REACTIVITY RATIO ESTIMATION IN COPOLYMERIZATION: A NEW ANALYSIS OF UNRESOLVED CONFLICTS

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REACTIVITY RATIO ESTIMATION IN COPOLYMERIZATION: A NEW ANALYSIS OF UNRESOLVED CONFLICTS†

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Using a stochastic approach, a fresh analysis has been provided to resolve the possible causes of the existing conflicts in the reactivity ratio estimation in copolymerization systems. The analysis provides some new clues regarding the inadequacy of a transient system (batch reactor) and suggests the use of a steady state operation (CSTR) as a more reliable method.

KEYWORDS   Copolymerization   Reactivity ratio   Stochastic approach.

INTRODUCTION

The knowledge of the reactivity ratios (r_1, r_2) is vital for the design of copolymerization reactors. Over the years a large number of experimental studies on wide ranging systems have been performed with a view to make an experimental determination (Brandup and Immergut, 1978) of the reactivity ratios. The evaluation of r_1 and r_2 has been conventionally carried out by an experimental measurement of the instantaneous concentration of the monomers in the feed (f_1) and copolymer (F_1) and subsequent use of copolymer composition equation.

Despite carefully controlled experimentation and use of sophisticated instrumental techniques, the estimated values of r_1 and r_2 indicate wide scatter (see Figure 1) even when the same experiments are repeated under identical conditions. This problem has worried the polymer scientists constantly and many attempts (e.g. Tidwell and Mortimer, 1970) have been made to identify the real cause for such discrepancies. Our aim is to take a completely fresh look at the problem. We model the copolymerization reacting systems as a Markovian birth-and-death process. The master equations appropriate to the batch and continuous stirred tank reactor systems have been solved by using the expansion method of Van Kampen (1975). The results obtained for the batch and continuous stirred tank reactors are analyzed by us and we have attempted to

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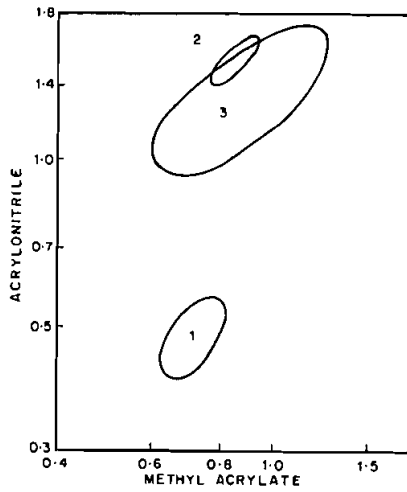
a.SYSTEM : ACRYLONITRILE -METHYL ACRYLATE
(1)-JOSHI AND KAPUR (1954). (2)-MARVEL AND SCHWEN (1957)
(3)-TAMIKADO AND IWAKURA (1959)
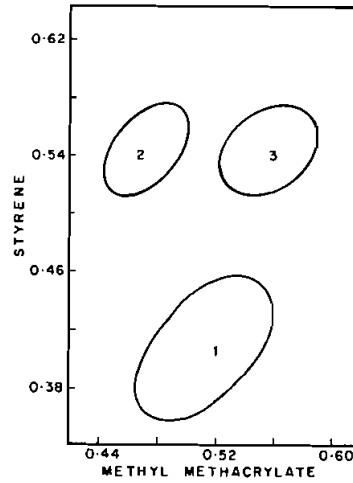
b.SYSTEM : STYRENE - METHYL METHACRYLATE
(1) - ITO AND YAMASHITA (1965).
(2) - MAYO AND LEWIS (1944).
(3) - MEYER (1966).
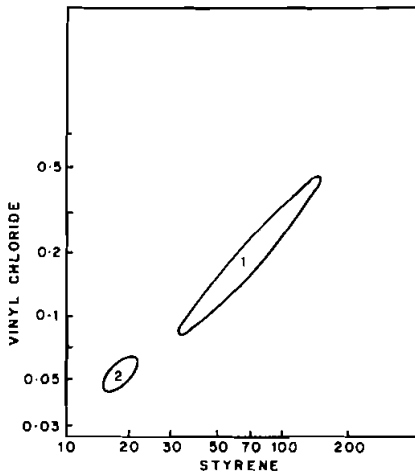
c.SYSTEM : VINYL CHLORIDE - STYRENE
(1)-CHAPIN , HAM AND FORDYCE (1948).
(2)-THOMPSON AND RAINES (1959).
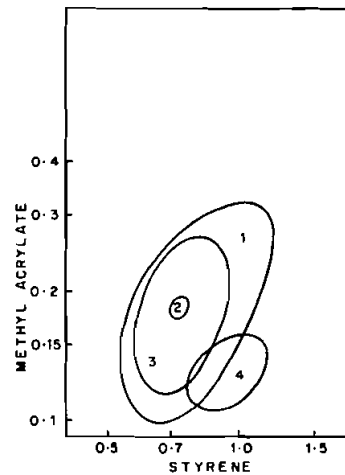
d.SYSTEM METHYL ACRYLATE-STYRENE
(1)- ALFREAY ET AL.(1946).(2)-LEWIS ET AL.(1948).
(3)-MARVEL ANO SHWEN (1957).
(4)-ITO AND YAMASHITA (1965).

FIGURE 1 r_1, r_2 confidence intervals for various copolymerization systems [Tidwell and Mortimer (1970)].

suggest a possible explanation for the observed scatter in the reactivity ratios. To our knowledge such analysis has not appeared in the literature previously.

BATCH COPOLYMERIZATION REACTOR

The phenomenological equations describing the conservation of monomers 1 and 2 in a batch copolymerization reactor can be written as

$$-\frac{dC_1}{dt} = k_1 C_1 C_k^{1/2}; \qquad -\frac{dC_2}{dt} = k_2 C_2 C_k^{1/2} \tag{1}$$

where the parameters k_1 and k_2 refer to the apparent rate constants defined as

$$k_1 = \left[\frac{(r_1-1)C_1}{C_1+C_2} + 1\right] \Big/ T_1^{1/2}; \qquad k_2 = \left[\frac{(1-r_2)C_1}{C_1+C_2} + r_2\right] \Big/ T_1^{1/2} \tag{2}$$

and

$$T_1 = (r_1\delta_1 C_1)^2 + 2\phi_2 r_2 r_1 C_1 C_2 \delta_1\delta_2 + (r_2\delta_2 C_2)^2/2fk_d[(C_1+C_2)]^2 \tag{3}$$

where δ_1, δ_2 refer to the homopolymerization rate constant ratios for monomers 1 and 2, respectively. ϕ_2 pertains to the terms relating to the cross termination process. f is the initiator efficiency, k_d is the rate constant for initiator decomposition, and C_k is the concentration of initiator k.

The above method of representing the rate of copolymerization reorganizes the original rate equations in a more familiar form involving the rate constants and the concentrations. It should be noted, however, that in this recast form the rate constant is not the intrinsic rate constant but involves a dependence on the concentrations of the monomers. This form is more convenient from operational point of view and has been widely employed in both basic and engineering studies (Mecklenburgh, 1970; Balaraman et al., 1983).

Equation (1) can be rewritten in terms of a single variable f_1 as

$$\frac{df_1}{dt} = \frac{af_1^3 + bf_1^2 + cf_1}{(ef_1^2 + gf_1 + h)^{1/2}} \tag{4}$$

where $f_1 = C_1/(C_1 + C_2)$ and $a - h$ are constants involving the reactivity ratios and several rate constants of the propagation and termination rate processes defined as follows:

$$\begin{aligned}
&a = r_1 + r_2 - 2, \qquad b = 3 - 2r_2 - r_1, \qquad c = r_2 - 1, \\
&e = (y_1 - 2\phi_2 + y_2), \qquad g = 2(\phi_2 - y_2), \qquad h = y_2 \\
&x_1 = (2k_{t_{11}}/k_{p_{11}}^2)r_1, \qquad x_2 = (2k_{t_{22}}/k_{p_{22}}^2)r_2, \\
&y_1 = x_1/x_2, \qquad y_2 = x_2/x_1 \quad \text{and} \quad \phi_2 = k_{t_{12}}/[2(k_{t_{11}}/k_{t_{22}})^{1/2}]
\end{aligned} \tag{5}$$

The constants appearing on the rhs of Eq. (4) are absorbed in t which is now defined as $t = t[R_k/x_1 x_2]^{1/2}$, where R_k is the rate of initiation $= 2fk_d C_k$. Equation (5) does not show any explicit dependence on the volume or the size of the

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system. In order to facilitate further calculations, it is necessary to show this dependence explicitly and for this purpose, we transform Eq. (4) using the relation $x = F_1 V$ where x now provides some measure of the partial volume of the size occupied by monomer 1 in the system. It is desirable to simplify Eq. (4) and retain only the dominant terms that would influence the system behaviour strongly. For this purpose we expand the denominator in a binomial series and rewrite Eq. (4) with terms upto second order as

$$\frac{dx}{dt} = 2cx + \left(\frac{2b - cg}{V}\right)x^2 \tag{6}$$

Higher order terms in this equation have been neglected for two reasons. All the terms of the order of (x^n) are accompanied by a factor $(1/V^{n-1})$. For a large volume system the contribution of these terms would therefore be negligible. Secondly the key point that we want to establish here can be better explained by reducing the mathematical algebraic manipulations to the minimum. The higher order terms can then be included to improve upon the approximation, if necessary.

For convenience of identifying the generation and consumption rates Eq. (6) can be written more explicitly as

$$\frac{dx}{dt} = r_2 x - x + \frac{\gamma_1}{V}x^2 - \frac{\gamma_2}{V}x^2 = Q(x) - R(x) \tag{7}$$

where

$$\gamma_1 = (3 + r_2 y_2 + \phi_2) \quad \text{and} \quad \gamma_2 = (2r_2 + r_1 + r_2\phi_2 + y_2) \tag{8}$$

and the constant 2 is absorbed in the time t. The generation and consumption of x as described by the macroscopic Eq. (7), can be modelled using a birth–death formalism as (Lax, 1960)

$$\frac{\partial p(x, t)}{\partial t} = Q(x + 1)p(x + 1, t) + R(x - 1)p(x - 1, t) - [Q(x) + R(x)]p(x, t) \tag{9}$$

where proper identification of Q and R and rearrangement leads to (Milne-Thompson, 1951)

$$\frac{\partial p(x, t)}{\partial t} = r_2(E_x^{-1} - 1)x + (E_x - 1)x + \frac{\gamma_1}{V}(E_x^{-1} - 1)x^2$$

$$+ \frac{\gamma_2}{V}(E_x - 1)x^2 \tag{10}$$

where E_x and E_x^{-1} refer to the difference operators defined as

$$(E_x - 1) = V^{-1/2}\frac{\partial}{\partial x} + \frac{V^{-1}}{2}\frac{\partial^2}{\partial x^2} + \cdots \tag{11}$$

$$(E_x^{-1} - 1) = -V^{-1/2}\frac{\partial}{\partial x} + \frac{V^{-1}}{2}\frac{\partial^2}{\partial x^2} + \cdots \tag{12}$$

The solution of Eq. (9) or (10) in a rigorous manner is rarely possible and a recourse to approximation schemes such as the one proposed by Van Kampen (1970) is necessary. The method (detailed elsewhere), expects the variable x to consist of a macroscopic part $V\phi(t)$ plus fluctuations of the order of $V^{1/2}$. This means that the probability $p(x, t)$ is assumed to be a sharp peak located roughly at $V\phi(t)$ with a width of $V^{1/2}$. Mathematically this can be written as

$$x = V\phi(t) + V^{1/2}y \tag{13}$$

where $V^{1/2}y$ refers to the fluctuating part of variable x. In view of Eq. (13) the probability $p(x, t)$ changes over to new probability $\pi(y, t)$ and the following relationship can be obtained by using a chain rule

$$\frac{\partial \pi}{\partial t} = V^{1/2}\left[V\frac{\partial \phi}{\partial t}\frac{\partial p}{\partial y} + \frac{\partial p}{\partial t}\right] \tag{14}$$

Equation (14) can be utilized in Eq. (10) where the difference operators E_x and E_x^{-1} are replaced using Eqs. (11) and (12) to obtain

$$\frac{\partial \pi}{\partial t} - V^{1/2}\frac{\partial \phi}{\partial t}\frac{\partial \pi}{\partial y} = r_2 V\left[-V^{-1/2}\frac{\partial}{\partial y} + \tfrac{1}{2}V^{-1}\frac{\partial^2}{\partial y^2}\right](\phi + V^{-1/2}y)\pi$$

$$+ V\left[V^{-1/2}\frac{\partial}{\partial y} + \tfrac{1}{2}V^{-1}\frac{\partial^2}{\partial y^2}\right](\phi + V^{-1/2}y)\pi$$

$$+ \gamma_1 V\left[-V^{-1/2}\frac{\partial}{\partial y} + \tfrac{1}{2}V^{-1}\frac{\partial^2}{\partial y^2}\right](\phi^2 + V^{-1}y^2 + 2\phi V^{-1/2}y)\pi$$

$$+ \gamma_2 V\left[V^{-1/2}\frac{\partial}{\partial y} + \tfrac{1}{2}V^{-1}\frac{\partial^2}{\partial y^2}\right](\phi^2 + V^{-1}y^2 + 2\phi V^{-1/2}y)\pi \tag{15}$$

Equation (15) refers to the transformed master Eq. (9) and can be further simplified. Thus all $V^{1/2}$ terms on rhs of Eq. (15) can be collected to obtain

$$-\frac{\partial \phi}{\partial t} = -r_2\phi + \phi + \gamma_2\phi^2 - \gamma_1\phi^2 \tag{16}$$

Equation (16) is identical to the macroscopic Eq. (7) and can be integrated subject to the initial condition $\phi = \phi_0$ at $t = 0$ to obtain

$$\phi = \frac{\phi_0 \exp[(r_2 - 1)t]}{1 + \phi_0[(\gamma_2 - \gamma_1)/(r_2 - 1)]\exp[(r_2 - 1)t] - 1} \tag{17}$$

A pictorial representation of the variation of the macroscopic part with time is shown in Figure 2. On examination of the curve for $r_2 < 1$, Eq. (17) suggests that the macroscopic part ϕ decays exponentially with time ($\phi_{st} = 0$). For $r_2 > 1$, the steady state solution tends to $\phi_{st} = (r_2 - 1)/(\gamma_2 - \gamma_1)$ and the solution exists provided $\gamma_2 > \gamma_1$.

The contributions of the fluctuating part of Eq. (7) can be obtained by collecting all the V^0 term in Eq. (15), i.e.,

$$\frac{\partial \pi}{\partial t} = [1 - r_2 + 2\phi(\gamma_2 - \gamma_1)]\frac{\partial y\pi}{\partial y} + \tfrac{1}{2}\phi(1 + r_2 + \gamma_1\phi + \gamma_2\phi)\frac{\partial^2 \pi}{\partial y^2} \tag{18}$$

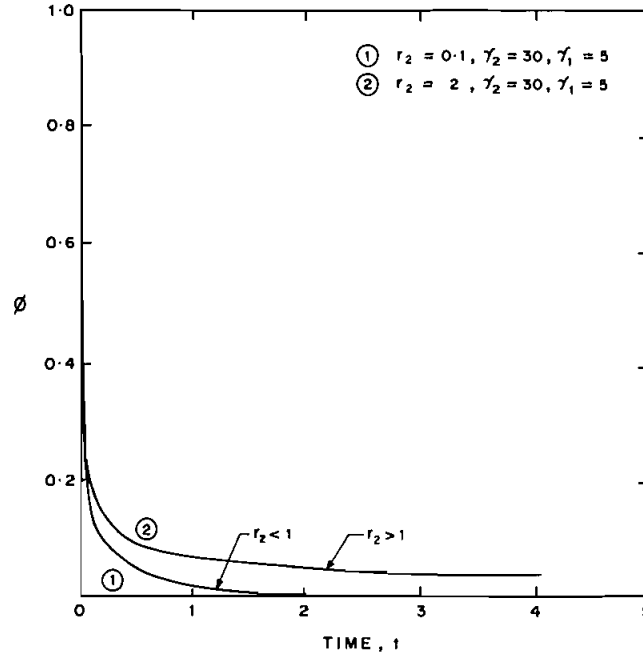## 34 B.D. KULKARNI, K.S. BALARAMAN AND R.A. MASHELKAR

FIGURE 2 Variation of the macroscopic part, ϕ with time.

The mean of the fluctuations ($\langle y \rangle$) is given by (Moyal, 1949)

$$\frac{d\langle y \rangle}{dt} = [r_2 - 1 - 2\phi(\gamma_2 - \gamma_1)]\langle y \rangle \tag{19}$$

Substituting the value of $\phi_{st} = 0$ in Eq. (19) we can obtain the fluctuation around the steady state as

$$\langle y \rangle = \langle y_0 \rangle \exp(r_2 - 1)t \tag{20}$$

Clearly $\phi_{st} = 0$, for $r_2 < 1$, represents a stable solution and according to Eq. (20) the fluctuations die out exponentially. For $r_2 > 1$, the solution $\phi_{st} = 0$ becomes unstable and the fluctuations grow. The system, however, possesses another solution, viz. $\phi_{st} = (r_2 - 1)/(\gamma_2 - \gamma_1)$ and all the branches would lead to this solution for $r_2 > 1$. It is interesting to note that the system possesses the second solution only if $\gamma_2 > \gamma_1$. In the event $\gamma_2 < \gamma_1$ we are left with a situation where only one unstable solution exists. Clearly, the macroscopic part would perform undamped oscillations for this case. In summary, the analysis reveals the following possibilities.

$r_2 < 1$,	$\gamma_2 > \gamma_1$	$\phi_{st} = 0$	Stable solution	
$r_2 > 1$,	$\gamma_2 > \gamma_1$	$\phi_{st} = 0$	Unstable solution	(21)

$$\phi_{st} = \frac{r_2 - 1}{\gamma_2 - \gamma_1} \qquad \text{Stable solution} \tag{22}$$

$r_2 > 1$,	$\gamma_2 < \gamma_1$	$\phi_{st} = 0$	Unstable solution	(23)

We shall pursue the implications of this further. The fact that for different values of parameters different steady states prevail may be considered to be equivalent to a phase transition. Thus for a given copolymer system, changing the temperature could change the equalities shown in Eqs. (21)–(23) leading to a change in the state of the system. The two states of the system are separated by a distance $(r_2 - 1)/(\gamma_2 - \gamma_1)$. Frequently an order of magnitude calculation of this distance reveals that the distance of separation between the states is not sufficient but is of the same order as the fluctuation themselves. This could arise for example when $\gamma_2 \gg \gamma_1$. In order to treat these cases we set $(r_2 - 1)$ equal to a certain multiple of the order of fluctuations as $(r_2 - 1) = V^{-1/2}\Delta$, where Δ is some constant. Following the general method employed earlier, we now obtain the macroscopic solution as

$$\phi = \frac{\phi_0}{1 + (\gamma_2 - \gamma_1)\phi_0 t} \tag{24}$$

while the fluctuations are described in the linear noise approximation as

$$\frac{d\langle y \rangle}{dt} = -\phi[2(\gamma_2 - \gamma_1)\langle y \rangle - \Delta] \tag{25}$$

or at steady state as

$$\langle y \rangle_{st} = \frac{\Delta}{2(\gamma_2 - \gamma_1)} \tag{26}$$

Clearly for this case the fluctuations do not die out but contribute finitely to the average value of the system.

The analysis thus far involves the variable x which is related to the instantaneous concentration of monomer in the feed f_1. These results can be transformed in terms of f_1, since it represents an experimentally measurable quantity. Further, the measured values of f_1 are frequently used in the estimation of r_1 and r_2. In view of the linear relationship between x and f_1, such a result can be obtained easily. It is important to note that the relative contributions of the macroscopic and fluctuating parts remain unaltered on such a transformation. The implications of the results obtained for x are therefore equally valid for f_1.

Let us now examine the implications of the results obtained to see if they can provide any rational explanation for the discrepancies in the values of r_1 and r_2. Most of the measurements for r_1, r_2 are carried out in a batch system. The processes are therefore inherently transient and neither the macroscopic part nor the fluctuating parts have reached any steady state. In a typical situation, where the first possibility in Eq. (21) exists, one would typically obtain ϕ and y profiles, both of which are exponentially decaying with time. It is important to note that the regression rates of both the macroscopic and fluctuating components are identical for this situation. The measured average value x of the system at any time therefore contains a contribution from both fluctuating and macroscopic parts. The extent of these contributions depends on the initial values $\langle x_0 \rangle$ and ϕ_0, and the only restriction imposed on these values is that they satisfy

$$x(0) = V\phi_0 + V^{1/2}\langle y_0 \rangle \tag{27}$$
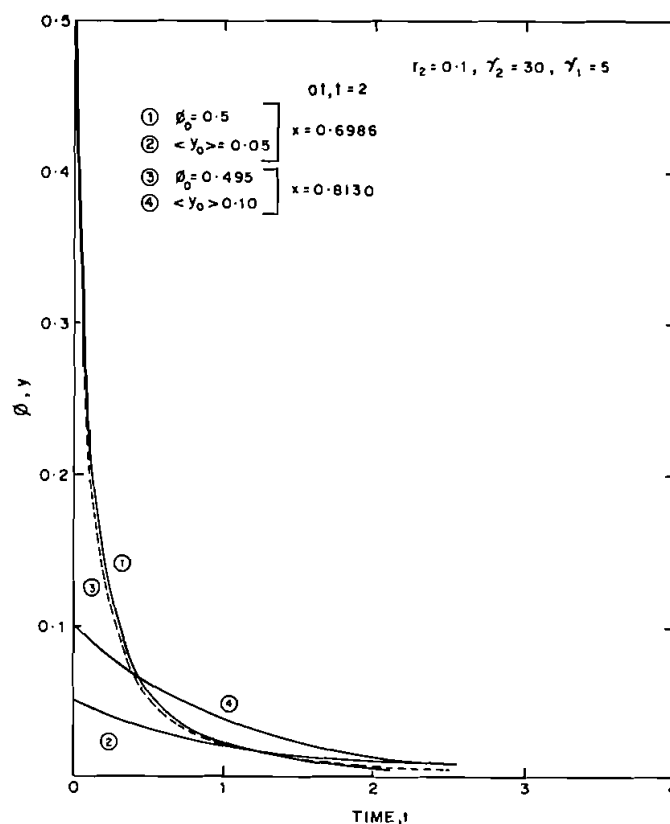
FIGURE 3   Variation of ϕ and y with time.

Many values of ϕ_0 and $\langle y_0 \rangle$ that satisfy this relation can exist. For identical experiments (same $\langle x_0 \rangle$, and other process conditions) this implies different contributions from the two parts. This may give rise to the discrepancy in the measured value of x and therefore the deduced values of the reactivity ratios.

To illustrate this point further, ϕ vs. t and y vs. t profiles for a set of parameter values have been drawn for two different initial conditions of $\phi(0)$ and $y(0)$ in Figure 3. The two initial values of $\phi(0)$ and $y(0)$ have been chosen such that Eq. (27) is satisfied. Let us now calculate the average value of x at some time t later. Thus with the first set of $\phi(0)$ and $y(0)$ as the initial conditions one obtains $x = 0.6986$ while for the second set we get $x = 0.8130$. The simple exercise indicates that despite carrying out identical experiments, the evolution of x can follow different trajectories leading to different values of x.

Similar reasoning applies to the second possibility [Eq. (22)] where additionally even the regression rates of the macroscopic and fluctuation parts are different. This further worsens the extent of discrepancies. In the third possibility the macroscopic part performs undamped oscillations and no information regarding the state of fluctuations can be obtained using the present method.

In essence, the foregoing stochastic analysis for the first time reveals that the existing problem might arise due to the transient measurements of f_1 (or x) where for similar experiments the contributions of the two parts turn out to be different for determination of reactivity ratios.

The use of the continuous stirred tank reactor (CSTR) to be operated under steady state conditions for measurement of r_1 and r_2 was advocated by the present authors (Balaraman *et al.*, 1982) recently. The authors had shown that the primary advantage of the use of CSTR lies in its adaptability to measure the reactivity ratios at all levels of conversion. The CSTR data could be processed easily to deduce the variation of the termination rate processes with extent of conversion. The present analysis favours the use of CSTR from a completely different angle. To prove this point more definitively, it is desirable to carry out a stochastic analysis for the case of CSTR and show that errors due to contributions from the fluctuating parts can be completely avoided. The following analysis demonstrates precisely this point.

CONTINUOUS STIRRED COPOLYMERIZATION REACTOR

Let us consider the case of a CSTR of volume V with input and output streams. The conservation equations for the monomers 1 and 2 are written as

$$V\frac{dC_1}{dt} = F(C_{1_f} - C_1) - Vk_1C_1C_k^{1/2} \tag{28}$$

$$V\frac{dC_2}{dt} = F(C_{2_f} - C_2) - Vk_2C_2C_k^{1/2} \tag{29}$$

where k_1 and k_2 refer to the individual rate constants for the copolymerization of monomers 1 and 2 and F is the volumetric input and output rate. Employing the parameter definitions

$$f_1 = \frac{C_1}{(C_1 + C_2)}; \qquad f_{s_1} = \frac{C_{1_f}}{(C_{1_f} + C_{2_f})}; \qquad \zeta = \frac{C_1 + C_2}{(C_{1_f} + C_{2_f})} \tag{30}$$

and expressing k_1 and k_2 in terms of r_1, r_2 and f_1, Eqs. (28) and (29) can be combined and written in terms of the copolymer composition as

$$\frac{df_1}{dt} = \frac{p - qf_1}{\zeta} + C_k^{1/2}\left[\frac{(r_1 + r_2 - 2)f_1^3 + (3 - r_1 - 2r_2)f_1^2 + (r_2 - 1)f_1}{(ef_1^2 + gf_1 + h)^{1/2}}\right] \tag{31}$$

where ζ refers to the extent of conversion and can be obtained as a solution of

$$\frac{d\zeta}{dt} = p - Ff_1\zeta - C_k^{1/2}\left[\frac{(r_1 - 1)f_1^2 + f_1}{(ef_1^2 + gf_1 + h)^{1/2}}\right]\zeta \tag{32}$$

Some of the coefficients in these equations are defined earlier and the newly introduced parameters are defined as

$$p = Ff_{s_1}, \qquad q = (Ff_{s_1} - Ff_{s_2}) \tag{33}$$

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Equations (31) and (32) can be suitably transformed by using $x = f_1 V$ and $z = \zeta V$

$$\frac{dx}{dt} = \frac{pV^2}{z} - \frac{qVx}{z} + \left[(r_2 - 1)x + \frac{[3 - 2r_2 - r_1 - 2(r_2 - 1)(\phi_2 - y_2)]x^2}{V} \right] \quad (34)$$

$$\frac{dz}{dt} = pV - \frac{Fxz}{V^2} - \left[\frac{x}{v} + \left(\frac{(r_1 - 1)}{V^2} - \frac{(\phi_2 - y_2)}{V^2} \right)x^2 \right] \frac{z}{V} \quad (35)$$

Here the last terms in Eqs. (31) and (32) have been expanded (as before) and only the dominant terms have been retained. The CSTR equation has two additional terms (first two terms in Eq. (34) over and above those corresponding to the batch system) which are related to the extent of conversion (z). The evolution of conversion in CSTR is described by Eq. (35). In contrast, the batch system does not contain these two terms and no explicit dependence on conversion exists. Consequently, a batch system leads to the case of a single component system. Unlike this, in the case of a CSTR we are led to write a multivariate master equation that now involves z and x as two components. This however, poses no problem and the master equation affording a stochastic description can be simply written as (Janssen, 1974)

$$\frac{\partial p(x, z, t)}{\partial t} = \frac{pV^2}{z}(E_x^{-1} - 1) + \frac{qVx}{z}(E_x - 1) + \frac{x(F + 1)}{V^2}$$

$$+ \frac{y_2 x^2 + r_2}{V^3}(E_z - 1)z + \left(pV + \frac{\phi_2 + 1}{V^3} z \right)(E_z^{-1} - 1)$$

$$+ [\ldots \text{ all the terms on rhs of Eq. (10)}] \quad (36)$$

Further defining

$$x = V\phi(t) + V^{1/2}y, \qquad z = V\Psi(t) + V^{1/2}y' \quad (37)$$

and employing the procedure as used earlier we obtain the macroscopic contributions to x and z, respectively, as

$$-\frac{\partial \phi}{\partial t} = -\frac{p}{\Psi} + \frac{q\phi}{\Psi} + \phi(r_2 - 1) + (\gamma_2 - \gamma_1)\phi^2 \quad (38)$$

$$-\frac{\partial \Psi}{\partial t} = -p + F\phi\Psi + [\phi + (r_2 - 1)\phi^2 - (\phi - y_2)\phi^2]\Psi \quad (39)$$

Comparison of Eq. (38) with Eq. (16) reveals that the macroscopic part of the variable x in batch and CSTR system again differs in that the latter contains two additional terms that involve Ψ. The net effect of these terms is to shift the steady state value of the macroscopic part which now is obtained as a solution of the cubic equation

$$\frac{q}{p}(r_2 - 1 - \phi_2 - y_2)\phi_{st}^3 + \left[\frac{q}{p}(F + 1) + (\gamma_2 - \gamma_1) - (r_2 - 1 - \phi_2 + y_2) \right]\phi_{st}^2$$

$$+ [(r_2 - 1) - (F + 1)]\phi_{st} = 0 \quad (40)$$

and Ψ_{st} is related to ϕ_{st} as

$$\Psi_{st} = p/[\phi_{st}(F+1) + \phi_{st}^2(r_2 - 1 - \phi_2 + y_2)] \tag{41}$$

Note that $\phi_{st} = 0$ still represents the solution of a CSTR. Additionally, however, we have two more solutions given by

$$(\phi_{st})_{1,2} = \frac{-l_2 \pm (l_2^2 - 4l_1l_3)^{1/2}}{2l_1} \tag{42}$$

where

$$l_1 = \frac{q}{p}(r_2 - 1 - \phi_2 - y_2); \qquad l_2 = \frac{q}{p}(F+1) + y_2 - y_1 - (r_2 - 1 - \phi_2 - y_2); \tag{43}$$

$$l_3 = (r_2 - 1) - (F+1)$$

The contributions of the fluctuating components to the variable x can be likewise obtained by balancing terms of the order of V^0 in Eq. (36). This leads to an equation for $\langle y \rangle$ which is exactly identical to Eq. (19). The result has important implications. The two additional terms in the CSTR equation alter the macroscopic contribution, but they do not alter the contribution of the fluctuating variable y. Stated simply this means that the evolution of fluctuations in the batch and CSTR systems are identical and in both systems the fluctuations die out if $r_2 < 1$. There is, of course, a vital difference. While the mean of the fluctuations remains unaffected, the spread around the mean value for the two systems is different. This is of course caused by the presence of the second additional term in the CSTR equations. For $r_2 > 1$ the fluctuations tend to grow and the state $\phi_{st} = 0$ becomes unstable. The solution given by Eq. (42) then represents the possible solution of the system and substituting Eq. (42) in Eq. (20) one can obtain the mean of the fluctuations around the steady state. A simple exercise indicates that again the fluctuations die out but now with a different regression rate.

The pathological discussion of what happens when one or the other parameters are changed can continue and can be followed from the equations derived. The essential point to note in the analysis is the fact that in a CSTR one could afford to wait to reach a steady state where contributions from the fluctuating variables are vanishingly small. The measured average value of the variable x would then correspond to the macroscopic value. Any error in estimation is now purely due to the systematic experimental error which can be avoided to a large extent. The data obtained under these conditions would be much more meaningful for estimation purposes and discrepancies can therefore be hopefully avoided.

CONCLUSIONS

Our school has been making a sustained effort towards developing analysis and design strategies for industrially important copolymerization systems. We were concerned for some time by the observation that the discrepancies in the

observed values of the reactivity ratios has triggered off a considerable controversy among polymer scientists over the past two decades. Invariably the errors in the experimental and numerical estimation procedures have been suggested as the possible reasons for this conflict. While those explanations have proved useful in development of more accurate experimental techniques and numerical estimation procedures, the existence of some kind of randomness in the observed values of r_1, r_2 has been generally ignored. It is this observation that led us to take a fresh and deeper look at this problem.

In the present analysis, we have logically incorporated the fluctuations leading to a stochastic formulation and adopted the expansion method that allowed a separate estimation of the macroscopic and fluctuating components. The experiments for obtaining the reactivity ratios are customarily carried out in a batch system, where the analysis indicated a finite contribution to the measured variables from a fluctuating component. Such a contribution depends on the initial level of fluctuation, which can be different, even for two 'identical' experiments. The analysis thus shows the inadequacy of the batch experiments and leads us to explore the use of a steady state technique using a CSTR. The fluctuations are shown to die out in this case, thus implying that data free from uncertainties could possibly be obtained by using such a technique.

It has to be emphasized that the present analysis, is a 'first order' analysis. However, we believe that without developing cumbersome details the key physical idea has been developed clearly. The same framework could be used for development of more elaborate analysis.

NOMENCLATURE

a, b, c parameters defined by Eq. (5)

C_1 concentration of monomer 1

C_2 concentration of monomer 2

e parameter defined by Eq. (5)

E_x operator defined by Eq. (11)

E_x^{x-1} operator defined by Eq. (12)

f initiator efficiency

f_1 composition of monomer 1 in the reactants

f_{s_1} composition of the monomer in the feed at $t = 0$, defined by Eq. (30)

f_2 composition of monomer 2 in the reactants

F flow rate

F_1, F_2 composition of monomers 1 and 2 in the copolymer

g, h parameters defined by Eq. (5)

k_d rate constant for the decomposition of the initiator

k_{11}, k_{12}
k_{21}, k_{22} 　　rate constants for propagation

$\left.\begin{array}{l} k_{t_{11}}, \\ k_{t_{12}}, \\ k_{t_{22}} \end{array}\right\}$ 　　rate constants for termination

l_1, l_2, l_3 　　constants defined by Eq. (43)

p 　　parameter defined by Eq. (33)

$p(x, t)$ 　　probability function defined by Eq. (9)

q 　　parameter defined by Eq. (33)

$Q(x)$ 　　consumption rate of the species, Eq. (9)

r_1, r_2 　　reactivity ratios

$R(x)$ 　　generation rate of the species, Eq. (9)

t 　　time

T 　　temperature

T_c 　　critical temperature

V 　　volume of the reactor

x 　　parameter defined as $f_1 V$

$x_1, x_2,$
y_1, y_2 　　parameters defined by Eq. (5)

y 　　fluctuating component contribution to the variable x defined by Eq. (13)

y' 　　fluctuating component contribution to the variable z defined by Eq. (37)

$\langle y \rangle$ 　　mean of fluctuations defined by Eq. (20)

z 　　parameter defined as V

Greek letters

γ_1, γ_2 　　parameters defined by Eq. (8)

δ_1, δ_2 　　parameters defined by Eq. (3)

$\pi(y, t)$ 　　transformed probability function defined by Eq. (14)

Ψ 　　function defined by Eq. (41)

ζ 　　extent of conversion defined by Eq. (30)

ϕ_2 　　parameter defined by Eq. (5)

$\phi(t)$ 　　macroscopic part of the variable x defined by Eq. (13)

λ 　　external parameter

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Subscripts

f	feed
st	steady state
1	monomer 1
2	monomer 2

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