

# Modeling the Effects of Micromixing and Start-Up Procedures on Bulk Copolymerization and Copolymer in a Tubular Reactor

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## SYNOPSIS

The combined effects of micromixing and start-up procedures on free radical, bulk copolymerization of styrene and acrylonitrile in an isothermal, premixed-feed tubular reactor have been theoretically analyzed. An axial dispersion model, which takes into account the entire range of backmixing, forms the basis of this analysis. Model predictions show that the overall conversion decreases with the increase of initial styrene content in the reactor, and is not affected by the degree of micromixing. However, for the nonazeotropic feed, the copolymer composition distribution becomes wider with the increase of initial acrylonitrile content in the reactor. For the azeotropic feed, broadening occurs with the decrease of initial acrylonitrile content in the reactor. Average copolymer composition is not affected either by micromixing or start-up procedure.

## INTRODUCTION

Copolymerization, which is an industrially important polymer manufacturing process, has several kinetic and phenomenological characteristics. For example, this is an epitome of multireaction systems which consist of free radical initiation, propagation, and termination steps. The participating monomers usually have varying degrees of reactivities. Moreover, the gel/autoacceleration effect occurs, especially in bulk copolymerization, as the conversion increases. This causes an increase in viscosity of the reaction mixture. The combined effect of all these factors is that the properties of the copolymers are mixing sensitive. Several authors<sup>1-5</sup> have modeled the effects of micromixing on copolymerization, and, in recent years, attention has been given to using continuous flow reactors for obvious advantages.

For a given feed composition, the performance of a continuous, copolymerization flow reactor may be intuitively dependent on the start-up procedure. It is to be noted that some polymerization reactions

have been experimentally found to be significantly affected by the start-up procedure.<sup>6</sup> Therefore, although modeling mixing affects copolymerization, the influence of initial feed condition in the reactor also needs to be considered. No modeling work, or theoretical analysis covering this particular aspect, has been reported in the literature. Hence, the objective of this study is to theoretically analyze the combined effects of micromixing and start-up procedure on bulk copolymerization in a tubular reactor. The axial dispersion model which takes into account the entire range of backmixing will be considered to evaluate the effects of backmixing. This model represents complete micromixing and plug flow for  $Pe \rightarrow 0$ , and  $Pe \rightarrow \infty$ , respectively. The bulk copolymerization of styrene and acrylonitrile will be considered because the high conversion kinetics of this system are available in the literature, and also it is industrially important.

## BULK COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE

Balaraman et al.<sup>7-9</sup> used a terminal model to develop the high conversion bulk copolymerization kinetics

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of styrene and acrylonitrile. Employing the  $\phi$  factor form of the termination model, the overall rate of copolymerization was expressed by Mayo and Walling<sup>10</sup> as

$$R_p = \frac{(r_1 c_1^2 + 2c_1 c_2 + r_2 c_2^2) R_1^{1/2}}{[(r_1 \delta_1 c_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 c_1 c_2 + (r_2 \delta_2 c_2)^2]^{1/2}} \quad (1)$$

where  $c_1$  and  $c_2$  are concentrations of monomers 1 and 2, respectively.  $R_1 = 2fk_d c_1$  is the rate of initiation where  $f$  is the initiator efficiency,  $k_d$  is the rate constant for initiator decomposition, and  $c_1$  is the concentration of the initiator I. The various rate groups that appear in eq. (1) are defined as

$$\begin{aligned} r_1 &= k_{p11}/k_{p12}, & r_2 &= k_{p22}/k_{p21} \\ \delta_1 &= (2k_{t11}/k_{p11}^2)^{1/2}, & \delta_2 &= (2k_{t22}/k_{p22}^2)^{1/2} \\ \phi &= k_{t12}/2(k_{t11}k_{t22})^{1/2} \end{aligned}$$

where  $r_1$  and  $r_2$  are called the reactivity ratios of monomers 1 and 2, respectively.  $k_{p11}$  and  $k_{p22}$  are the propagation rate constants for the homopolymerization of monomers 1 and 2, respectively.  $k_{t11}$  and  $k_{t12}$  are the termination rate constants for the homopolymerization of monomers 1 and 2, respectively.  $k_{t12}$  is the termination rate constant for the cross reaction. Equation (1) can be expressed in terms of the rates of consumption of the reacting monomers as follows:

$$R_1 = \frac{-dc_1}{dt} = k_1 c_1 c_1^{1/2} \quad (2)$$

$$R_2 = \frac{-dc_2}{dt} = k_2 c_2 c_1^{1/2} \quad (3)$$

where  $k_1$  and  $k_2$  are the apparent rate constants related to the rates of monomer consumption  $R_1$  and  $R_2$ , respectively. Balaraman et al.<sup>7-9</sup> defined  $k_1$  and  $k_2$  as follows:

$$k_1 = \frac{[(r_1 - 1)f_1 + 1]}{T_1^{1/2}} \quad (4)$$

$$k_2 = \frac{[(1 - r_2)f_1 + r_2]}{T_1^{1/2}} \quad (5)$$

where

$$f_1 = \frac{c_1}{(c_1 + c_2)} \quad (6)$$

$$T_1 = \frac{T_{10}}{(2fk_d)} \quad (7)$$

and

$$T_{10} = (r_1 \delta_1 f_1)^2 + 2\phi r_1 r_2 \delta_1 \delta_2 f_1 (1 - f_1) + [r_2 \delta_2 (1 - f_1)]^2 \quad (8)$$

The values of the various kinetic parameters appearing in the above equations are reported elsewhere.<sup>7-9,11</sup>

## MATHEMATICAL DESCRIPTION OF THE PROBLEM

The following assumptions have been made to formulate the problem.

1. The system is isothermal, and the monomers and the initiator are fed in a premixed mode.
2. The diffusivity of the monomers, and that of the initiator, are the same and do not depend on concentration.
3. The polymer chains do not diffuse.
4. The volume of the reaction mass remains constant.

Literature survey shows that, although extensive modeling work has been conducted in the area, there exists hardly any model which does not consider diffusivity to be constant.<sup>4,5,12,13</sup> However, this assumption may indeed be a good approximation for any real system. In free radical polymerization of methyl methacrylate in tubular reactor studies, Baillagou and Soong<sup>13</sup> pointed out that, in order to avoid the difficult multicomponent diffusion problem, the polymerizing solution can be treated as a pseudobinary system. The polymer molecules and radicals may be treated as one component (the high molecular weight component) and the initiator solvent and monomer molecules as the second constituent (the low molecular weight component) of the mixture. The same diffusivity (the binary mutual diffusivity), can, therefore, be used in all mass balance equations. The mutual diffusion coefficient is a complex function of the concentration, temperature, and molecular weight of the polymer. Diffusivity versus polymer concentration have been plotted for many different systems.<sup>14-16</sup> The plots revealed only weak conversion dependence except at the extremes of the composition domain. This suggests the approximation of constant diffusivity over the entire range of polymer concentration.

Further, for tubular reactors,<sup>17</sup> the axial diffusivity  $D_a$  is related to molecular diffusivity  $D_m$  as

$$D_a = D_m + U^2 \frac{d}{1.92} D_m \quad (9)$$

In the laminar region that is normally experienced in such systems, this equation suggests that, at very low Reynolds number,  $D_a$  approaches  $D_m$  and at higher Reynolds number ( $D_a \propto D_m$ ). As pointed out by Baillagou and Soong,<sup>13</sup>  $D_m$  can be considered independent of concentration and, therefore, the axial diffusivity  $D_a$  may also be assumed reasonably constant for practical situations.

The unsteady state mass balance equations for the monomers and the initiator, using the axial dispersion model, may be written as follows:

$$\frac{\partial c_1}{\partial t} = D_a \frac{\partial^2 c_1}{\partial z^2} - u \frac{\partial c_1}{\partial z} + R_1 \quad (10)$$

$$\frac{\partial c_2}{\partial t} = D_a \frac{\partial^2 c_2}{\partial z^2} - u \frac{\partial c_2}{\partial z} + R_2 \quad (11)$$

$$\frac{\partial c_I}{\partial t} = D_a \frac{\partial^2 c_I}{\partial z^2} - u \frac{\partial c_I}{\partial z} + R_I \quad (12)$$

where  $z$  and  $t$  represent the axial and time coordinates, respectively.  $D_a$  is the axial diffusivity, and  $u$  is the axial velocity of the polymerizing fluid.

Introducing the following dimensionless variables,

$$C_1 = \frac{c_1}{c_{10}}, \quad C_2 = \frac{c_2}{c_{20}}, \quad C_I = \frac{c_I}{c_{10}},$$

$$\bar{z} = \frac{z}{L}, \quad \text{and} \quad \tau = \frac{ut}{L}$$

Equations (10)–(12) can be written as

$$\frac{\partial C_1}{\partial \tau} = \frac{1}{\text{Pe}} \frac{\partial^2 C_1}{\partial \bar{z}^2} - \frac{\partial C_1}{\partial \bar{z}} + \frac{R_1 \bar{t}}{c_{10}} \quad (13)$$

$$\frac{\partial C_2}{\partial \tau} = \frac{1}{\text{Pe}} \frac{\partial^2 C_2}{\partial \bar{z}^2} - \frac{\partial C_2}{\partial \bar{z}} + \frac{R_2 \bar{t}}{c_{20}} \quad (14)$$

$$\frac{\partial C_I}{\partial \tau} = \frac{1}{\text{Pe}} \frac{\partial^2 C_I}{\partial \bar{z}^2} - \frac{\partial C_I}{\partial \bar{z}} + \frac{R_I \bar{t}}{c_{10}} \quad (15)$$

where  $\text{Pe} = uL/D_a$  is the Peclet number,  $L$  is the length of the reactor, and  $\bar{t}$  is the mean residence time. Equations (13)–(15) have the following dimensionless boundary conditions. The initial conditions are to be determined in accordance with the start-up procedures which are given in Table I.

### Boundary Conditions

$$\frac{\partial C_1}{\partial \bar{z}}(\tau, 0) = \text{Pe} \{C_1(0^+) - 1\} \quad (16)$$

$$\frac{\partial C_2}{\partial \bar{z}}(\tau, 0) = \text{Pe} \{C_2(0^+) - 1\} \quad (17)$$

$$\frac{\partial C_I}{\partial \bar{z}}(\tau, 0) = \text{Pe} \{C_I(0^+) - 1\} \quad (18)$$

$$\frac{\partial C_1}{\partial \bar{z}}(\tau, 1) = 0 \quad (19)$$

$$\frac{\partial C_2}{\partial \bar{z}}(\tau, 1) = 0 \quad (20)$$

$$\frac{\partial C_I}{\partial \bar{z}}(\tau, 1) = 0 \quad (21)$$

**Table I Initial Start-Up Conditions of the Reactor**

Case No. <sup>a</sup>	Initial Concentration (mol/L)	Inlet Feed Composition, $\bar{f}_1$ , Molar Fraction	Initial Start-Up Conditions, $\bar{f}_1$ , Molar Fraction
1a	0.0267	0.424	0.000
1b	0.0267	0.424	0.424
1c	0.0267	0.424	0.604
1d	0.0267	0.424	1.000
2a	0.0267	0.604	0.000
2b	0.0267	0.604	0.424
2c	0.0267	0.604	0.604
2d	0.0267	0.604	1.000

<sup>a</sup> 1 = nonazeotropic; 2 = azeotropic.

Equations (16)–(18) represent the Danckwerts boundary conditions,<sup>18</sup> which are widely applied to the axial dispersion model. Note that eqs. (13)–(15) can be solved simultaneously for various values of Pe using the initial conditions given in Table I and the above boundary conditions.

For the axial dispersion model, it is possible to mathematically correlate Pe to the degree of segregation,  $J$ , using the micromixing concepts of Danckwerts<sup>18</sup> and Zwietering.<sup>19</sup> When Pe approaches zero and infinity,  $J$  approaches zero and unity, respectively.

The final relationships may be expressed as follows<sup>20</sup>:

For  $Pe < 16$ ,

$$\frac{\bar{\alpha}}{\bar{t}} = 128 Pe^2 e^{Pe/2} \times \sum_{n=1}^{\infty} \frac{w_n \sin w_n}{(Pe^2 + 4Pe + 4w_n^2)(Pe^2 + 4w_n^2)} \quad (22)$$

$$\frac{\alpha_P(\bar{Z})}{\bar{t}} = 64 Pe^2 e^{Pe\bar{Z}/2} \times \sum_{n=1}^{\infty} \frac{w_n(2w_n \cos w_n \bar{Z} + Pe \sin w_n \bar{Z})}{(Pe^2 + 4Pe + 4w_n^2)(Pe^2 + 4w_n^2)} \quad (23)$$

where  $w_n$ , the eigenvalues, are the positive roots of

$$2w_n \tan \frac{w_n}{2} - Pe = 0 \quad (24)$$

$$2w_n \cot \frac{w_n}{2} + Pe = 0 \quad (25)$$

$$\frac{\text{var } \alpha_P}{\bar{t}^2} = \int_0^1 \left[ \frac{\alpha_P(Z)}{\bar{t}} - \frac{\bar{\alpha}}{\bar{t}} \right]^2 d\bar{Z} \quad (26)$$

$$\frac{\text{var } \alpha}{\bar{t}^2} = 8 Pe \frac{\bar{\alpha}}{\bar{t}} \quad (27)$$

$$J = \frac{\text{var } \alpha_P}{\bar{t}^2} / \frac{\text{var } \alpha}{\bar{t}^2} \quad (28)$$

For  $Pe > 16$ ,

$$\frac{\bar{\alpha}}{\bar{t}} = \frac{1}{2} \left( 1 + \frac{2}{Pe} \right) \quad (29)$$

$$J = \frac{1}{3} \left[ \left( 1 - \frac{\bar{\alpha}}{\bar{t}} \right)^3 + \left( \frac{\bar{\alpha}}{\bar{t}} \right)^3 \right] / \left( \frac{1}{12} + \frac{1}{Pe} + \frac{3}{Pe^2} \right) \quad (30)$$

## CALCULATION OF COMPOSITION DISTRIBUTION

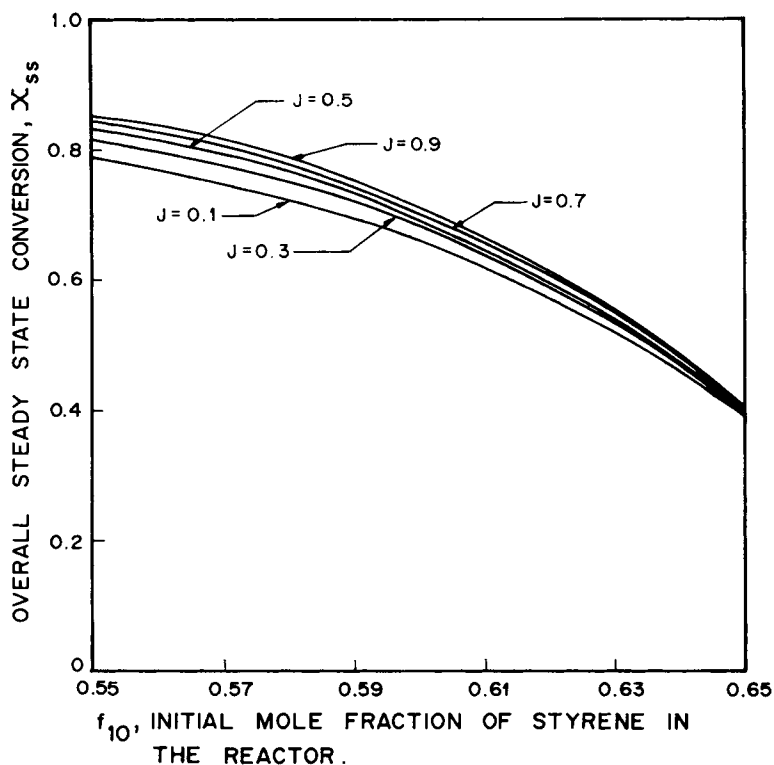
Depending on the start-up procedure and the deviation of the propagation and termination processes at high conversion with the onset of the gel effect, the composition of the molecules is most likely to be random along the length of the reactor. This does not permit the use of the conventional copolymer composition eq. (16). However, all the copolymer molecules will have mole fractions varying between  $0 \leq F_1(\bar{z}) \leq 1$ , where  $F_1(\bar{z}) = R_1(\bar{z}) / \{R_1(\bar{z}) + R_2(\bar{z})\}$ . Therefore, the composition distributions are to be determined by sorting the copolymer molecules into the cells of a histogram based on the value of  $F_1(\bar{z})$ . The number of molecules formed at a given  $\bar{z}$  at steady state is  $m(\bar{z}) \propto \{R_1(\bar{z}) + R_2(\bar{z})\}$ . Thus the composition histogram can be formed. The differential composition distribution,  $g(F_1)$ , is calculated by normalizing the histogram with cumulative moles of copolymer formed. The integral composition distribution  $G(F_1)$  is then calculated by summing the  $g(F_1)$ . The average copolymer composition will be given by  $\bar{F}_1 = \sum g(F_1)F_1$ .

Equations (16)–(21) have been solved from transient to steady state conditions by the method of orthogonal collocation which has been described in detail elsewhere.<sup>11,21–23</sup> The model predictions calculated using the various start-up procedures (see Table I),  $\bar{t} = 1$  h, and temperature = 60°C are discussed in the following section.

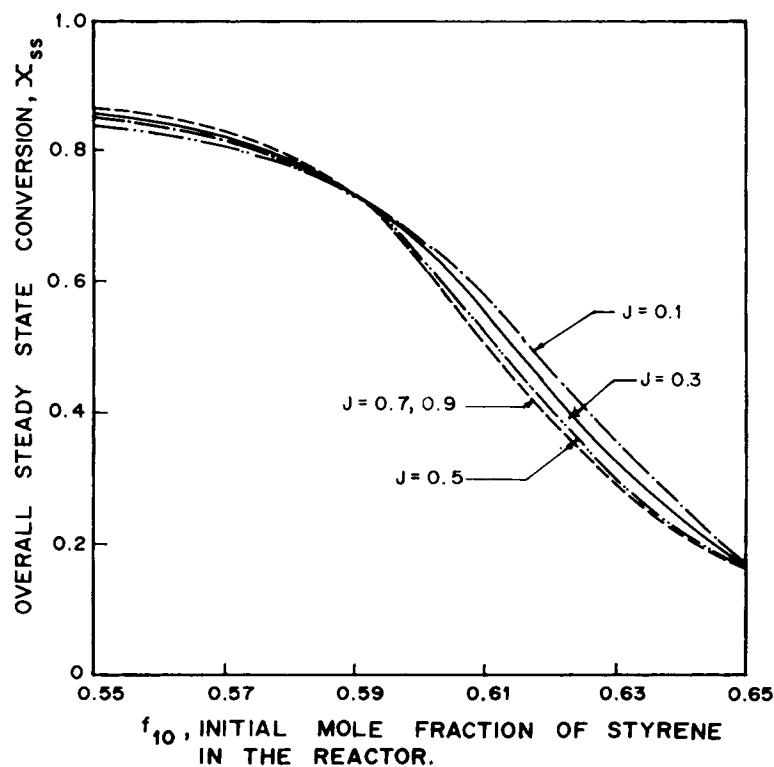
## RESULTS AND DISCUSSION

Figures 1 and 2 show the effects of initial styrene composition in the reactor, and extent of micromixing, in terms of degree of segregation  $J$ , on the overall conversion  $X_{ss}$  for both nonazeotropic and azeotropic feeds, respectively. It is noticed in either case that the overall conversion decreases with the increase of initial styrene content in the reactor. However, the rate of decrease of conversion as a function of initial styrene content is somewhat higher for the azeotropic case. Micromixing happens to have lesser effect on the overall conversion. This point is more evidently shown by Figures 3 and 4 for nonazeotropic and azeotropic cases, respectively.

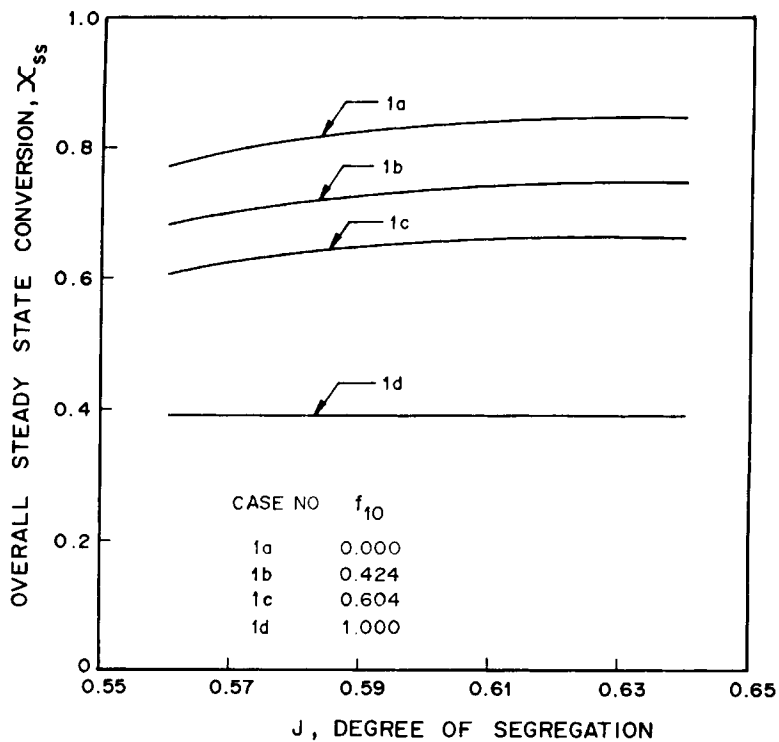
Figures 5 and 6 demonstrate the influence of degree of segregation and the start-up procedures on the copolymer composition distributions for nonazeotropic and azeotropic feed compositions, re-



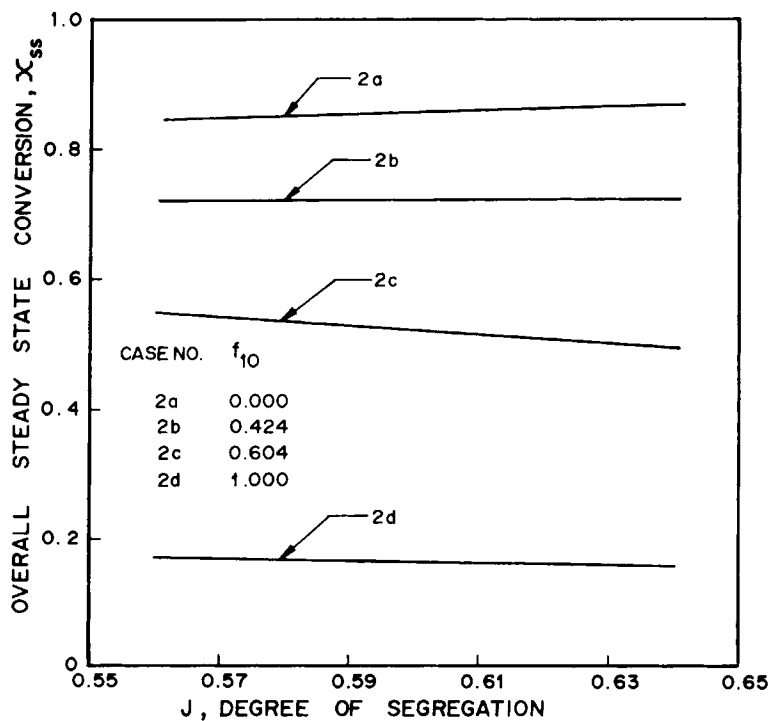
**Figure 1** Effect of start-up conditions on overall steady-state conversion for nonazeotropic feed.



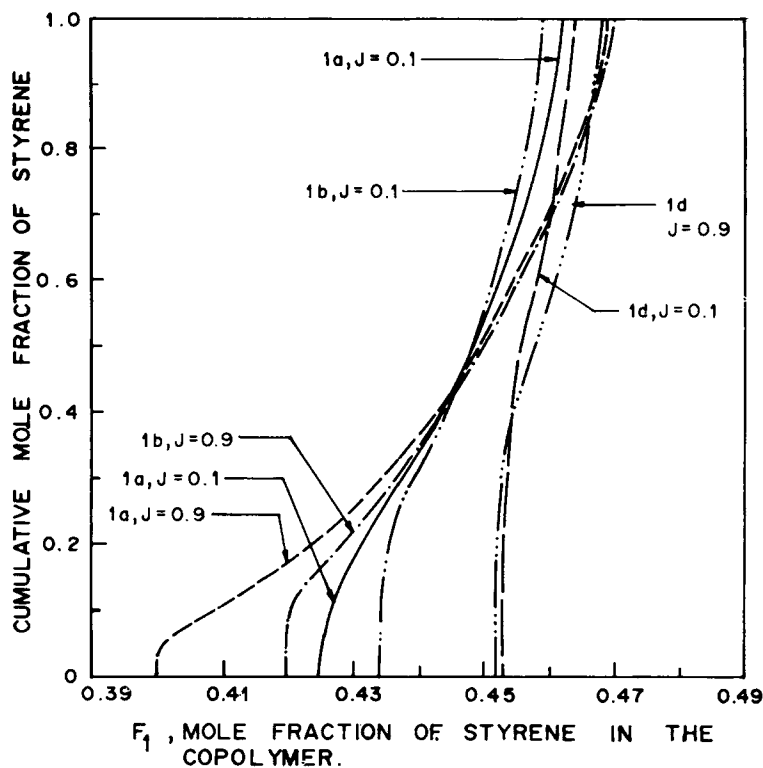
**Figure 2** Effect of start-up conditions on overall steady-state conversion for azeotropic feed.



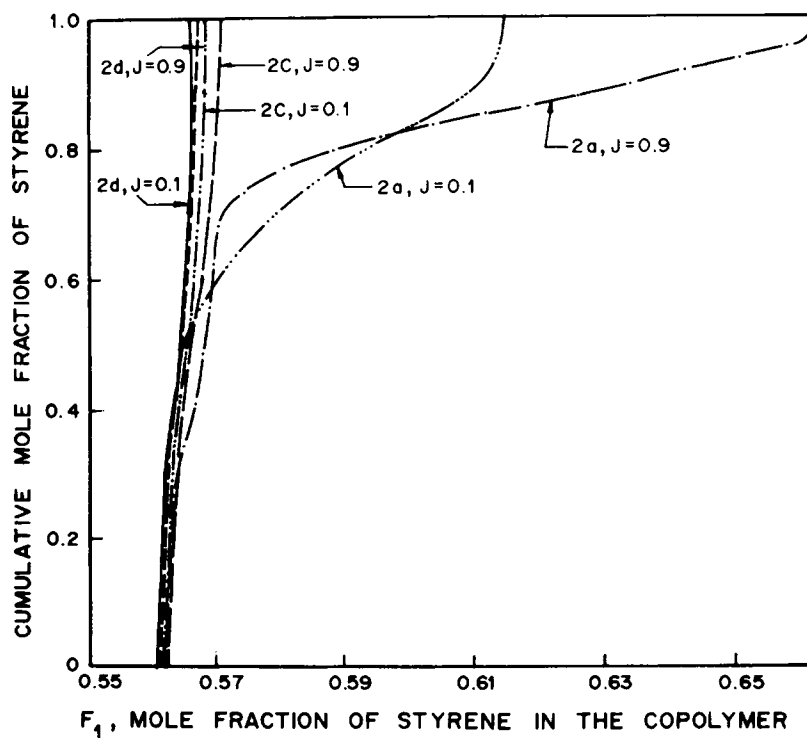
**Figure 3** Variation of overall steady-state conversion as a function of degree of segregation  $J$  for nonazeotropic feed.



**Figure 4** Variation of overall steady-state conversion as a function of degree of segregation  $J$  for azeotropic feed.



**Figure 5** Influence of degree of segregation and start-up conditions on copolymer composition distributions for nonazeotropic feed.



**Figure 6** Influence of degree of segregation and start-up conditions on copolymer composition distributions for azeotropic feed.

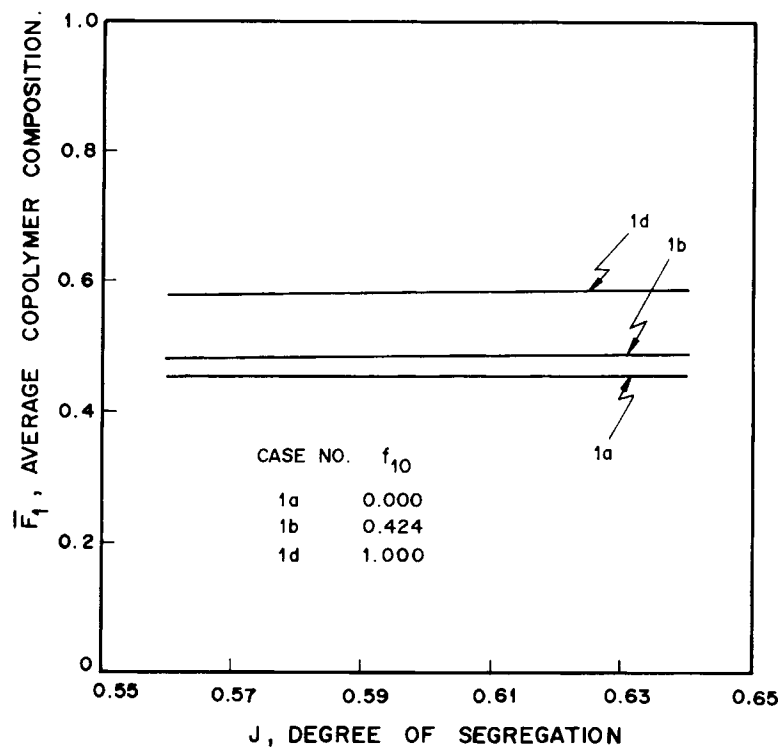


Figure 7 Micromixing effects on average copolymer composition for nonazeotropic feed.

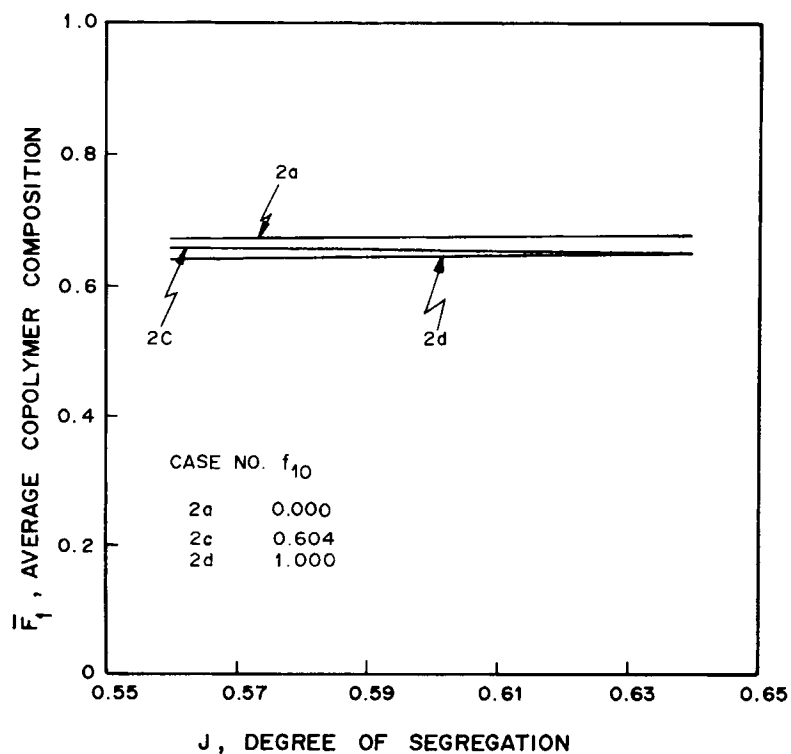
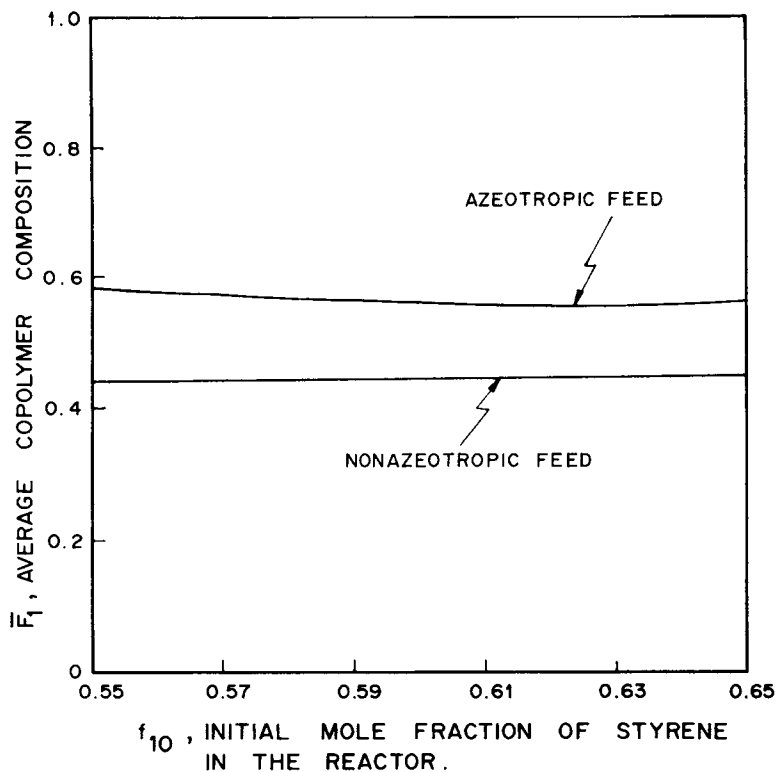


Figure 8 Micromixing effects on average copolymer composition for azeotropic feed.





**Figure 9** Effect of start-up conditions on average copolymer composition for nonazeotropic and azeotropic feeds.

spectively. Two limiting cases have been presented here for each start-up procedure. These are  $J = 0.9$  and  $0.1$ , which correspond to the situations when the reactor approaches plug flow and perfect mixing, respectively. For the same degree of micromixing, the composition distribution becomes broader, for the nonazeotropic feed, with the increase of initial acrylonitrile content in the reactor. However, the model prediction is somewhat different for the azeotropic feed composition. In this case, for the same level of micromixing, the composition distribution becomes wider with the decrease of initial acrylonitrile composition in the reactor. It may be noted that, for the azeotropic feed, micromixing has hardly any effect on the composition distribution when the reactor is initially full of styrene. This may be attributed to the comparatively low overall conversion which probably does not make the reaction mixture highly viscous. Another noteworthy point is the case when both the feed and the reactor bed have monomer composition equal to that of the azeotropic composition. The model prediction exhibits moderate micromixing effects on the copolymer composition distribution. This phenomenon has been reflected because the gel effect has been incorporated into the copolymerization kinetics.

Figures 7 and 8 predict the influence of the micromixing effects on the average copolymer composition  $\bar{F}_1$  for the nonazeotropic and azeotropic feeds, respectively. It may be noted that  $\bar{F}_1$  does not practically vary with the degree of segregation,  $J$ , irrespective of the start-up conditions.

Figure 9 shows the effect of the start-up procedures on the average copolymer composition  $\bar{F}_1$ . It is found that  $\bar{F}_1$  does not, as a matter of fact, change with the variation in the start-up procedures.

## CONCLUSIONS

The combined effects of micromixing and start-up procedures on the bulk copolymerization and copolymer have been mathematically predicted for an isothermal, premixed-feed tubular reactor. An axial dispersion model has been used to evaluate the influence of micromixing. The high conversion kinetics of free radical, bulk copolymerization of styrene and acrylonitrile have been considered for the case study. The model predictions can be summarized as follows:

1. The overall conversion, either for nonazeotropic or azeotropic feed compositions, de-

- creases with the increase of initial styrene content in the reactor.
2. Micromixing does not influence the overall conversion for a given start-up procedure.
  3. The copolymer composition distribution for nonazeotropic feed becomes broader with the increase of initial acrylonitrile content in the reactor. For the azeotropic feed, it becomes so with the increase of styrene content. However, in this case micromixing does not affect the copolymer composition distribution when the reactor initially contained acrylonitrile.
  4. Average copolymer composition is not affected either by micromixing or start-up procedure.

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## NOMENCLATURE

- |                |  |                |   |
|----------------|--|----------------|---|
| $c_1$          | concentration of monomer 1   | $k_{p22}$      | propagation rate constant for homopolymerization monomer 2                      |
| $c_{10}$       | concentration of monomer 1 in the feed   | $p_{p21}$      | propagation rate constant between free radical of monomer 2, and pure monomer 1 |
| $C_1$          | dimensionless concentration of monomer 1, $c_1/c_{10}$                         | $k_{t11}$      | termination rate constant for homopolymerization of monomer 1                   |
| $c_2$          | concentration of monomer 2   | $k_{t22}$      | termination rate constant for homopolymerization of monomer 2                   |
| $c_{20}$       | concentration of monomer 2 in the feed   | $k_{t12}$      | termination rate constant for the cross reaction                                |
| $C_2$          | dimensionless concentration of monomer 2, $c_2/c_{20}$                         | $L$            | length of the reactor   |
| $c_I$          | concentration of initiator I   | $m(\bar{z})$   | moles of copolymer formed at $\bar{z}$ at steady state                          |
| $c_{I0}$       | concentration of the initiator in the feed                                     | Pe             | Peclet number   |
| $C_I$          | dimensionless concentration of the initiator I, $c_I/c_{I0}$                   | $r_1$          | reactivity ratio of monomer 1   |
| $D_a$          | axial diffusivity of the reacting monomers and the initiator                   | $r_2$          | reactivity ratio of monomer 2   |
| $f$            | initiator efficiency   | $R_1$          | rate of initiation  |
| $f_1$          | mole fraction of the polymer-free reaction mixture, $c_1/(c_1 + c_2)$          | $R_p$          | overall rate of copolymerization  |
| $f_{10}$       | mole fraction of the entering feed   | $R_1$          | rate of consumption of monomer 1  |
| $\bar{F}_1$    | average copolymer composition  | $R_2$          | rate of consumption of monomer 2  |
| $F_1(\bar{z})$ | instantaneous copolymer composition  | $T_{10}, T_1$  | rate parameter [see eqs. (7) and (8), respectively]                             |
| $g(F_1)$       | differential copolymer composition distribution                                | $X_{ss}$       | steady state overall conversion   |
| $G(F_1)$       | cumulative copolymer composition distribution                                  | $t$            | time coordinate   |
| $J$            | degree of segregation  | $\bar{t}$      | mean residence time   |
| $k_{p11}$      | propagation rate constant for homopolymerization of monomer 1                  | var $\alpha$   | variances of $\alpha$   |
| $k_{p12}$      | propagation rate constant between free radical of monomer 1 and pure monomer 2 | var $\alpha_p$ | variances of $\alpha_p$   |
|                |  | $z$            | axial coordinate  |
|                |  | $\bar{z}$      | dimensionless axial coordinate, $z/L$   |

## Greek Symbols

- |                      |  |
|----------------------|--|
| $\bar{\alpha}$       | age of a molecule in the reactor         |
| $\alpha_p$           | average age of a molecule within a point |
| $\delta_1, \delta_2$ | ratios of kinetic rate parameters        |
| $\tau$               | dimensionless time coordinate            |
| $\phi$               | cross termination rate constant          |

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