	$P_{m,r,d} + P_{n,s,e} \xrightarrow{(rs)k_{tc}} P_{m+n,r+s-2,d+e}$
Dimer proton abstraction by nitroxide	$D + \bullet ON_x \xrightarrow{kh_3} D^\bullet + HON_x$
Alkoxyamine decomposition	$P_{m,r,d} \xrightarrow{(d)k_{decomp}} P_{m,r,d-1} + HON_x$
Addition of nitroxide to monomer	$M + \bullet ON_x \xrightarrow{k_{iNO}} P_{1,1,0}$
Promoted dissociation of BPO	$I + \bullet ON_x \xrightarrow{k_{pr}} R_{in} + B + N$

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TABLE 12.7 Balance and Moment Equations in the Nitroxide-Mediated Radical Copolymerization of Vinyl/Divinyl Monomers

Component	Equation
Chemical initiator	$\frac{1}{V} \frac{d(V[I])}{dt} = -k_d [I] - k_{fin} Y_{010} [I] - k_{pr} [I] [\bullet\text{ON}_x]$
Monomer conversion	$\frac{dx}{dt} = 2k_{dim} [M]_0 (1-x)^2 + k_{thi} [D] (1-x) + k_i ([R_{in}] + [D^\bullet] + [S^\bullet]) (1-x) + (k_p + k_{fm}) (1-x) Y_{010} + k_{iNO} [\bullet\text{ON}_x] (1-x)$
Dimer	$\frac{1}{V} \frac{d(V[D])}{dt} = k_{dim} [M]^2 - k_{thi} [M] [D] - k_{fd} Y_{010} [D] - k_{h3} [D] [\bullet\text{ON}_x]$
Solvent	$\frac{1}{V} \frac{d(V[S])}{dt} = -k_{fs} Y_{010} [S]$
Primary radical	$\frac{1}{V} \frac{d(V[R_{in}])}{dt} = 2fk_d [I] - k_i [R_{in}] [M] + k_{fin} Y_{010} [I] + fk_{pr} [I] [\bullet\text{ON}_x] - k_{da3} [R_{in}] [\bullet\text{ON}_x] + k_{a3} [R_{in} \text{ON}_x]$
Dimer radical	$\frac{1}{V} \frac{d(V[D^\bullet])}{dt} = k_{thi} [D] [M] - k_i [M] [D^\bullet] + k_{fd} Y_{010} [D] + k_{h3} [D] [\text{NO}_x] - k_{da3} [D^\bullet] [\bullet\text{ON}_x] + k_{a3} [\text{DON}_x]$
Solvent radical	$\frac{1}{V} \frac{d(V[S^\bullet])}{dt} = -k_i [M] [S^\bullet] + k_{fs} Y_{010} [S] - k_{da3} [S^\bullet] [\bullet\text{ON}_x] + k_{a3} [\text{SON}_x]$
Dormant primary radical	$\frac{1}{V} \frac{d(V[R_{in} \text{ON}_x])}{dt} = k_{da3} [R_{in}] [\bullet\text{ON}_x] - k_{a3} [R_{in} \text{ON}_x]$
Dormant dimer radical	$\frac{1}{V} \frac{d(V[\text{DON}_x])}{dt} = k_{da3} [D^\bullet] [\bullet\text{ON}_x] - k_{a3} [\text{DON}_x]$
Dormant solvent radical	$\frac{1}{V} \frac{d(V[\text{SON}_x])}{dt} = k_{da3} [S^\bullet] [\bullet\text{ON}_x] - k_{a3} [\text{SON}_x]$
Nitroxyl radical	$\frac{1}{V} \frac{d(V[\bullet\text{ON}_x])}{dt} = k_a Y_{001} - k_{da} Y_{010} [\bullet\text{ON}_x] + k_{a3} ([R_{in} \text{ON}_x] + [\text{DON}_x] + [\text{SON}_x]) - k_{da3} ([R_{in}] + [D^\bullet] + [S^\bullet]) [\bullet\text{ON}_x] - k_{h3} [D] [\bullet\text{ON}_x] - k_{pr} [I] [\bullet\text{ON}_x] - k_{iNO} [\bullet\text{ON}_x] [M]$
Zeroth-order moment	$\frac{1}{V} \frac{d(VY_{000})}{dt} = k_{thi} [M] [D] + k_i [M] ([R_{in}] + [D^\bullet] + [S^\bullet]) - \frac{1}{2} \overline{k_{tcn}} Y_{010}^2 - k_p^* Y_{100} Y_{010} + k_{fm} Y_{010} [M] + k_{iNO} [\bullet\text{ON}_x] [M]$
First-order moments	$\frac{1}{V} \frac{d(VY_{100})}{dt} = k_p [M] Y_{010}$ $\frac{1}{V} \frac{d(VY_{010})}{dt} = k_{thi} [M] [D] + k_i [M] ([R_{in}] + [D^\bullet] + [S^\bullet]) - (\overline{k_{tcn}} + \overline{k_{tdn}}) Y_{010}^2 - k_{da} Y_{010} [\bullet\text{ON}_x] + k_a Y_{001} + k_{iNO} [\bullet\text{ON}_x] [M] - (k_{fin} [I] + k_{fd} [D] + k_{fs} [S]) Y_{010}$
Second-order moments	$\frac{1}{V} \frac{d(VY_{001})}{dt} = k_{da} Y_{010} [\bullet\text{ON}_x] - k_a Y_{001} - k_{decomp} Y_{001}$ $\frac{1}{V} \frac{d(VY_{200})}{dt} = 2k_p [M] Y_{110} + k_p [M] Y_{010} + \overline{k_{tcw}} Y_{110}^2 + 2k_p^* Y_{110} Y_{200}$ $\frac{1}{V} \frac{d(VY_{020})}{dt} = k_{thi} [M] [D] + k_i [M] ([R_{in}] + [D^\bullet] + [S^\bullet]) - 2\overline{k_{tdw}} Y_{020} Y_{010} + \overline{k_{tdw}} Y_{010}^2 + 2\overline{k_{tcw}} Y_{010}^2 - 4\overline{k_{tcw}} Y_{020} Y_{010} + \overline{k_{tcw}} Y_{020}^2 + 2k_p^* Y_{020} Y_{110} + k_{da} (Y_{010} - 2Y_{020}) [\bullet\text{ON}_x] + k_a (Y_{001} + 2Y_{011}) + k_{fp} (2Y_{010} Y_{100} + 2Y_{010} Y_{110} - 2Y_{020} Y_{100}) + k_{iNO} [\bullet\text{ON}_x] [M] + k_{fm} [M] Y_{010} + (k_{fm} [M] + k_{fin} [I] + k_{fd} [D] + k_{fs} [S]) (Y_{010} - 2Y_{020})$ $\frac{1}{V} \frac{d(VY_{002})}{dt} = \overline{k_{tcw}} Y_{011}^2 + 2k_p^* Y_{011} Y_{101} + k_{da} (Y_{010} + 2Y_{011}) [\bullet\text{ON}_x] + k_a (Y_{001} - 2Y_{002}) + k_{decomp} (Y_{001} - 2Y_{002})$ $\frac{1}{V} \frac{d(VY_{110})}{dt} = k_p [M] Y_{020} - \overline{k_{tdw}} Y_{110} Y_{010} + \overline{k_{tcw}} Y_{110} Y_{020} - 2\overline{k_{tcw}} Y_{110} Y_{010} + k_p^* Y_{200} Y_{020} + k_p^* Y_{110}^2 - k_{da} Y_{110} [\bullet\text{ON}_x] + k_a Y_{101} + k_{fp} (Y_{010} Y_{200} - Y_{100} Y_{110}) - (k_{fm} [M] + k_{fin} [I] + k_{fd} [D] + k_{fs} [S]) Y_{110}$ $\frac{1}{V} \frac{d(VY_{101})}{dt} = k_p [M] Y_{011} + \overline{k_{tcw}} Y_{110} Y_{011} + k_p^* Y_{200} Y_{011} + k_p^* Y_{110} Y_{101} + k_{da} Y_{110} [\bullet\text{ON}_x] - k_a Y_{101} - k_{decomp} Y_{101}$ $\frac{1}{V} \frac{d(VY_{011})}{dt} = -\overline{k_{tdw}} Y_{011} Y_{010} + \overline{k_{tcw}} Y_{011} Y_{020} - 2\overline{k_{tcw}} Y_{011} Y_{010} + k_p^* Y_{011} Y_{110} + k_p^* Y_{020} Y_{101} + k_{da} (Y_{020} - Y_{010} - Y_{011}) [\bullet\text{ON}_x] + k_a (Y_{002} - Y_{001} - Y_{011}) - k_{decomp} Y_{011} + k_{fp} (Y_{010} Y_{101} - Y_{011} Y_{100}) - (k_{fm} [M] + k_{fin} [I] + k_{fd} [D] + k_{fs} [S]) Y_{011}$

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TABLE 12.8 Definition of the PseudoKinetic Rate Constants Needed in the Model

Pseudokinetic Rate Constant	Mathematical Expression
Dimerization	$k_{\text{dim}} = k_{\text{dim}11} f_1^2 + \frac{1}{2}k_{\text{dim}12} f_1 f_2 + \frac{1}{2}k_{\text{dim}21} f_2 f_1 + k_{\text{dim}22} f_2^2$
Thermal initiation	$k_{\text{thi}} = \sum_{j=1}^M k_{\text{thij}} f_j$
Propagation	$k_p = \sum_{i=1}^R \sum_{j=1}^M k_{ij} p_i f_j$
Crosslinking	$k_p^{*o} = \sum_{i=1}^R k_{pi3} p_i$
Deactivation	$k_{\text{da}} = \sum_{i=1}^R k_{\text{dai}} p_i$
Activation	$1k_a = \sum_{i=1}^R k_{ai} q_i$
Chain transfer to initiator	$k_{\text{fin}} = \sum_{i=1}^R k_{\text{fini}} p_i$
Chain transfer to monomer	$k_{\text{fm}} = \sum_{i=1}^R \sum_{j=1}^M k_{\text{fmij}} p_i f_j$
Chain transfer to dimer	$k_{\text{fD}} = \sum_{i=1}^R k_{\text{fDi}} p_i$
Chain transfer to solvent	$k_{\text{fS}} = \sum_{i=1}^R k_{\text{fSi}} p_i$
Chain transfer to polymer	$k_{\text{fp}} = \sum_{i=1}^R k_{\text{fpj}} p_i F_j$
Number-average termination by disproportionation	$\overline{k_{\text{tdn}}} = \sum_{i=1}^R \sum_{j=1}^R \overline{k_{\text{tcn}ij}} p_i p_j$
Weight-average termination by disproportionation	$\overline{k_{\text{tdw}}} = \sum_{i=1}^R \sum_{j=1}^R \overline{k_{\text{tcw}ij}} p_i p_j$
Number-average termination by combination	$\overline{k_{\text{tcn}}} = \sum_{i=1}^R \sum_{j=1}^R \overline{k_{\text{tc}ij}} p_i p_j$
Weight-average termination by combination	$\overline{k_{\text{tcw}}} = \sum_{i=1}^R \sum_{j=1}^R \overline{k_{\text{tcw}ij}} p_i p_j$

TABLE 12.9 Specific Cases That Can be Analyzed with the General Model Presented in Tables 12.6 and 12.7

Conventional Systems	Conventional homopolymerization	Conventional copolymerization (without crosslinking)
	Required initial conditions: $[M]_0, [I]_0, [S]_0$ Fixed initial conditions: $f_{20} = 0, [\text{NOx}]_0 = 0$ Comments: pseudokinetic rate constants method not required.	Required initial conditions: $[M]_0, [I]_0, f_{20}, [S]_0$ Fixed initial conditions: $[\text{NOx}]_0 = 0$ Comments: pseudokinetic rate constants method required. If two monomers are employed, $M = 2, R = 2$ in the definitions.
Controlled Systems	Homopolymerization in the presence of NMRP controllers Required initial conditions: $[M]_0, [I]_0, [\text{NOx}]_0, [S]_0$ Fixed initial conditions: $f_{20} = 0$ Comments: pseudokinetic rate constants method not required	Copolymerization in the presence of NMRP controllers (without crosslinking) Required initial conditions: $[M]_0, [I]_0, [\text{NOx}]_0, f_{20}, [S]_0$ Comments: pseudokinetic rate constants method required. If two monomers are employed, $M = 2, R = 2$ in the definitions.
Crosslinked Systems (With or Without Controller)	Copolymerization of vinyl/divinyl monomers Required initial conditions: $[M]_0, [I]_0, f_{20} = 0, [S]_0$ Fixed initial conditions: $[\text{NOx}]_0 = 0$ Comments: pseudokinetic rate constants method required. $M = 2, R = 3$ in the definitions.	Copolymerization of vinyl/divinyl monomers in the presence of NMRP controllers Required initial conditions: $[M]_0, [I]_0, [\text{NOx}]_0, f_{20}, [S]_0$ Comments: pseudokinetic rate constants method required. $M = 2, R = 3$ in the definitions.

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REFERENCES

1. The American Heritage[®] Dictionary of the English Language. 4th ed., Houghton Mifflin Company; 2000. Available at <http://www.thefreedictionary.com/chemical+engineering>. Accessed 2012 Apr 6.
2. Penlidis A. *Can J Chem Eng* 1994;72:385.
3. Ray WH, Soares JBP, Hutchinson R. *Macromol Symp* 2004;206:1.
4. Hrymak A, Pelton R, Zhu S. 2005. Compilers, Collected Works of Archie Hamielec. McMaster University, Hamilton, Ontario, Canada. Available at <http://chemeng.mcmaster.ca/departments/Collected%20Works%20of%20Archie%20Hamielec.pdf>. Accessed 2012 Apr 6.
5. Hungenberg K-D. *Macromol React Eng* 2009;3:220.
6. Ray WH. *J Macromol Sci Rev Macromol Chem* 1972; C8:1.
7. Penlidis A, MacGregor JF, Hamielec AE. *AIChE J* 1985;31:1547.
8. Kiparissides C. *Chem Eng Sci* 1996;51:1637.
9. Dubé MA, Soares JBP, Penlidis A, Hamielec AE. *Ind Eng Chem Res* 1997;36:966.
10. Yoon WJ, Kim YS, Kim IS, Choi KY. *Korean J Chem Eng* 2004;21:147.
11. Asua J. *Polymer Reaction Engineering*. Hoboken: Wiley-Blackwell; 2007.
12. Bausa J. *Macromol Symp* 2007;259:42.
13. Mueller PA, Richards JR, Congalidis JP. *Macromol React Eng* 2011;5:261.
14. Penlidis A, editor. *Polymer Reaction Engineering*. Taylor & Francis. ISSN 1054-3414 (Print), 1532-2408 (Online). Available at http://www.tandfonline.com/loi/lree20?open=10#vol_10. Accessed 2012 Apr 6.
15. Spiegel S, editor. *Macromolecular Materials & Engineering*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA. Online ISSN 1439-2054. Available at [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1439-2054](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1439-2054). Accessed 2012 Apr 6.
16. Spiegel S, editor. *Macromolecular Reaction Engineering*. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA. Online ISSN 1862-8338. Available at [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1862-8338](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1862-8338). Accessed 2012 Apr 6.
17. Hill CG Jr., *Chemical Engineering Kinetics and Reactor Design*. New York: John Wiley & Sons; 1977.
18. Smith JM. *Chemical Engineering Kinetics*. 3rd ed. New York: McGraw Hill; 1981.
19. Bird RB, Stewart WE, Lightfoot EN. *Transport Phenomena*. 2nd ed. New York: John Wiley & Sons; 2007.
20. Ballard MJ, Napper DH, Gilbert RG. *J Polym Sci Polym Chem Ed* 1981;19:939.
21. Hamielec AE, MacGregor JF. In: Reichert KH, Geiseler W, editors. *Polymer Reaction Engineering, Modelling Copolymerizations*. Munich: Hanser Publishers; 1983. p 21ff.
22. Hamielec AE, MacGregor JF, Penlidis A. *Makromol Chem Macromol Symp* 1987;10/11:521.
23. [a] Arriola DJ. Modeling of addition polymerization systems [Ph. D. thesis]. Madison (WI): University of Wisconsin; 1989; [b] Saldívar E, Dafniotis P, Ray WH. *J Macromol Sci Rev Macromol Chem Phys* 1998;C38:207.
24. Storti G, Carrá S, Morbidelli M, Vita G. *J Appl Polym Sci* 1989;37:2443.
25. Li W-H, Hamielec AE, Crowe CM. *Polymer* 1989;30: 1518.
26. Tobita H, Hamielec AE. *Macromolecules* 1989;22:3098.
27. Tobita H, Hamielec AE. *Polymer* 1991;32:2641.
28. Zabisky RCM, Chan WM, Gloor PE, Hamielec AE. *Polymer* 1992;33:2243.
29. Xie T, Hamielec AE. *Makromol Chem Theory Simul* 1993;2:421.
30. Xie T, Hamielec AE. *Makromol Chem Theory Simul* 1993;2:455.
31. [a] Penlidis A, MacGregor JF, Hamielec AE. *J Appl Polym Sci* 1988;35:2009. [b] Penlidis A, MacGregor JF, Hamielec AE. *J Appl Polym Sci* 1988;35:2023.
32. [a] Chien DCH, Penlidis A. *Polym React Eng* 1994;2:163. [b] Chien DCH, Penlidis A. *Chem Eng Sci* 1994;49:1855.
33. Dubé MA, Penlidis A. *J Polym Sci A Polym Chem* 1997;35:1659.
34. Palmer DE, McManus NT, Penlidis A. *J Polym Sci A Polym Chem* 2000;38:1981.
35. Palmer DE, McManus NT, Penlidis A. *J Polym Sci A Polym Chem* 2001;39:1753.
36. McManus NT, Hsieh G, Penlidis A. *Polymer* 2004;45: 5837.
37. Leamen MJ, McManus NT, Penlidis A. *J Polym Sci A Polym Chem* 2005;43:3868.
38. Leamen MJ, McManus NT, Penlidis A. *Chem Eng Sci* 2006;61:7774.
39. Scoria MJ, Dhib R, Penlidis A. Branching level detection in polymers. In: Lee S, editor. *Encyclopedia of Chemical Processing (EChP)*. London: Taylor & Francis; 2005. p 251ff.
40. Scoria MJ, Tzoganakis C, Dhib R, Penlidis A. *J Appl Polym Sci* 2007;103:1340.
41. Polic AL, Duever TA, Penlidis A. *J Polym Sci A Polym Chem* 1998;36:813.

42. [a] Dubé MA, Penlidis A. *Polymer* 1995;36:587. [b] Dubé MA, Penlidis A. *Macromol Chem Phys* 1995;196:1101. [c] Dubé MA, Penlidis A. *Polym Int* 1995;37:235.
43. Fujisawa T, Penlidis A. *J Macromol Sci Pure Appl Chem* 2008;45:115.
44. Vivaldo-Lima E, Hamielec AE, Wood PE. *Polym React Eng* 1994;2(1&2):87.
45. Vivaldo-Lima E, García-Pérez R, Celedón-Briones OJ. *Rev Soc Quím Mex* 2003;47:22.
46. Quintero-Ortega IA, Vivaldo-Lima E, Luna-Bárcenas G, Alvarado JFJ, Louvier-Hernández JF, Sanchez IC. *Ind Eng Chem Res* 2005;44:2823.
47. Hernández-Ortiz JC, Vivaldo-Lima E, Penlidis A. *Macromol Theory Simul* 2012;21:302.
48. Hernández-Ortiz JC, Vivaldo-Lima E, Lona LMF, McManus NT, Penlidis A. *Macromol React Eng* 2009;3:288.