

Copolymer Composition Control Policies for Semibatch Free Radical Copolymerization Processes

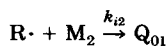
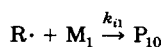
It is well known that a significant copolymer composition drift occurs in batch free-radical copolymerization processes due to the different reactivities of comonomers. Since such composition drift may lead to the copolymers of heterophases and poor physical and mechanical properties, it is very important to operate the polymerization reactor to maintain constant desired copolymer composition. One of the techniques to prevent the composition drift is to operate the reactor in a semibatch mode; i.e., more reactive monomer of monomer mixture is added to the reactor to maintain constant monomer ratio during the course of polymerization. When one designs the semibatch reactor control system, it is first required to obtain feedforward monomer addition policies using accurate kinetic and reactor models. If the molecular weight and molecular weight distribution are also to be controlled, one faces more complex multivariable or multiobjective control problems which require, in general, extensive computation.¹⁻⁴

In this paper, we shall present analytical solutions to the copolymer composition control problems for the semibatch process for two cases: i.e., varying initiator concentration case and constant initiator concentration case. The methodology introduced in this paper will provide a tool useful for the rapid estimation of monomer addition policies in any semibatch free-radical copolymerization processes.

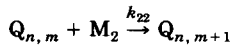
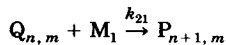
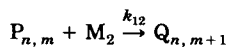
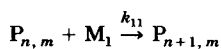
COPOLYMERIZATION KINETICS AND REACTOR MODELS

The following kinetics scheme is used to describe the free radical copolymerization of vinyl monomers:

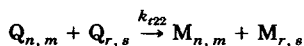
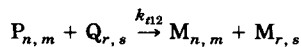
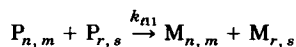
Initiation:



Propagation:



Termination:



Here I is the initiator, $R\cdot$ is the free radical species, and M_1 and M_2 are the monomers. $P_{n,m}$ is a polymer (concentration = $P_{n,m}$) with n units of M_1 and m units of M_2 and terminal M_1 , while $Q_{n,m}$ is a polymer (concentration = $Q_{n,m}$) with n units of M_1 and m units of M_2 and terminal M_2 . Here disproportionation termination and chain transfer reactions are assumed negligible.

Then, the semibatch reactor model for isothermal free radical copolymerization takes the following form:

$$\frac{dM_1}{dt} = \frac{u}{V}(M_{1f} - M_1) - (k_{11}P + k_{21}Q)M_1 \quad (1)$$

$$\frac{dM_2}{dt} = \frac{u}{V}(M_{2f} - M_2) - (k_{12}P + k_{22}Q)M_2 \quad (2)$$

$$\frac{dI}{dt} = \frac{u}{V}(I_f - I) - k_d I \quad (3)$$

$$\frac{dV}{dt} = u \quad (4)$$

where u is the volumetric addition rate of monomer (or monomer mixture) and P and Q are the concentrations of live polymers having terminal M_1 and M_2 units, respectively, represented by the following forms obtained by applying pseudosteady state approximation for live polymer radicals:

$$P = \frac{k_{21} M_1}{k_{12} M_2} Q \quad (5)$$

$$Q = \left[2 f_i k_d I / k_{t11} \left(\frac{k_{21} M_1}{k_{12} M_2} \right)^2 + 2 k_{t12} \left(\frac{k_{21} M_1}{k_{12} M_2} \right) + k_{t22} \right]^{1/2} \quad (6)$$

where f_i is the initiator efficiency.

Now the problem is to find monomer feedrate [$u(t)$] required to maintain constant copolymer composition (or constant comonomer composition in bulk reaction mixture). In other words, the objective is to find the addition rate of monomer such that the desired monomer mole ratio

$$\phi = M_1/M_2 \quad (7)$$

is held constant during the polymerization period. On such polymerization trajectory, the following equation is also valid:

$$\phi = \frac{dM_1}{dM_2} \quad (8)$$

From eqs. (1) and (2), we obtain

$$V = \frac{u(M_{1f} - M_{2f}\phi)}{\phi M_2(k_{11}P + k_{21}Q - k_{12}P - k_{22}Q)} \quad (9)$$

Note that it is not possible to operate the semibatch copolymerization reactor if the feed monomer ratio is the same as the desired monomer mole ratio in the reactor. This is also intuitively obvious. Therefore, more reactive monomer or monomer mixture should be added to the reactor with some nonzero initial reactor volume.

Let us define

$$\alpha \triangleq \left[2f_i k_d / k_{t11} \left(\frac{k_{21}}{k_{12}} \phi \right)^2 + 2k_{t12} \left(\frac{k_{21}}{k_{12}} \phi \right)^2 + k_{t22} \right]^{1/2} \quad (10)$$

$$\beta \triangleq k_{21} [(r_1 - 1)\phi + 1 - r_2] \quad (11)$$

where r_1 and r_2 are reactivity ratios, i.e., $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. Since we are searching deductively for the monomer feedrate which will result constant value of ϕ , those parameters α and β are now considered to be constant. Then the copolymerization modeling equations are reduced to

$$\frac{dM_2}{dt} = \frac{u}{V} (M_{2f} - M_2) - \alpha M_2 I^{1/2} (k_{21}\phi + k_{22}) \quad (12)$$

$$\frac{dI}{dt} = \frac{u}{V} (I_f - I) - k_d I \quad (13)$$

$$\frac{du}{dt} = \frac{\alpha\beta\phi M_2 I^{1/2} u}{M_{1f} - M_{2f}\phi} + \frac{u}{M_2} \left(\frac{dM_2}{dt} \right) + \frac{u}{2I} \left(\frac{dI}{dt} \right) \quad (14)$$

and the reactor volume is given by

$$V = V_0 + \int_0^t u(t) dt \quad (15)$$

where V_0 is the initial reactor volume. If the polymerization is started with initial reactor volume V_0 , then the corresponding initial monomer feed rate is

$$u_0 = \frac{V_0 \phi \alpha \beta I_0^{1/2} M_{20}}{M_{1f} - M_{2f} \phi} \quad (16)$$

Note that $\phi \neq M_{1f}/M_{2f}$. We also observe

$$\text{if } \beta > 0, M_{1f}/M_{2f} > \phi \quad (17a)$$

$$\text{if } \beta < 0, M_{1f}/M_{2f} < \phi \quad (17b)$$

$$\text{if } \beta = 0, \phi = (1 - r_2)/(1 - r_1) \quad (17c)$$

Equation (17c) corresponds to the azeotropic composition, i.e.,

$$x_1 = \frac{\phi}{1 + \phi} = \frac{1 - r_2}{2 - r_1 - r_2} \quad (18)$$

where x_1 is the mole fraction of M_1 . Equations (17a)–(17c) confirm our intuition that the feed stream must be rich in more reactive monomer to maintain constant monomer mole ratio in the bulk reaction mixture.

Therefore, once the initial reactor volume, initial reactant and initiator concentrations, and feed conditions are given, the feed rate of monomers $[u(t)]$ is determined by numerically solving eqs. (12), (13), and (14).

SPECIAL CASE

When the initiator concentration is assumed constant, the monomer addition policy can be determined analytically. The effective initiator concentration in the reactor can be maintained nearly constant over a wide range of conversion by using a high initial concentration of slowly decomposing initiators. For isothermal copolymerization with constant initiator concentration, only eqs. (1), (2), and (4) are considered. In this example, let us assume that only the more reactive monomer (M_1) is added to the reactor, which already contains both comonomers and initiators. Again, it is desired to find monomer addition policy which will lead to the constant monomer mole ratio (ϕ) in the bulk phase. From eqs. (1) and (2), we obtain

$$\frac{dM_1}{dt} = -Qk_{21}M_1 \left\{ \phi + r_2 + [\phi(r_1 - 1) + 1 - r_2] \frac{M_1}{M_{1f}} \right\} \quad (19)$$

and the solution to this equation is given by

$$M_1 = M_{1f} \frac{r_2 + \phi}{\phi(r_1 - 1) + 1 - r_2} \left[\left(1 + \frac{M_{1f}}{M_{10}} \frac{(r_2 + \phi)}{(\phi r_1 - \phi + 1 - r_2)} \right) \exp[Qk_{21}(r_2 + \phi)t] - 1 \right]^{-1} \quad (20)$$

where M_{10} represents the initial concentration of M_1 in the reactor. The volume of the reaction mixture at time t is determined from eqs. (4), (9), and (20):

$$V(t) = V_0 \left(\frac{\lambda - \exp[-Qk_{21}(r_2 + \phi)t]}{\lambda - 1} \right) \quad (21)$$

where

$$\lambda \triangleq 1 + \frac{M_{1f}(r_2 + \phi)}{M_{10}(\phi r_1 - \phi + 1 - r_2)} \quad (22)$$

Thus, the monomer addition rate is represented as follows:

$$u(t) = \frac{VQk_{21}(r_2 + \phi)}{\lambda \exp[Qk_{21}(r_2 + \phi)t] - 1} \quad (23)$$

The concentration of the second monomer is given by

$$M_2 = \frac{M_{1f}(r_2 + \phi)}{\phi(\phi r_1 - \phi + 1 - r_2) \{ \lambda \exp[Qk_{21}(r_2 + \phi)t] - 1 \}} \quad (24)$$

In operating the semibatch copolymerization reactor of varying volume, it is desired to achieve the prespecified conversion of M_2 (i.e. M_{2f}') at the end of polymerization when the reactor reaches its full capacity (V_f). If we specify the desired fractional conversion of M_2 at the end of polymerization,

$$x_{2f} \triangleq \frac{V_0 M_{20} - V_f M_{2f}'}{V_0 M_{20}} \quad (25)$$

then the total polymerization time required to achieve x_{2f} is easily computed from eqs. (21), (24), and (25):

$$t_f = \frac{1}{Qk_{21}(r_2 + \phi)} \ln \left[\frac{M_{10}}{M_{20}\phi(1 - x_{2f})} \right] \quad (26)$$

If $M_{10}/M_{20} = \phi$, then eq. (26) is further reduced to

$$t_f = \frac{1}{Qk_{21}(r_2 + \phi)} \ln \left[\frac{1}{1 - x_{2f}} \right] \quad (27)$$

and the required initial reactor volume (V_0) is

$$V_0 = \frac{V_f(1 - \lambda)}{(1 - x_{2f}) - \lambda} \quad (28)$$

It is interesting to note that the total reaction time (t_f) is independent of feed monomer concentration (M_{1f}) in this case.

Although this special case has some limitations because of the assumption of constant initiator concentration, this analytical solution is useful to quickly estimate the desired reaction time, monomer feed rate, and initial reactor volume.

References

1. A. Tsoukas, M. Tirrell, and G. Stephanopoulos, *Chem. Eng. Sci.*, **37**, 1785-1795 (1982).
2. M. Tirrell and K. Gromely, *Chem. Eng. Sci.*, **36**, 367-375 (1981).
3. K. Y. Choi and D. Butala, *Proc. Am. Automatic Control Conference*, American Automatic Control Council, Minneapolis, MN, June 1987, pp. 307-312.
4. D. Butala, K. Y. Choi, and M. K. H. Fan, *Comput. Chem. Eng.*, (1988), in press.

K. Y. CHOI

Department of Chemical and Nuclear Engineering
and Systems Research Center
University of Maryland
College Park, Maryland 20742

Received January 5, 1988

Accepted March 18, 1988