Composition Control in Emulsion Copolymerization. I. Optimal Monomer Feed Policies

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SYNOPSIS

The problem of producing polymers with constant instantaneous composition in semibatch reactors has been addressed in the most general terms. A rigorous procedure for determining *a priori* the monomer feed policy that allows one to produce, with a minimum reaction time, a given amount of polymer, with constant instantaneous composition and complete monomer depletion, has been developed. The procedure involves the knowledge of only the monomer reactivity ratios and the interphase partition laws. Its practical implementation needs the on-line monitoring of conversion. The reliability of the theoretical approach has been tested by comparison with the optimal policies obtained in the literature, for three different binary systems, as the result of various experimental iterative procedures. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

When producing copolymers in batch reactors, the different reactivity values of the involved monomers lead to a drift in the copolymer composition. The consequent dishomogeneity in the composition of the final product is often unacceptable in view of its final applications. Heterogeneous systems are further complicated by the interphase partition equilibria that affect the monomer concentration in the reaction locus and then the composition of the produced copolymer.

In principle, composition deviations can be corrected through appropriate monomer additions using a semibatch reactor. This is best operated in the case of low viscosity systems, such as emulsion polymerizations. The difficulty is in the evaluation of the monomer addition flow rate, because of the lack of genuinely predictive models of the reaction kinetics and of instruments for real-time composition measurement.

The simplest approach, widely adopted in applications, is to feed a monomer mixture with composition equal to the desired copolymer composition.[1-3] By keeping the reaction starved, i.e., with a feed rate much lower than the polymerization rate, the composition of the copolymer matches that of the monomer mixture continuously fed to the reactor. This procedure allows one to prevent uncontrolled monomer buildup in the system, which may shift the copolymer composition. However, due to the very low concentration of monomers in the reaction locus, this mode of operation may affect significantly the molecular weight distribution.[4] The addition of preemulsified mixtures has been used as well. In this case, secondary nucleation may arise, which affects the final particle-size distribution.[5]

The basic disadvantage of starved copolymerizations is the loss of productivity. The process is, in fact, operated below the maximum reaction rate that would be attainable with higher local concentration of monomers. In some cases, however, this choice is imposed by a limitation in the reactor cooling capability. Thus, in order to prevent thermal runaway, it is necessary to keep the polymerization rate low, so that the heat-generation rate does not exceed the maximum possible cooling rate.

In general, a more attractive objective is to produce a copolymer with a given composition while keeping the polymerization rate maximum. In this

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case, in order to maintain constant the copolymer composition, we keep the corresponding monomer composition in the reaction locus constant by feeding the monomers at an appropriate rate. In principle, this requires a detailed knowledge of the reaction kinetics as well as of the interphase monomer partitioning, which is needed to account for the monomer accumulation in the nonreacting phases. In this regard, it is worth noting that the major difficulty in determining the polymerization kinetics is to estimate the number of active radicals per particle, $\bar{n}$, and the number of particles in the latex, N_p.

In homogeneous systems, a constant composition copolymer can be obtained through independent monomer additions, so as to keep the monomer composition in the reactor constant. The same approach has been proposed for emulsion polymerization systems[6-9] using on-line gas chromatography to monitor the overall monomer composition. In heterogeneous systems, the control of the overall monomer composition in the reactor is not sufficient. In this case, we need to introduce suitable interphase partition laws to estimate the monomer composition in the polymer particles, i.e., in the reaction locus, from the overall monomer composition measurement, and then to evaluate the rate of monomer addition so as to keep this constant.

Dimitratos et al.[10,11] combined model predictions of monomer consumption with experimental measurements of overall residual monomers through a Kalman filtering technique. The model for the rate of polymerization was based on equilibrium partition relationships and on literature correlations for the evaluation of the average number of active chains per particle, $\bar{n}$. The model error was corrected by the filtering algorithm using the measured values of the overall monomer composition inside the reactor. The procedure was illustrated for the binary system vinyl acetate–butyl acrylate, where independent monomer additions were designed so as to maintain the desired ratio of monomer concentrations in the reaction locus.[12]

A similar model was used by Arzamendi and Asua[13] to control the composition of a vinyl acetate–methyl acrylate copolymer. Having recognized the difficulties involved in the evaluation of $\bar{n}$, an iterative experimental procedure was developed[14] to estimate the change of $\bar{n}$ as a function of conversion during the polymerization.

A modification of this approach was introduced by Van Doremaele et al.[15] with reference to the binary system styrene–methyl acrylate, where the monomers exhibit largely different water solubilities. The $\bar{n}$ evaluation was avoided through a direct empirical correlation between conversion and monomer feed rate. This procedure requires an initial estimate of $\bar{n}$ to obtain a first trial addition policy. Then, from the conversion values measured experimentally after each run, an improved monomer addition policy can be calculated for the subsequent run using only monomer interphase partition laws and reactivity ratios. Also, this procedure is experimentally iterative. Besides its fast convergence, a fundamental concern, common to all iterative experimental procedures, arises from possible irreproducibilities among subsequent reactions.

In this work, a different approach is proposed. The monomer addition policy is determined a priori as a function of conversion, rather than time, through a model that involves only monomer interphase partition laws and reactivity ratios, thus avoiding the estimate of the number of active chains per particles and the number of polymer particles.[16] This idea has been implicitly recognized by Guillot[17] and by Van Doremaele et al.,[15] whereas some preliminary results of its application have been discussed in Storti et al.[18] Taking advantage of the simplified model, it is possible to solve the classical optimization problem of determining monomer feed policies that minimize the reaction time needed to complete monomer depletion while producing a constant composition copolymer. The obtained results confirm that in most operating conditions the optimal monomer feed policy requires to feed all the less reactive monomer at the beginning of the reaction. This result is in agreement with common practice in homogeneous systems,[19] which has also been applied to systems in emulsion.[14] Using the rigorous solution of the optimization problem, some unusual behaviors originated from the different water solubilities of the monomers, which are peculiar of emulsion processes, are identified. The results of some parametric calculations are discussed in the case of a binary system so as to further clarify this aspect. Finally, the reliability of the proposed approach has been tested by comparing the monomer addition policies calculated a priori through the proposed procedure with those obtained earlier in the literature through experimental iterations as discussed above.

It is worth noting that, since the monomer addition policies are obtained as a function of conversion, the practical implementation of this approach needs the on-line monitoring of conversion. This can be obtained using various techniques, such as densimetry, gas chromatography, mass flow measurements for gaseous monomers, and heat balance on the cooling system (cf. Ref. 20). On the other

hand, the proposed approach is fully predictive, it does not require any kind of trial and error procedure (neither computational nor experimental), it does not suffer from irreproducibilities in subsequent polymerization reactions, and it can be applied to cases involving any number of monomer species, as long as reactivity ratios and interphase partition parameters are known.

THE COMPOSITION-CONVERSION MODEL

The proposed method for controlling a heterogeneous copolymerization reaction relies on a predictive model of copolymer composition as a function of monomer conversion.[16] The material balance of the i-th monomer species in a semibatch reactor is given by

$$\frac{dM_i}{dt} = Q_i - R_{c_i} V_w MW_i \quad i = 1 \cdots N_m \quad (1)$$

where monomer accumulation results from a balance between the rate of the polymerization reaction, R_{c_i}, and the feed flow rate, Q_i, whereas all the remaining symbols are explained in the Nomenclature section. The monomer present in the reactor is partitioned among three phases, i.e., polymer particles, oil droplets, and water phase, so that

$$M_i = M_i^p + M_i^d + M_i^w \quad i = 1 \cdots N_m \quad (2)$$

The time evolution of the copolymerization reaction is fully specified by the $2 \times N_m$ differential-algebraic equations above, where N_m is the number of monomer species, once the expressions of the copolymerization rate, R_{c_i}, the monomer feed, Q_i, and the interphase partition laws are specified.

By assuming that the reaction takes place only in the polymer particles, the ultimate model applies, and the latex is monodisperse, the rate of monomer consumption is given by

$$R_{c_i} = \left(\sum_{j=1}^{N_m} k_{p_{ji}} \bar{n}_j \right) [M_i]^p \frac{N_p}{N_A} \quad (3)$$

This relation involves the concentration of each monomer species in the polymer particles $[M_i]^p$, as well as the average number of radicals of different types per particle, $\bar{n}_j$. According to the pseudohomopolymerization approach[16] (also referred to as pseudokinetic approximation in the context of ho-

mogeneous systems[21]), we can introduce the following average propagation rate constants:

$$\bar{k}_{p_i} = \sum_{j=1}^{N_m} k_{p_{ji}} \mathcal{P}_j \quad (4)$$

so that

$$\sum_{j=1}^{N_m} k_{p_{ji}} \bar{n}_j = \sum_{j=1}^{N_m} k_{p_{ji}} (\bar{n} \mathcal{P}_j) = \bar{n} \sum_{j=1}^{N_m} k_{p_{ji}} \mathcal{P}_j = \bar{k}_{p_i} \bar{n} \quad (5)$$

where $\mathcal{P}_j$ stands for the probability of having a growing radical with a terminal unit of type j, i.e., $\mathcal{P}_j = \bar{n}_j / \bar{n}$. The vector of N_m probabilities, $\mathbf{P}$, can be evaluated through the procedure developed in Ref. 16, which leads to the following linear system of equations:

$$\mathbf{AP} = \mathbf{b} \quad (6)$$

where the elements of the matrix $\mathbf{A}$ and the vector $\mathbf{b}$ are given by

$$a_{ij} = \begin{cases} \sum_{j \neq i} k_{p_{ij}} [M_j]^p \\ -k_{p_{ji}} [M_i]^p \\ 1 \end{cases} \begin{array}{l} , \\ \text{for } i < N_m \\ \text{for } i = N_m \end{array} \quad (7)$$

$$b_i = \begin{cases} 0 & \text{for } i < N_m \\ 1 & \text{for } i = N_m \end{cases} \quad (8)$$

The equations above apply to the most general case where any number of monomer species, N_{mi}, is involved. Note that, in the case where the reactions of chain transfer to monomer are present, eqs. (3)–(8) should be modified by adding to each propagation constant, $k_{p_{ij}}$, the corresponding chain-transfer constant, $k_{tr_{ij}}$. Substituting eq. (5), eq. (3) reduces to

$$R_{c_i} = \bar{k}_{p_i} \bar{n} [M_i]^p \frac{N_p}{N_A} \quad (9)$$

and the overall rate of polymer production is given by

$$R_c = \sum_{i=1}^{N_m} R_{c_i} = \left(\sum_{i=1}^{N_m} \bar{k}_{p_i} [M_i]^p \right) \bar{n} \frac{N_p}{N_A} \quad (10)$$

Thus, the instantaneous molar composition of the polymer, y_i, is given by a relation that involves only the monomer concentration in the polymer particles,

$[M_i]^p$, and the average propagation rate constants, $\bar{k}_{p_i}$:

$$y_i = \frac{R_{c_i}}{R_c} = \frac{\bar{k}_{p_i}[M_i]^p}{\sum_j \bar{k}_{p_j}[M_j]^p} \qquad (11)$$

Note that, in the case of a binary system, the above relationship reduces to the well-known equation originally developed for homogeneous systems (cf. Refs. 22 and 23).

Using the polymer mass balance,

$$\frac{dM_c}{dt} = V_w \sum_{j=1}^{N_m} R_{c_j} MW_j \qquad (12)$$

together with the monomer mass balance (1) and eq. (11), the amount of the i-th monomer, M_i, as a function of the overall mass of polymer produced, M_c, is given by

$$\begin{cases} \dfrac{dM_i}{dM_c} = \hat{Q}_i - Y_i \\ M_i = M_i^p + M_i^d + M_i^w \end{cases} \quad i = 1 \cdots N_m \quad (13)$$

where Y_i is the instantaneous weight fraction of monomer i in the polymer, while $\hat{Q}_i$ is the amount of monomer fed to the reactor per unit mass of produced polymer. In order to be completed, the system of equations above requires two sets of N_m interphase partition equations to evaluate the amount of each monomer present in the three phases inside the reactor.

The use of system (13) is twofold: given a feed policy, $\hat{Q}_i$, it provides the composition Y_i of the polymer produced during the reaction or, alternatively, for a given composition objective, $\bar{Y}_i$, it provides the required monomer additions as a function of the amount of polymer produced. The important aspect of this model is that it involves only the propagation rate constants, besides the interphase partition laws, i.e., both $\bar{n}$ and N_p have been eliminated. Accordingly, the results of this model are highly reliable, as shown by the extensive comparisons with experimental data reported in the literature (cf. Ref. 16). Of course, the cost of this simplification is that we can compute the consumption of each monomer as a function of overall conversion, but not of time.

OPTIMAL MONOMER FEED POLICIES

The Constant Composition Copolymerization

The final aim of composition control is to produce tailored polymers identified through proper rela-

tionships between molecular structure and application properties. The composition objective reduces frequently to maintain constant the fraction of each monomer species in each polymer chain. For this reason, we address the design of a constant composition polymerization, though such restriction does not pertain to the procedure developed in this work.

To complete the system of eqs. (13), we need to specify the interphase monomer partition laws. Among the various options that have been developed in the literature, ranging from thermodynamic models[24] to empirical correlations of experimental data,[15] it is possible to represent the monomer partitioning through linear relationships between the concentrations in the two involved phases as follows:

$$[M_i]^p = m_i^p [M_i]^w \qquad (14)$$

$$[M_i]^d = m_i^d [M_i]^w \qquad (15)$$

where the concentrations in the water phase have been taken as the reference concentration, since this is present in the reactor throughout the entire polymerization process. Such empirical representations of the equilibrium data have been found satisfactory for several systems and, therefore, have been widely adopted in applications.[17,25,26]

Let us introduce the volumetric composition of monomer droplets and polymer particles as follows:

$$\alpha_i = \frac{V_i^d}{V_d} \qquad (16)$$

$$\phi_i = \frac{V_i^p}{V_p} \qquad (17)$$

where $\sum_{i=1}^{N_m} \alpha_i = 1$. In these terms, the concentration of each monomer in the aqueous phase, $[M_i]^w$, can be assumed to be equal to a fraction of the saturation value, $[M_i]^{w,*}$, proportional to the droplets composition, i.e.:

$$[M_i]^w = \alpha_i [M_i]^{w,*} \qquad (18)$$

On the other hand, the simple equipartition between monomer droplets and polymer particles has been found adequate for many systems,[27] due to the natural affinity of the two organic phases, i.e.:

$$\frac{\phi_i}{\alpha_i} = \phi^* = \text{constant} \qquad (19)$$

where ϕ^*, independent of the index i, represents the overall swelling of the polymer particles at satura-

tion, i.e., $\phi^* = \sum\limits_{i=1}^{N_m} \phi_i$. In the case where the amount of monomers is not sufficient to saturate the system, so as to form a separate oil phase, using the equipartition eqs. (19), eq. (18) becomes

$$[M_i]^w = \frac{\phi_i}{\phi^*} [M_i]^{w,*} \tag{20}$$

It can be seen that the relations above can be recasted in the form of the interphase monomer partition laws (14) and (15) by taking the following expressions for the partition coefficients:

$$m_i^d = \frac{\tilde{\rho}_i}{[M_i]^{w,*}} \tag{21}$$

$$m_i^p = \frac{\phi^* \tilde{\rho}_i}{[M_i]^{w,*}} \tag{22}$$

It is worth stressing the simplicity of the above equations that requires one to know only the saturation concentration of each monomer in water, $[M_i]^{w,*}$, the maximum swelling of the polymer particles, ϕ^*, and the molar density of the monomers, $\tilde{\rho}_i$.

By noting that the overall amount of monomer i in phase l is given by

$$M_i^l = [M_i]^l V_l MW_i \tag{23}$$

the substitution of eqs. (14) and (15) in the second of eqs. (13) leads to

$$M_i = \left(V_p \frac{m_i^p}{V_w} + V_d \frac{m_i^d}{V_w} + 1 \right) M_i^w \tag{24}$$

Since the amount of water in the reactor remains constant, we can introduce the following constant ratios:

$$K_i^l = \frac{m_i^l}{V_w} \tag{25}$$

so that the system (13) can be rewritten as

$$\begin{cases} \dfrac{dM_i}{dM_c} = \hat{Q}_i - Y_i \\ M_i = (V_p K_i^p + V_d K_i^d + 1) M_i^w \end{cases} \quad i = 1 \cdots N_m \tag{26}$$

which holds true for any number of monomer species and any type of monomer addition policy, $\hat{Q}_i$.

Let us now introduce the requirement of producing a polymer with constant instantaneous composition, i.e., y_i = constant. This implies a constraint on the monomer composition in the polymer particles that, as shown in the Appendix, can be written using eq. (11) in terms of the following N_m relations:

$$\phi_i = C_i \phi, \tag{27}$$

where the monomer specific constant C_i involves kinetic copolymerization constants, monomer molar densities, and the desired values of the polymer composition.

Semibatch emulsion polymerization reactors can be operated either in the starved or in the flooded interval. As mentioned earlier, it is possible to keep the reaction starved by feeding the monomers at a rate much smaller than the potential maximum rate of polymerization. In this case, a complete control of the composition is readily obtained, at the cost of a large process time. The flooded interval is obtained through larger feed rates that lead to the buildup of unreacted monomers in the reactor; in this case, monomers accumulate as a separate phase, in the form of droplets. Monomer addition policies for composition control change depending upon the regime at which the reactor is operated. In the following, the monomer feed policies as a function of the amount of polymer produced are obtained in explicit form for both intervals.

Flooded Interval

When the reactor is operated in the flooded interval, monomer droplets are present and, hence, the polymer particles are saturated with monomers, i.e.:

$$V_d > 0 \quad \text{and} \quad \phi = \phi^* \tag{28}$$

In this case, the constraint of constant composition (27), together with the equilibrium equations (19), leads to

$$\alpha_i = C_i \tag{29}$$

Recalling that V_w is constant, eqs. (29) can be substituted in eqs. (18) and (23), leading to

$$M_i^w = C_i M_i^{w,*} = \text{constant} \tag{30}$$

By differentiating the second of eqs. (26) with respect to the polymer mass, M_c, and using eqs. (21)–(23), (25), and (30), we obtain

$$\frac{dM_i}{dM_c} = \left(K_i^p \frac{dV_p}{dM_c} + K_i^d \frac{dV_d}{dM_c} \right) M_i^w$$

$$= \rho_i C_i \left(\phi^* \frac{dV_p}{dM_c} + \frac{dV_d}{dM_c} \right) \qquad (31)$$

Since the particle volume, V_p, can be represented in terms of the overall amount of polymer in the reactor, M_c, as follows:

$$V_p = \frac{V_c}{1 - \phi} = \frac{M_c}{\rho_c(1 - \phi)} , \qquad (32)$$

for $\phi = \phi^*$, eq. (31) reduces to

$$\frac{dM_i}{dM_c} = \rho_i C_i \left(\frac{\phi^*}{\rho_c(1 - \phi^*)} + \frac{dV_d}{dM_c} \right) \qquad (33)$$

Substituting eq. (33), the first of eqs. (26) leads to

$$\hat{Q}_i = Y_i + \rho_i C_i \left[\frac{dV_d}{dM_c} + \frac{\phi^*}{\rho_c(1 - \phi^*)} \right]$$

$$= Y_i + \frac{Y_i}{A_i} \left[\rho_c \frac{dV_d}{dM_c} + \frac{\phi^*}{1 - \phi^*} \right] \qquad (34)$$

where the new parameter

$$A_i = \frac{\rho_c Y_i}{\rho_i C_i} \qquad (35)$$

has been introduced. Note that this is related to the ratio between the desired copolymer composition and the corresponding monomer mixture composition in the reaction locus. Since it can be easily shown that A_i is proportional to $\bar{k}_{p_i}$, this can be regarded as an index of the monomer reactivity evaluated at the monomer mixture composition that produces the desired polymer composition. Equation (34) is the basic equation for the flooded interval. It provides the feed flow rate of each monomer species, per unit mass of produced polymer, $\hat{Q}_i$, in terms of the desired polymer composition, Y_i, and of the accumulation of monomers in the oil droplets and in the polymer particles. To fully determine the monomer feed policy, we have to first choose the desired evolution of the volume of oil droplets in the system, i.e., $V_d = V_d(M_c)$. Let us consider two different choices of interest in applications:

Case 1.1. The volume of oil droplets remains constant, i.e.:

$$V_d = \text{constant}. \qquad (36)$$

In this case, eq. (34) reduces to

$$\hat{Q}_i = Y_i + \frac{Y_i \phi^*}{A_i(1 - \phi^*)} \qquad (37)$$

It is seen that the monomer feed rate is determined by the instantaneous consumption of monomers due to the polymerization reaction and by the accumulation of monomers in the growing polymer particles.

It is worth noting that there is no advantage in keeping a large oil phase in the reactor, since it is, anyway, impossible to increase the concentration of monomers in the polymer particles above saturation. On the other hand, getting close to the droplets' disappearance threshold makes the reactor behavior sensitive. The reactor regime may, in fact, switch to starved conditions as a consequence of small errors in the monomer feed rates, thus slowing down the reaction rate and requiring different values of $\hat{Q}_i$ to match the composition assignment. In conclusion, a small amount of monomer droplets guarantees stable operating conditions, but an excess of it bears no advantage and actually reduces the fraction of reactive volume available in the system.

Case 1.2. One of the monomers is fed all at once, at the beginning of the reaction.[13,14] Let us indicate this monomer with the index j. We can evaluate the total volume of droplets at the beginning of the reaction, V_d^0, from the partition eq. (24) for monomer j with $V_p = 0$ as follows:

$$\hat{M}_j^0 = \rho_j \alpha_j V_d^0 + M_j^{w,0} \qquad (38)$$

where eqs. (18) and (23) have been used. By setting $\hat{Q}_j$ equal to zero in eq. (34) for $i = j$ and solving the corresponding differential equation for V_d with the initial condition $V_d = V_d^0$, as given by eq. (38), we obtain

$$V_d(M_c) = V_d^0 - \left(\frac{Y_j}{\rho_j C_j} + \frac{\phi^*}{\rho_c(1 - \phi^*)} \right) M_c \qquad (39)$$

This equation provides the variation of the droplets volume as a function of conversion. Substituting eq. (39) in eqs. (34) and solving for the remaining monomers leads to

$$\hat{Q}_i = Y_i - \frac{\rho_i C_i}{\rho_j C_j}$$

$$Y_j = \frac{Y_i}{A_i} (A_i - A_j) \quad \text{for} \quad i \neq j \qquad (40)$$

This relation provides the flow rate of each monomer, which should be fed to the reactor in order to

maintain the instantaneous polymer composition constant in the case where the j-th monomer is entirely charged to the reactor at the beginning of the process, i.e., $\hat{Q}_j = 0$.

It is seen that the operation above is actually feasible only in the case where the j-th monomer, which is that not fed to the reactor, corresponds to the smallest value of the parameter A_j, i.e., to the less reactive monomer under the selected composition conditions. Any other choice would, in fact, lead to negative flow rates of at least one of the remaining monomer species. Moreover, since A_j is constant during the reaction, the selection above can be made once and for all at the beginning of the process. It does not need to be changed as the reaction proceeds, at least as long as the reactor operates in the flooded interval.

It is worth noticing that the above result provides the rigorous criterion for determining the monomer species that should be entirely charged to the reactor at the beginning of the process and not fed subsequently. We should emphasize that this criterion arises from the constraint of producing a polymer with constant instantaneous composition and is not related to the minimization of the reaction time. This aspect will be, in fact, accounted for subsequently, in the section Minimization of the Batch Time.

Starved Interval

When the monomer feed flow rate is lower than the maximum potential polymerization rate, the reactor operates in the starved interval, where no monomer droplets are present, i.e., $V_d = 0$. The application of this condition, together with the constant composition constraint (27), to eqs. (26) allows one to evaluate the required feed flow rate $\hat{Q}_i$. Using eq. (20) and the partition eq. (24), the overall amount of monomer i in the reactor can be expressed as follows:

$$M_i = V_p \rho_i \phi_i + M_i^w$$

$$= \rho_i \left(V_p + \frac{B_i}{\rho_c} \right) \phi_i \qquad (41)$$

where the coefficient $B_i = \rho_c M_i^w / \rho_i \phi = \rho_c M_i^{w,*} / \rho_i \phi^*$, representative of the monomer solubility in the aqueous phase, remains constant during the reaction. By differentiating the previous equations with respect to the polymer mass, M_c, and substituting in the monomer mass balances (26), we obtain

$$\frac{B_i}{\rho_c} \rho_i \frac{d\phi_i}{dM_c} + \rho_i \frac{d(\phi_i V_p)}{dM_c} = \hat{Q}_i - Y_i \qquad (42)$$

Using eq. (32) for the volume of the polymer particles and recalling that now ϕ varies, it follows that

$$\frac{B_i}{\rho_c} \rho_i \frac{d\phi_i}{dM_c} + \frac{\rho_i}{\rho_c} \frac{d}{dM_c} \left(\frac{M_c \phi_i}{1 - \phi} \right) = \hat{Q}_i - Y_i \qquad (43)$$

which, using the constant composition requirement (27), reduces to

$$\hat{Q}_i = Y_i + \frac{Y_i}{A_i} \left[\frac{d\phi}{dM_c} \left(B_i + \frac{M_c}{(1 - \phi)^2} \right) + \frac{\phi}{1 - \phi} \right] \qquad (44)$$

It can be seen that the feed flow rate, $\hat{Q}_i$, needed to maintain the polymer composition constant depends upon the actual swelling of the polymer particles, $\phi(M_c)$. Similarly to the monomer droplets volume in the case of flooded interval, here the evolution of the monomer swelling in the polymer particles, $\phi(M_c)$, remains as a degree of freedom. Thus, we can select any desired $\phi(M_c)$ or, alternatively, we can choose $\hat{Q}_j$ for a particular monomer species and compute, from eqs. (44), $\phi(M_c)$ and $\hat{Q}_i$ for all remaining monomers. These two situations are analyzed in the following:

Case 2.1. The overall swelling ratio of the polymer particles, ϕ, remains constant during the polymerization reaction, i.e.:

$$\phi = \bar{\phi} = \text{constant} \qquad (45)$$

Thus, the derivative of ϕ with respect to the copolymer mass vanishes and the monomer feed policies are readily obtained from eqs. (44) as follows:

$$\hat{Q}_i = Y_i + \frac{Y_i \bar{\phi}}{A_i (1 - \bar{\phi})} \qquad (46)$$

Note that the feed policy (46) is identical to that obtained earlier for the flooded interval (37), except for the different value of ϕ, i.e., $\bar{\phi}$ instead of ϕ^*. Again, the monomer feed rate is determined by two contributions: the instantaneous monomer consumption due to the polymerization reaction and the accumulation of monomer in the growing polymer particles. Using this monomer feed policy, in fact, the size of the polymer particles increases continuously. This behavior is obviously due to the continuous addition of monomer needed to keep constant the particle swelling. It is worth noting that this situation occurs in applications where the value $\bar{\phi}$ is selected so as to maintain a significant gel effect,

which allows one to operate at higher rate of polymerization. We will come back to this issue in the next section.

Case 2.2. Let us assume that we have operated the reactor in the flooded interval up to a conversion value where $V_d = 0$ and $\phi > 0$. Now we want to fully deplete the monomer inside the reactor, while maintaining the composition of the produced polymer constant, and we decide to do so by stopping the feed of the j-th monomer species. Thus, from eq. (44) with $i = j$, by setting $\hat{Q}_j = 0$, we obtain

$$\frac{d\phi}{dM_c} = -\frac{A_j(1 - \phi)^2 + \phi(1 - \phi)}{B_j(1 - \phi)^2 + M_c} = -\gamma_j \quad (47)$$

where the new parameter γ_j has been introduced. Integrating with the final condition,

$$\phi = 0 \quad \text{at} \quad M_c = M_c^f \quad (48)$$

where M_c^f is the total mass of polymer produced, we obtain

$$\phi(M_c) = \frac{1}{2B_j} [A_j(M_c^f - M_c) + M_c + B_j +$$

$$-\sqrt{(A_j(M_c^f - M_c) + M_c - B_j)^2 + 4B_j M_c}] \quad (49)$$

Using eqs. (49) and (44), we can determine the required feed policies for the remaining monomer species, i.e., $i = 1, N_m$ with $i \neq j$. In particular, by substituting eq. (47) in eqs. (44), we obtain

$$\hat{Q}_i = \frac{Y_i}{A_i}\left(B_i + \frac{M_c}{(1 - \phi)^2}\right)(\gamma_i - \gamma_j) \quad \text{for } i \neq j \quad (50)$$

where the value of ϕ for each M_c value is given by eq. (49). Similarly to Case 1.2 in the flooded interval, we note that the condition of constant instantaneous polymer composition can be satisfied in practice only in the case where the j-th monomer, i.e., that whose flow rate is $\hat{Q}_j = 0$, is the one characterized by the smallest value of the parameter γ_j. Any other choice would, in fact, lead to negative values of the flow rate of at least one of the other monomers.

However, in this case, since γ_j is a function of conversion, it is possible that the monomer with the smallest value of γ_j, hereafter referred to as the *critical monomer*, changes during the polymerization reaction. For example, the critical monomer changes from j to k at the conversion value where γ_k becomes first equal to γ_j and then $\gamma_k < \gamma_j$. At this point, the feed rate of the k-th monomer vanishes and this becomes the new critical monomer, while the j-th

one starts to be fed to the system. In order to find all possible locations ($\phi - M_c$ pair of values) where a change in the critical monomer occurs, we set $\gamma_k = \gamma_j = \bar{\gamma}$. From eq. (47),

$$\bar{\gamma} = \frac{A_j(1 - \phi)^2 + \phi(1 - \phi)}{B_j(1 - \phi)^2 + M_c}$$

$$= \frac{A_k(1 - \phi)^2 + \phi(1 - \phi)}{B_k(1 - \phi)^2 + M_c} \quad (51)$$

and eliminating the quantity M_c, we obtain

$$\bar{\gamma} = \frac{A_j - A_k}{B_j - B_k} \quad (52)$$

Since the parameter γ is positive, this relation indicates that a necessary condition for the exchange of critical monomer to occur is that the differences between A and B for the monomer pair under examination have the same sign.

Thus, summarizing, the determination of the critical monomer in the starved interval is performed as follows:

1. The γ value corresponding to each monomer species is first computed at the end of the reaction (i.e., $\phi = 0$, $M_c = M_c^f$) using eq. (47):

$$\gamma_j = \frac{A_j}{B_j + M_c^f} \quad \text{for} \quad j = 1 \cdots N_m \quad (53)$$

   The critical monomer is identified as the one characterized by the minimum value of γ. Note that the desired polymer composition, monomer reactivities, water solubilities, and reactor productivity (M_c^f) all contribute to determine the critical monomer.

2. We can now integrate eq. (47) backward and compute, at each conversion value M_c, the corresponding value of the parameter γ for each monomer species. If one of them, say γ_k, becomes lower than that corresponding to the critical monomer, then k becomes the critical monomer.

3. The procedure at the previous point is iterated up to reaching the value $\phi = \phi^*$.

Finally, it is worth noting two particular cases arising when the two monomers have similar water solubilities, i.e., $B_k \simeq B_j$.

The first one concerns the exchange of critical monomer. Since $\bar{\gamma}$ is finite, eq. (52) indicates that, in order to have a change in the critical monomer, the two monomers must have also similar values of

A. Using eq. (35), we see that the condition $A_k = A_j$ implies that

$$\frac{Y_k}{\rho_k \phi_k} = \frac{Y_j}{\rho_j \phi_j} \tag{54}$$

which means equal ratios of the monomer weight fractions in the polymer and in the monomer mixture. This corresponds to the case of azeotropic system. The two monomer species j and k are both "critical" all along the reaction and therefore we may charge both of them to the reactor at the beginning of the reaction.

The second case concerns the optimal monomer feed policy. Under the condition of similar or negligible monomer water solubilities, the term $[B_i(1 - \phi)^2 + M_c]$ becomes practically independent of the monomer type. Thus, from eqs. (44), we see that

$$\frac{\hat{Q}_i - Y_i}{C_i \rho_i} = \frac{\hat{Q}_j - Y_j}{C_j \rho_j} \tag{55}$$

which, by setting $\hat{Q}_j = 0$, reduces to eq. (40). Thus, the feed policy becomes identical to that obtained earlier for case 1.2 in the flooded interval. This result is a direct consequence of the assumption of monomer equipartition between the two organic phases stated by eq. (19).

Minimization of the Batch Time

In the previous section, we determined the monomer addition policies that allow us to maintain the instantaneous polymer composition constant throughout the entire polymerization process. These are given as a function of the mass of polymer produced, M_c, and depend on whether the reactor is operated in the flooded [eq. (34)] or in the starved [eq. (44)] interval. In applications, it is usually required to reach very high conversion values, so as to reduce the amount of unreacted monomer in the final product. Accordingly, also in the case where the reactor is initially operated in the flooded interval, we should account for a final stage of the process where the monomer is depleted and the reactor operates in the starved interval. This situation has been analyzed earlier in case 2.2.

In this section, we address the issue of minimizing the batch time, so as to maximize the reactor productivity. For this, we take advantage of the degrees of freedom that are still available after having applied the constant composition constraint as described in the previous sections. In particular, these are provided by the evolution of the monomer drop-

lets volume, $V_d(M_c)$, in eq. (34) for the flooded interval and of the monomer swelling ratio, $\phi(M_c)$, in eq. (44) for the starved interval.

To minimize the time needed to produce a given amount of constant composition polymer, we need to maximize the rate of polymerization. Usually, the initial concentrations of initiator, emulsifier, chain-transfer agent, and temperature are given, so as to obtain a polymer with desired application properties, such as, e.g., molecular weight or particle size. Thus, we can assume that the only operating variables that can be used to minimize the reaction time are the feed flow rates of the monomer species, $\hat{Q}_i$. However, since we want the polymer instantaneous composition to be constant, the values of $\hat{Q}_i$ should also satisfy the corresponding constraints given by eqs. (34) and (44), depending on whether the reactor is operated in the flooded or in the starved interval, respectively. Since the monomer feed flow rates, $\hat{Q}_i$, can affect only the term $(\bar{n} \phi)$ in the expression of the overall polymerization rate (10), our optimization problem reduces to maximize the value of the product $(\bar{n} \phi)$ throughout the entire polymerization process.

We next consider the case where no significant gel effect is present, so that the average number of active chains per particles, $\bar{n}$, is independent of the overall fraction of monomers in the polymer particles, ϕ. In this case, the maximum polymerization rate is obtained when the monomer swelling, ϕ, is maximum.

The Case Without Autoacceleration

The swelling of polymer particles by monomer species has an upper bound corresponding to saturation conditions, i.e., $\phi \leq \phi^*$. Thus, in the case where no gel effect is present, the maximum rate of polymerization is achieved when the polymer particles are saturated by the monomer mixture. In principle, by continuously feeding fresh monomers to the reactor, we can maintain this condition for an indefinite time. However, as mentioned above, saturation conditions cannot be kept until the end of the process and we have to consider a final stage where the monomers are depleted. Note that this usually takes a significant fraction of the total process time, since the rate of polymerization vanishes along with the monomer concentration.

The problem is to identify the most efficient procedure to drive ϕ from its saturation value ϕ^* to zero, while keeping the polymerization rate as large as possible. For this, let us assume that the reactor is first operated in the flooded interval so as to produce a given amount of polymer, M_c^*, as yet un-

known. At this point, the reactor switches to the starved interval and, hereafter, ϕ decreases so as to reach the final desired conversion value, M_c^f, with no unreacted monomer in the polymer particles, i.e., $\phi = 0$. Accordingly, the problem of minimizing the batch reaction time becomes equivalent to maximizing the following functional:

$$J = \int_0^{M_c^f} \phi \, dM_c = \phi^* \, M_c^* + \int_{M_c^*}^{M_c^f} \phi \, dM_c \quad (56)$$

To evaluate the monomer fraction in the polymer particles as a function of the amount of produced polymer, i.e., $\phi = \phi(M_c)$, we use the material balances for the starved interval (44), which may be rewritten in the form

$$\frac{d\phi}{dM_c} = \frac{A_i(\hat{Q}_i - Y_i)(1 - \phi)^2 - \phi(1 - \phi)Y_i}{Y_i[B_i(1 - \phi)^2 + M_c]}$$

$$= G_i(\hat{Q}_i, \phi, M_c) \quad i = 1 \cdots N_m, \quad (57)$$

where

$$\phi = 0 \quad \text{at} \quad M_c = M_c^f \quad (58)$$

and

$$\phi = \phi^* \quad \text{at} \quad M_c = M_c^* \quad (59)$$

In the equations above, the N_m monomer feed flow rates, $\hat{Q}_i$, are the control variables. However, since eqs. (57) provide $N_m - 1$ constraints, we can take one of them, say the j-th flow rate, $\hat{Q}_j$, as the optimization variable. We then maximize the functional (56) with respect to $\hat{Q}_j$, using eqs. (57)–(59) to compute the flow rates of the remaining $N_m - 1$ monomers, i.e., $\hat{Q}_i$ with $i \neq j$, as well as the monomer swelling ratio, $\phi(M_c)$. Thus, with reference to the generic monomer j, the optimization problem can be reduced to minimize the following functional:

$$I(\hat{Q}_j) = z^*\phi^* - \int_0^{z^*} \phi(z, \hat{Q}_j)dz$$

$$= \int_0^{z^*} [\phi^* - \phi(z, \hat{Q}_j)]dz \quad (60)$$

with the constraints

$$\frac{d\phi}{dz} = h_j(\phi, z)\hat{Q}_j + g_j(\phi, z) \quad (61)$$

$$\phi = 0 \quad \text{at} \quad z = 0 \quad (62)$$

$$\phi = \phi^* \quad \text{at} \quad z = z^* \quad (63)$$

where

$$z = M_c^f - M_c \quad (64)$$

$$z^* = M_c^f - M_c^* \quad (65)$$

$$h_j(\phi, z) = -\frac{A_j(1 - \phi)^2}{Y_j[B_j(1 - \phi)^2 + M_c^f - z]} \quad (66)$$

$$g_j(\phi, z) = \frac{A_j(1 - \phi)^2 + \phi(1 - \phi)}{[B_j(1 - \phi)^2 + M_c^f - z]} \quad (67)$$

We also see that, based on physical considerations, the control variable $\hat{Q}_j$ is upper and lower bounded by

$$0 \leq \hat{Q}_j \leq Y_j \quad (68)$$

The problem stated above belongs to a particular class of variational problems that allow a special solution.[28] The corresponding Hamiltonian is, in fact, *linear* in the control variable, and since the terminal value z^* is unspecified, it must equal zero all along the optimal trajectory. This result allows us to conclude that the optimal policy $\hat{Q}_j(M_c)$ belongs to one of the two extrema of the admissible interval (68), depending on the sign of $h(\phi, z)$ in eq. (61). Since $h(\phi, z) < 0$, the optimal policy is given by

$$\hat{Q}_j^{\text{opt}}(M_c) = 0 \quad (69)$$

The corresponding feed flow rates for all remaining monomer species are determined from eqs. (57), which may be rewritten concisely as follows:

$$G_i(\hat{Q}_i, \phi, M_c) = G_j(\hat{Q}_j = 0, \phi, M_c)$$

$$i = 1, N_m; \quad i \neq j \quad (70)$$

where the monomer swelling ratio, ϕ, is obtained as a function of M_c by integrating eq. (57) with $i = j$ and, therefore, $\hat{Q}_j = 0$. It can be readily seen that eq. (70) is equivalent to eq. (50) with $\phi(M_c)$ given by eq. (49).

In principle, the procedure above can be applied to each monomer independently. However, as we discussed in the context of case 2.2 above, only in the case where the selected monomer j corresponds to the critical monomer do we obtain a physically acceptable solution. For any other selection of the monomer j, eq. (70) would, in fact, lead to a negative flow rate for at least one of the remaining monomer species.

In conclusion, the procedure for determining the optimal monomer policy for producing a given

amount of polymer, M_c^f, with constant instantaneous composition, Y_i, in the shortest possible time can be summarized as follows:

1. Determine the critical monomer j as the one for which the A_j value given by eq. (35) is minimum.
2. Compute the conversion value M_c^* where the transition from flooded to starved interval occurs by solving eq. (49) with $\phi = \phi^*$.
3. The flow rates of the monomer species in the flooded interval, i.e., for $M_c \leq M_c^*$, are computed from eq. (40) (except for $\hat{Q}_j$, which is zero).
4. The flow rates of the monomer species in the starved interval, i.e., for $M_c \geq M_c^*$, are computed from eqs. (49) and (50) (except for $\hat{Q}_j = 0$).

Note that in the procedure above we assumed that the critical monomer does not change during the polymerization process. Actually, it is possible that, during the starved interval, the critical monomer changes, say from j to k. In this case, the optimal monomer feed policy is again given by eqs. (49) and (50), with j replaced by the new critical monomer, for each conversion interval characterized by a different definition of the critical monomer. In this context, it is worth noting that the change in the critical monomer definition can arise also at the conversion value where the transition from flooded to starved interval occurs. Let us assume, e.g., that $A_j \leq A_k$ while $\gamma_j \geq \gamma_k$. Thus, from eqs. (40) and (50), we readily see that during the flooded interval the critical monomer is j, while, as the reactor enters the starved interval ($M_c = M_c^*$), it becomes the monomer k. It should be recognized that, from a physical point of view, the occurrence of this exchange requires the water solubility of monomer k to be much larger than that of monomer j (i.e., $B_k \gg B_j$). After the exchange, in fact, no more additions of monomer, k, are needed during the starved interval, since the amount of this component required by the reaction to be completed is provided by the aqueous phase.

The Case with Autoacceleration

A specific situation of practical interest is one where a strong gel effect is present, so as to compensate for monomer depletion with a corresponding increase of the number of active chains per polymer particle, $\bar{n}$. For example, this may be the case for systems containing acrylates, which typically exhibit a large reduction of the termination rate during the

starved interval of the reaction. In these cases, the maximization of the polymerization rate requires one to maximize the product ($\bar{n} \phi$), and we need to evaluate the average number of active chains per particle, $\bar{n}(\phi)$. Thus, the main advantage of the approach proposed in this work vanishes. On the other hand, whatever be the mechanism determining the $\bar{n}$ increase, this problem may be overcome, at the expenses of one experimental run only, as follows:

1. A semibatch polymerization reaction is performed using the monomer feed policy developed in the previous section. This allows us to obtain the desired copolymer composition, even though the required reaction time is not minimized. However, we use this experimental run to determine the kinetic behavior of the system with the required monomer mixture composition.
2. By inspection of the curve conversion vs. time, it can be seen whether the reaction rate exhibited its maximum value during the flooded or the starved interval. If the second case applies, we can calculate the monomer swelling ratio corresponding to the maximum reaction rate. Thus, we design the optimal monomer feed policy so as to perform most of the polymerization in the starved interval with constant ϕ equal to this value, using the relations developed earlier in case 2.1. In the last portion of the polymerization process, where ϕ is driven to zero so as to fully deplete the monomer in the reactor, the optimal monomer feed policy is obtained through the same procedure outlined in the previous section.

SOME NUMERICAL EXAMPLES

In this section, a few numerical examples are considered, so as to better illustrate the procedure for determining the optimal monomer feed policy developed earlier, with particular reference to possible changes in the critical monomer definition during the reaction. Note that this problem has never been considered in previous studies in the literature. The numerical values of the model parameters used in all reported calculations are summarized in Table I. These have been arbitrarily chosen so as to enhance, for illustration purposes, each specific behavior under examination.

All the examined situations refer to binary systems where the less reactive monomer is the first one (i.e., $A_1 < A_2$) and, therefore, this is always the

Table I **Numerical Values of the Model Parameters Used in Figures 1–3, When Not Differently Specified in the Figure Caption**

Parameter	Numerical Value
Reactivity Ratios	
r_{12}	0.4
r_{21}	0.6
Monomer Solubilities in Aqueous Phase	
$[M]_1^{w,*}$	$9.0 \cdot 10^{-2}$ mol L^{-1}
$[M]_2^{w,*}$	$9.0 \cdot 10^{-5}$ mol L^{-1}
Monomer Densities	
ρ_1	0.9 g cm^{-3}
ρ_2	0.9 g cm^{-3}
Polymer Density	
ρ_c	1.1 g cm^{-3}
Monomer Solubilities in Particle (Volume Fraction)	
ϕ_1^*	0.80
ϕ_2^*	0.80
Monomer Molecular Weight	
MW_1	100 g mol^{-1}
MW_2	100 g mol^{-1}
Volume of Water	
V_w	1.0 L
Polymer Composition (Weight Fraction)	
$Y_1 = Y_2$	0.50

critical monomer in the flooded interval. Thus, in the following, we examine the effect of water solubility and polymer composition on the optimal monomer feed policy during the starved interval.

In Figure 1, the effect of an inversion in the monomer solubilities in the aqueous phase, with constant polymer composition, is illustrated. In Figure 1(a) ($B_1 = 13.8$ g; $B_2 = 13.8 \cdot 10^{-3}$ g), the solubility of the noncritical monomer (monomer 2) is much lower than that of monomer 1. This is reflected by the increase in the flow rate of monomer 2 when passing from the flooded to the starved interval, due to the limited amount of this monomer solubilized in the aqueous phase when oil droplets disappear. The opposite behavior, observed in the case where the water solubility of the noncritical

monomer is large with respect to that of monomer 1 ($B_1 = 13.8 \cdot 10^{-3}$ g; $B_2 = 13.8$ g), is shown in Figure 1(b). A significant amount of monomer 2 becomes available to the reaction when oil droplets disappear, so that a flow rate equal to about one-half of the preceding one is required for composition control.

As discussed in the previous section, a change in the definition of the critical monomer can occur when the differences between the two parameters A and B have the same sign. This situation is illustrated in Figure 1(b). However, in order to observe this phenomenon, we have to consider even larger values of the solubility of monomer 2. In Figure 2(a), where $B_2 = 27.6$ g, a change in the critical monomer
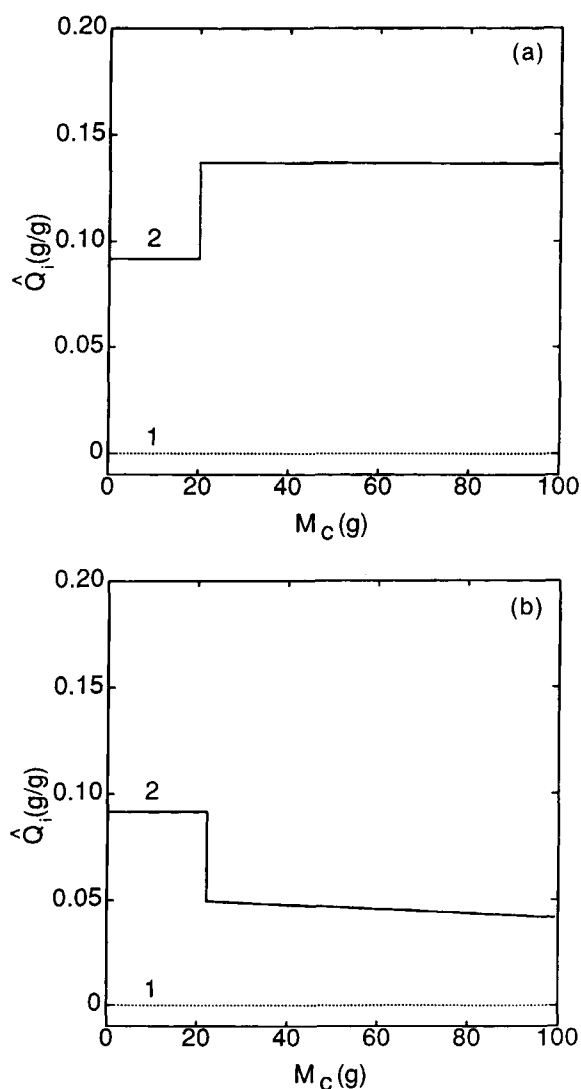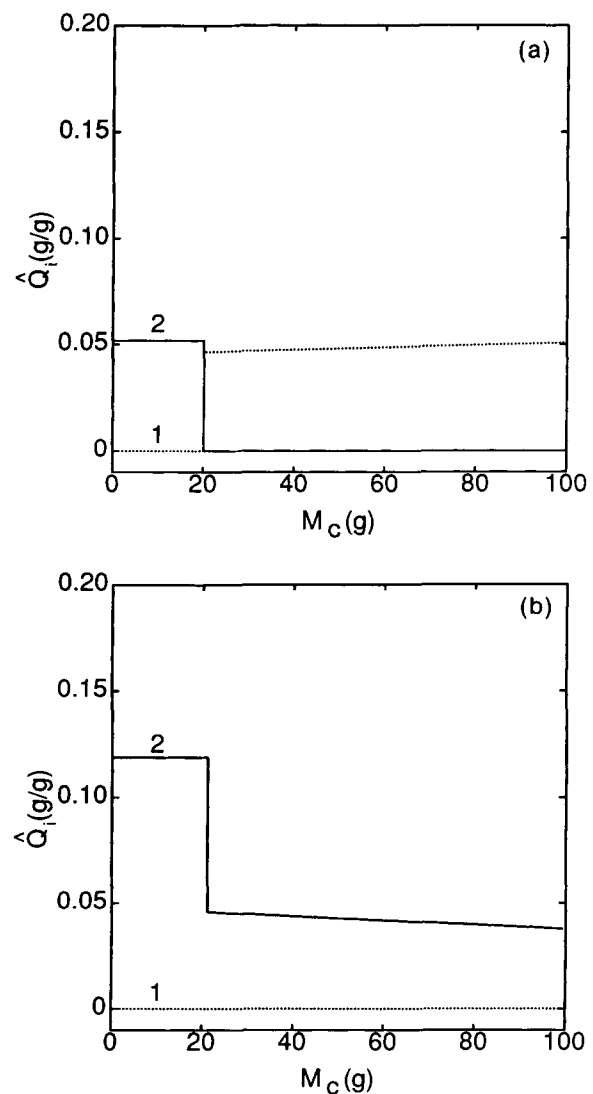

Figure 1 Calculated monomer feed flow rates, $\hat{Q}_i$ as a function of the amount of polymer produced, M_c. ($\cdots$) Monomer 1; (———) monomer 2. Parameter values as reported in Table I. (a) $B_1 = 13.8$ g; $B_2 = 13.8 \cdot 10^{-3}$ g; (b) $B_1 = 13.8 \cdot 10^{-3}$ g, $B_2 = 13.8$ g.
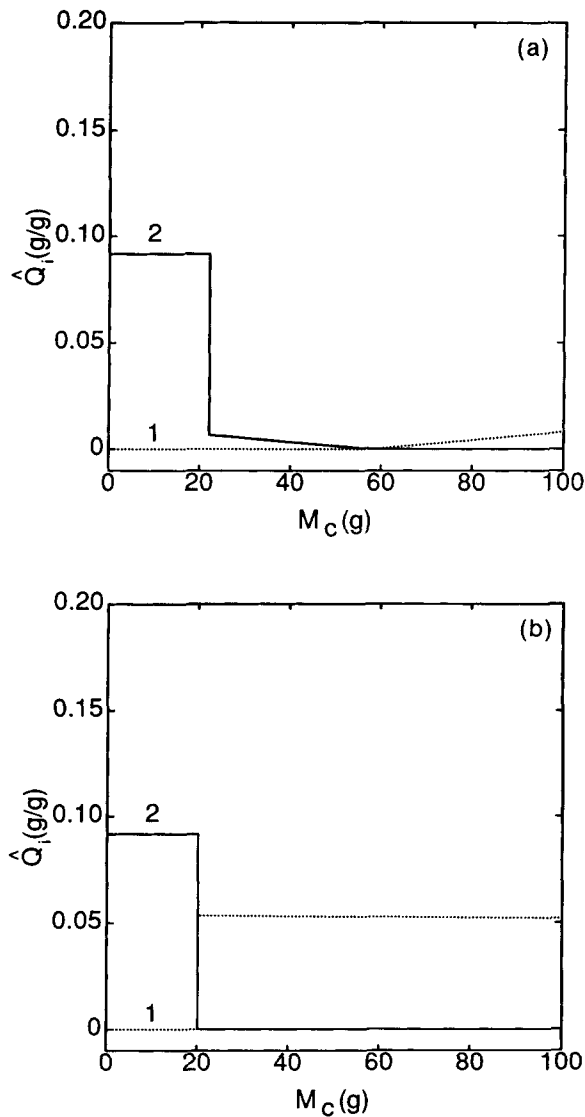
Figure 2 Calculated monomer feed flow rates, $\hat{Q}_i$ as a function of the amount of polymer produced, M_c. ($\cdots$) Monomer 1; (———) monomer 2. Parameter values as reported in Table I. (a) $B_1 = 13.8$ g, $B_2 = 27.6$ g; (b): $B_1 = 13.8 \cdot 10^{-3}$ g; $B_2 = 41.4$ g.

tical. It appears that as the fraction of monomer 1 in the polymer increases the conversion value where the critical monomer inversion occurs increases, up to the situation shown in Figure 3(b), where monomer 1 remains the critical one throughout the entire polymerization reaction.

We have seen that the optimal monomer feed policies are significantly affected by the monomer water solubilities. In particular, the phenomenon of a change in the critical monomer definition during the polymerization reaction can occur only in heterogeneous polymerization systems. However, it should be noted that this phenomenon can occur only when the reactivity differences among the var-

definition is observed at a conversion value equal to about 60%. This phenomenon is further enhanced in Figure 2(b), where $B_2 = 41.4$ g, and the critical monomer change occurs at the transition from the flooded to the starved interval. From this point on, the critical monomer becomes monomer 2 and then monomer 1 is fed to the reactor during the entire starved interval.

In Figure 3, the effect of polymer composition is illustrated. In particular, with reference to Figure 2(a), where $Y_1 = 0.50$, we consider the case where $Y_1 = 0.45$ in Figure 3(a) and that where $Y_1 = 0.55$ in Figure 3(b), all the other parameters being iden-

Figure 3 Calculated monomer feed flow rates, $\hat{Q}_i$, as a function of polymer produced, M_c. ($\cdots$) Monomer 1; (———) monomer 2. Parameter values as reported in Table I. (a) $Y_1 = 0.45$; (b) $Y_1 = 0.55$.

ious monomer species are not too large, which corresponds to the situation where the composition control is not a significant issue. When the values of the reactivity parameter A are, in fact, quite different, it becomes rather difficult to have differences in the solubility parameters B so large as to lead to significant changes in the parameters γ.

COMPARISON WITH EXPERIMENTAL DATA

Let us now verify the reliability of the theoretical results obtained above by comparison with experimental data reported in the literature for three different binary systems. These include styrene (STY)–methyl acrylate (MA),[15] methyl methacrylate (MMA)–ethyl acrylate (EA),[29] and MA–vinyl acetate (VA).[30] For each of these systems, in the original studies, the optimal monomer feed policy was determined so as to obtain a good composition control while minimizing the reaction time. This policy was obtained following an iterative experimental procedure, which involved the adjustment of the monomer feed policy in each reaction batch based on the results obtained in the preceding one. However, in general, and particularly in industrial environments, this procedure may not be reliable because of the occurrence of irreproducibilities between two subsequent reactions. This point has been well illustrated by Van Doremaele et al.[15] through a pair of polymerization reactions with different induction times.

In the following, we compare the optimal monomer feed policy obtained experimentally in the studies mentioned above with that predicted *a priori* following the procedure developed in this work. In particular, after identifying the critical monomer to be charged at the beginning of the reaction and checking for possible critical monomer changes, the flow rate of each remaining monomer has been calculated using eqs. (40) when the reactor operates in the flooded interval, and eqs. (50), when it operates in the starved interval. It should be mentioned that in all the cases examined we observed that the optimal monomer feed flow rate remains substantially constant as a function of the amount of polymer produced. This result makes very simple the practical implementation of these optimal monomer feed policies, which, we iterate once again, has the unavoidable requirement of the on-line monitoring of conversion, i.e., of the overall amount of polymer formed in the reactor.

Finally, note that no fitting of the model parameter values has been performed. These have all been

Table II Numerical Values of the Model Parameters Used in Figures 4–6 (1 = STY; 2 = MA; 3 = MMA; 4 = EA; 5 = VA) and Corresponding Literature Sources

Parameter	Numerical Value	Source
Reactivity Ratios		
r_{12}	0.75	31
r_{21}	0.18	31
r_{34}	2.03	31
r_{43}	0.24	31
r_{25}	9.00	31
r_{52}	0.10	31
Monomer Concentrations in Aqueous Phase at Saturation		
$[M]_1^{w,*}$	$3.65 \cdot 10^{-3}$ mol L^{-1}	32
$[M]_2^{w,*}$	$6.04 \cdot 10^{-1}$ mol L^{-1}	32
$[M]_3^{w,*}$	$1.60 \cdot 10^{-1}$ mol L^{-1}	32
$[M]_4^{w,*}$	$1.50 \cdot 10^{-1}$ mol L^{-1}	32
$[M]_5^{w,*}$	$2.79 \cdot 10^{-1}$ mol L^{-1}	33
Monomer Densities		
ρ_1	0.88 g cm^{-3}	31
ρ_2	0.95 g cm^{-3}	31
ρ_3	0.91 g cm^{-3}	31
ρ_4	0.92 g cm^{-3}	31
ρ_5	0.94 g cm^{-3}	31
Polymer Density		
ρ_c	1.10 g cm^{-3}	Average value[31]
Monomer Concentrations in Particles at Saturation (Volume Fraction)		
ϕ_1^*	0.60	32
ϕ_2^*	0.85	32
ϕ_3^*	0.71	32
ϕ_4^*	0.85	32
ϕ_5^*	0.85	32

estimated from independent literature sources, as indicated in Table II. Note that the value of ϕ^* has been estimated by averaging the corresponding values of the pure components based on the final polymer composition; moreover, the polymer density has been assumed constant for each examined system.

Styrene–Methyl Acrylate (Van Doremaele et al.[15]).

The objective is to produce $M_c^f = 179$ g of the binary copolymer STY-MA, with constant instantaneous

composition Y_{STY} = 0.29 and minimum batch time. In this case, the values of the parameter A, defined by eq. (35), are 3.51 and 0.87 for STY and MA, respectively, thus indicating that MA is the critical monomer in the flooded interval. Even though the monomer species exhibit rather different water solubilities, the values of the parameter γ, computed through eq. (47) as a function of conversion, indicate that the critical monomer does not change during the reaction. This result is in agreement with the experimental findings, since in the optimal polymerization procedure determined experimentally by Van Doremaele et al.,[15] all the MA was charged in the reactor at the beginning of the reaction.

We can now proceed to calculate the flow rate of STY needed to minimize the reaction time while keeping constant the instantaneous polymer composition through eqs. (40) and (50). In particular, it is found that the value of the monomer flow rate in the flooded interval is $\hat{Q}_{STY}$ = 0.261, while in the starved interval, it remains in the interval 0.236 $\leq \hat{Q}_{STY} \leq$ 0.260. The amount of produced polymer, where the transition from flooded to starved interval occurs, is found to be given by M_c^* = 29.7 g. The amount of STY to be charged initially in the reactor is obtained by subtracting the overall amount of styrene fed to the reactor according to the predicted optimal feed policy from the corresponding amount present in the final copolymer at the desired composition (51.9 g). The obtained value (8.25 g) is in good agreement with that found experimentally (8.0 g).

Finally, in Figure 4, the predicted optimal feed policy is compared with that determined experimentally in terms of the amount of STY fed to the reactor as a function of the amount of polymer pro-
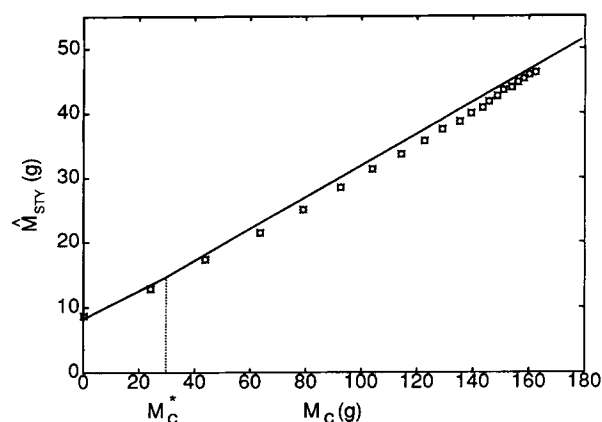
Figure 4 Amount of styrene fed to the reactor, $\hat{M}_{STY}$ as a function of the polymer produced, M_c. ($\square$) Experimental data by Van Doremaele et al.;[15] (———) calculated feed policy.

duced. A satisfactory agreement between model predictions and experimental data is observed. It is worth noting that the curve shown in Figure 4 approaches a straight line, thus indicating that, as mentioned above, the feed flow rate tends to remain substantially constant as a function of conversion. Also, the discontinuity in the value of $\hat{Q}_{STY}$ at M_c = M_c^*, where the transition from flooded to starved interval occurs, accounts for the slope discontinuity in the curve shown in Figure 4. It is worth mentioning that in the simulation above the effect of the seed, used in the experimental run, has been neglected since its overall amount was rather small (less than 2 g of polymer).
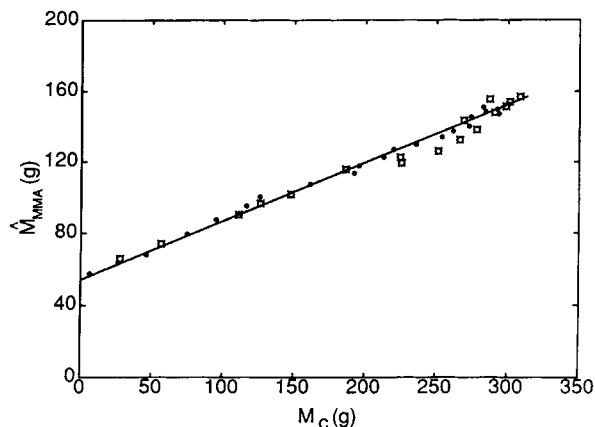
Methyl Methacrylate–Ethyl Acrylate (Arzamendi et al.[29]).

In this case, we consider the production of M_c^f = 389 g of the copolymer MMA–EA with composition Y_{MMA} = 0.5. Note that in the experimental run the reaction was started with 75 g of a prepolymerized seed with the desired composition.

Since the two monomers have similar densities and water solubilities, no change of critical monomer is expected during the reaction. From eq. (35) we see that A_{MMA} = 2.56 and A_{EA} = 0.88, thus indicating that EA is the critical monomer. This monomer was, in fact, entirely charged to the reactor at the beginning of the reaction in the experimental work.

In this case, due to the significant amount of the seed with respect to water and the monomer, the flooded interval is not present. In other words, all the monomer species initially charged in the reactor are fully solubilized by the prepolymerized seed and the water phase, so that no monomer droplets are formed. Accordingly, only the optimal monomer feed policy corresponding to the starved interval (50) has been used. The calculated flow rate of MMA fed to the reactor as a function of conversion ranges from 0.326 to 0.327. The initial value of ϕ is slightly less than the saturation value and is equal to about 0.77. The estimated amount of the noncritical monomer (MMA) to be charged at the beginning of the reaction (53.5 g) is in good agreement with that adopted experimentally (53.8 g).

The detailed comparison between model predictions and experiments is shown in Figure 5 in terms of the amount of MMA added to the reactor as a function of the net amount of produced polymer, i.e., overall amount of polymer in the reactor excluding the seed. Two experimental runs corresponding to two subsequent iterations of the optimization procedure are reported. In general, the agreement between model and experimental results

Figure 5 Amount of methyl methacrylate fed to the reactor, $\hat{M}_{MMA}$, as a function of the polymer produced, M_c. Experimental data by Arzamendi et al.:[29] ($\square$) run 4; ($\bullet$) run 5; (————) calculated feed policy.

is satisfactory. Note that the experimental data corresponding to the fifth experiment (run 5) are closer to the theoretical results than those of the fourth one (run 4), thus confirming that as the number of experimental iterations increases the correct optimal policy was, in fact, approached in the original experimental work.

Methyl Acrylate–Vinyl Acetate (Arzamendi and Asua[30])

The objective is to produce 314 g of an MA–VA copolymer with composition Y_{MA} = 0.5 (in addition to 75 g of a prepolymerized seed with the desired composition). In the examined experiment (run II-1 in Ref. 30), the optimal monomer feed policy, corresponding to minimum reaction time and constant polymer composition, was obtained. In this case, by comparing the values of the parameter A (A_{MA} = 6.13 and A_{VA} = 0.65) given by eq. (35), we see that the critical monomer is VA. Since the two monomers exhibit again very similar water solubilities, this does not change during the reaction, as is it can be readily verified by computing the relevant values of the parameter γ. Similarly to the previous case, the reaction operates in the starved interval throughout the entire process, due to the significant amount of seed initially charged in the reactor.

In Figure 6, the experimental values of the amount of MA added to the reactor as a function of the produced polymer are compared with those predicted through eq. (50). The monomer swelling ratio, ϕ, decreases continuously during the reaction, starting from the initial value ϕ = 0.70, which is lower than the saturation value. A practically constant monomer flow rate is obtained as a function

of conversion, with $\hat{Q}_{MA}$ ranging from 0.435 to 0.442. The predicted amount of MA initially introduced in the reactor (19.1 g) is in good agreement with the corresponding experimental value (18.5 g).

CONCLUSIONS

A general model for semibatch copolymerization reactions has been formulated, by taking the mass of polymer produced (equivalent to conversion) as the evolutionary coordinate. This model includes only a few physicochemical parameters: the reactivity ratios and the monomer water solubilities, whose values are usually available in the literature. It provides an accurate description of the copolymer composition evolution, without involving the uncertain estimation of quantities such as the number of polymer particles or the number of radicals per particle.

The developed model provides the framework for a generalized approach to composition control in emulsion copolymerization. This allows us to realize predefined composition patterns of the produced copolymers by simply operating on the monomer feed rates. In particular, the optimal procedure, in terms of feed policies of the monomer species, for producing with minimum reaction time a given amount of copolymer with constant instantaneous composition and complete monomer depletion has been determined. This result arises as the rigorous solution of the relevant variational problem and applies to any number of monomer species.

The reliability of the theoretical approach has been tested by comparison with experimental data reported in the literature. It is found that, for three
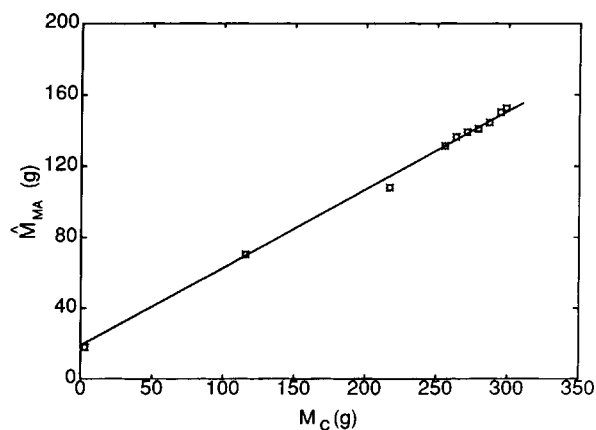
Figure 6 Amount of methyl acrylate fed to the reactor $\hat{M}_{MA}$ as a function of the polymer produced, M_c. ($\square$) experimental data by Arzamendi and Asua[30] (run II-1); (————) calculated feed policy.

different binary systems, the optimal monomer feed policies predicted *a priori* by the developed procedure are in good agreement with those obtained in the original studies through various types of optimization techniques based on experimental iterations of the reaction. It is worth reiterating that the implementation of the procedure developed in this work requires on-line measurement of the amount of polymer produced.

NOMENCLATURE

A_i = $Y_i \rho_c / C_i \rho_i$

B_i = $M_i^{w,*} \rho_c / \phi^* \rho_i$ [g]

C_i polymer-free volume fraction of monomer i in polymer particles

$k_{p_{ji}}$ propagation rate constant of radical j with monomer i [cm^3 (mol s)$^{-1}$]

$\bar{k}_{p_i}$ average propagation rate constant defined by eq. (4) [cm^3 (mol s)$^{-1}$]

$k_{tr_{ji}}$ chain-transfer rate constant of radical j with monomer i [cm^3 (mol s)$^{-1}$]

K_i^l = m_i^l / V_w [cm^{-3}]

m_i^l partition coefficient for monomer i between phase l and aqueous phase, defined by eqs. (14) and (15)

M_c overall amount of polymer produced [g]

M_i overall amount of monomer i in the reactor [g]

$\hat{M}_i$ overall amount of monomer i fed to the reactor [g]

M_i^l amount of monomer i in phase l [g]

$[M_i]^l$ concentration of monomer i in phase l [mol cm$_l^{-3}$]

MW_i molecular weight of monomer i [g mol^{-1}]

$\bar{n}_j$ average number of radicals with terminal unit of type j per polymer particle

$\bar{n}$ average number of radicals per polymer particle

N_m number of monomer species

N_A Avogadro's number [molecules mol^{-1}]

N_p number of particles per unit volume [particles cm$_w^{-3}$]

Q_i massive feed flow rate of monomer i [g s^{-1}]

$\hat{Q}_i$ mass of monomer i fed to the reactor per unit mass of polymer produced [g g^{-1}]

r_{ij} reactivity ratio ($=k_{p_{ii}} / k_{p_{ij}}$)

R_{c_i} overall rate of monomer i consumption [mol s^{-1} cm$_w^{-3}$]

R_c overall polymerization rate [mol s^{-1} cm$_w^{-3}$]

t time [s]

V_c overall volume of polymer [cm^{-3}]

V_l overall volume of phase l [cm$_l^{-3}$]

V_i^l volume of monomer i in phase l [cm$_l^{-3}$]

x_i^l mole fraction of monomer i in phase l

y_i mole fraction of monomer i in the polymer

Y_i weight fraction of monomer i in the polymer = $(y_i MW_i) / (\Sigma_j y_j MW_j)$

z = $M_c^f - M_c$

Greek Letters

α_i volume fraction of monomer i in oil droplets

γ parameter defined by eq. (47)

ρ density [g cm^{-3}]

ϕ_i volume fraction of monomer i in polymer particles

ϕ overall volume fraction of monomer species in polymer particles = $\Sigma_i^{N_m} \phi_i$

Subscripts

c copolymer

d oil droplets

i, j, k monomer species

l generic phase ($d, p,$ or w)

w aqueous phase

p polymer particle

m monomer

Superscripts

d oil droplets

f final

l generic phase ($d, p,$ or w)

p polymer particle

w aqueous phase

$*$ saturation

$\underset{\sim}{0}$ initial

molar

APPENDIX: DETERMINATION OF THE MONOMER COMPOSITION IN THE POLYMER PARTICLES, C_i

In the following, we determine the monomer composition in the polymer particles that allows one to produce a copolymer, with given composition, y_i, in terms of polymer-free volume fractions, $C_i = \phi_i / \phi$. This is the dual of the usual problem of evaluating the polymer composition produced by a given monomer mixture that, with reference

to bulk systems and two monomer species, leads to the classical equation by Mayo and Lewis[22] and Alfrey and Goldfinger.[23]

In the general case of the N_m monomer species, the composition C_i can be evaluated numerically by a successive substitution method. A similar approach was previously reported by Pawda and Schwier[34] with reference to ternary systems. Its formulation arises naturally by rewriting eq. (11) in terms of C_i values, i.e., by expressing the monomer concentrations in the polymer particles, $[M_i]^P$, as $C_i \phi \tilde{\rho}_i$. This leads to

$$C_i = y_i \frac{\sum_j \bar{k}_{p_j} C_j \tilde{\rho}_j}{\bar{k}_{p_i} \tilde{\rho}_i} \quad (A.1)$$

The corresponding solution algorithm results in the following sequence of operations [the apex (n) indicates the set of C_i values corresponding to the generic n-th iteration and the numbers above the arrows refer to the involved equations]:

$$\mathbf{C}^{(n)} \overset{(6)}{\to} \mathbf{P} \overset{(4)}{\to} \bar{\mathbf{k}}_p \overset{(A.1)}{\to} \mathbf{C}^{(n+1)} \quad (A.2)$$

A good first trial solution $\mathbf{C}^{(0)}$ is given by

$$C_i = \frac{y_i/\tilde{\rho}_i}{\sum_j y_j/\tilde{\rho}_j} \quad (A.3)$$

which corresponds to assume equal reactivity values for all monomer species and, therefore, a volume fraction composition of the monomer phase equal to that of the desired polymer. No problem of convergence was found using this first trial solution even in the case of largely different monomer reactivity values.

Finally, let us consider the case where only two monomer species are involved, since it leads to an analytical solution. Equation (A.1) leads to

$$\frac{y_1}{y_2} = \frac{\bar{k}_{p_1} \tilde{\rho}_1 C_1}{\bar{k}_{p_2} \tilde{\rho}_2 C_2} = \text{constant} \quad (A.4)$$

The average rate constants, $\bar{k}_{p_i}$, are evaluated according to eqs. (4)-(8) as follows:

$$\bar{k}_{p_1} = k_{p_{11}} \mathcal{P}_1 + k_{p_{21}} \mathcal{P}_2$$

$$\bar{k}_{p_2} = k_{p_{12}} \mathcal{P}_1 + k_{p_{22}} \mathcal{P}_2 \quad (A.5)$$

where the probability values $\mathcal{P}_i$ are given by

$$\mathcal{P}_1 = \frac{k_{p_{21}} C_1 \tilde{\rho}_1}{k_{p_{21}} C_1 \tilde{\rho}_1 + k_{p_{12}} C_2 \tilde{\rho}_2} \quad \text{and}$$

$$\mathcal{P}_2 = \frac{k_{p_{12}} C_2 \tilde{\rho}_2}{k_{p_{21}} C_1 \tilde{\rho}_1 + k_{p_{12}} C_2 \tilde{\rho}_2} \quad (A.6)$$

By substituting these expressions for $\mathcal{P}_i$ in eqs. (75) and (74) and using the consistency condition

$$C_1 + C_2 = 1 \quad (A.7)$$

a quadratic equation for C_1 (or C_2) is obtained, which can be solved analytically. This represents the dual version of the classical copolymerization equation.[22,23]

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