

# Modeling of Bulk Copolymerization Reactor Using Chain-Length-Dependent Rate Constants

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**ABSTRACT:** A mathematical model is developed for a batch reactor in which binary free radical copolymerization occurs. The diffusion-controlled features of the propagation and termination reactions are taken into account by applying the free volume theory, whereas the chain-length-dependent termination rate constant is formulated by using the continuous probability function. Application of the pseudokinetic rate constant method, as well as the terminal model, reduces the complex rate expressions for the copolymerization system to those for the corresponding homopolymerization system. In addition, the moment equations of the living and dead polymer concentrations, as well as the equation for copolymer composition, are derived to compute the average molecular weight and the copolymer composition. The model is proven adequate when applied to the copolymerization system of styrene and acrylonitrile with AIBN(2,2'-azobisisobutyronitrile) initiator. The results of model prediction clearly show that even the propagation reaction is limited by the diffusion of monomers at higher conversion and that the azeotropic fraction of styrene is about 0.6. It is noticed that as the monomer conversion increases, the molecular weight distribution tends to become broader because the weight-average molecular weight increases at a faster rate than the number-average molecular weight. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1015–1027, 1997

**Key words:** copolymerization; styrene–acrylonitrile; chain-length dependence; batch reactor

## INTRODUCTION

Some understanding of polymer structures, polymer kinetics, and polymer properties has been achieved through mathematical modeling of the copolymerization reactor.<sup>1</sup> At high conversions, however, the reaction kinetics shows considerable deviations from the conventional kinetics due to its chain-length-dependent and diffusion-controlled features. Therefore, molecular diffusion behavior in polymer–monomer mixtures has been studied for several decades.<sup>2</sup> Based on the results

of these studies, various models have been proposed to give quantitative descriptions of the rate constants in which chain-length dependency of termination rate constant is neglected.<sup>2</sup> Obviously, these models are inadequate to describe autoacceleration in the copolymerization of styrene and acrylonitrile (SAN).

In this study, it is aimed to develop a mathematical model for a batch reactor in which bulk free radical copolymerization takes place. Application of the free volume theory<sup>3</sup> and the reptation theory<sup>4</sup> makes it possible to describe quantitatively the diffusion-controlled nature of the propagation and termination reactions and also the chain-length dependency of the

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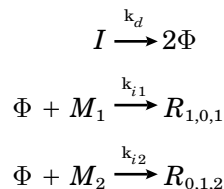
termination reaction rate constant. When these effects on both the propagation and termination reactions are considered, the kinetic expressions for copolymerization system is very much involved. In order to relax the complexity of the kinetic expressions, the pseudokinetic rate constant method (PKRCM), which was introduced by Hamielec and MacGregor<sup>1</sup> and developed further by Tobita and Hamielec,<sup>2</sup> is applied to the binary copolymerization system. The model also contains the moment equations of the living and dead polymer concentrations and the equation for copolymer composition.

The model is then applied to the copolymerization system of SAN and numerical analysis is performed to determine the histories of monomer and initiator conversions and residual styrene mole fraction in a batch reactor. The result turns out to be in good agreement with experimental data reported in the literature.<sup>5</sup> By using this model, both the copolymer composition and the number- and weight-average molecular weights are also predicted under various reaction conditions.

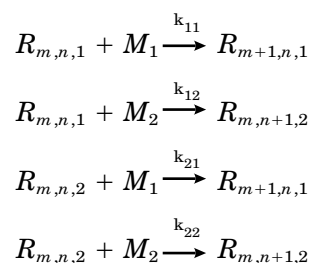
## REACTION KINETICS

In this work, focus is placed on a binary copolymerization in a batch reactor producing linear chains on the basis of the terminal model. Penultimate effects are ignored in all reactions; i.e., the reactivity of the polymer radical is assumed to depend solely on its terminal monomer unit. In the terminal model, the reactivities of two monomers, styrene ( $M_1$ ) and acrylonitrile ( $M_2$ ), and those of the two types of polymeric radicals carrying each of the monomers at the growing chain end, respectively, are distinguished. No chain transfer agent is used. Since the rates of chain transfers to the monomer, initiator, or dead polymer are small, we neglect chain transfer effects. Hence, the binary copolymerization reactions to be considered are as follows.

1. *Initiation reaction.* The bulk copolymerization for SAN with AIBN (2,2'-azobisisobutyronitrile) initiator in a batch reactor is to be considered. The first step is the formation of free radicals  $\Phi$  by decomposition of initiator  $I$  with rate constant  $k_d$ , and then free radical reacts with monomer to form primary radicals.

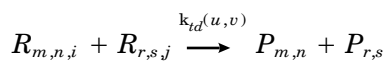


2. *Propagation reaction.* Monomer additions to free radicals  $R_{m,n,i}$  proceed with rate constant  $k_{ij}$ . Terminal model thus gives four distinct propagation rate constants  $k_{11}$ ,  $k_{12}$ ,  $k_{21}$ , and  $k_{22}$ , where  $k_{ij}$  indicates the reaction of polymeric radical  $i$  with monomer  $j$ . It is to be noted that the mechanism assumes a chain-length-independent propagation rate constant. We consider the following four reactions.

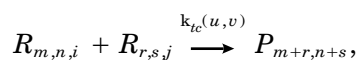


Each of the  $R_{m,n,i}$ s and  $M_j$ s may be comprised of one or more kinetically distinguishable species; hence, the rate constant  $k_{ij}$  is generally a function of composition.

3. *Bimolecular termination.* In the termination reaction, the end monomer unit of polymeric radicals need not be considered since the termination rate constant  $k_t$  is dependent upon the diffusion rate of the growing polymeric radicals in the reaction medium.<sup>5</sup> The chain-length dependence of  $k_t$  begins to appear due to the different translational diffusion rates of polymeric radicals after the onset of entanglement. In the terminal model for copolymerization, there are two possible termination reactions: one by disproportionation; the other by combination. They are as follows:



(disproportionation reaction) and



(combination reaction)

where  $u = m + r$ ,  $v = n + s$ , and  $k_{td}(u, v)$  and  $k_{tc}(u, v)$  are the termination rate constants between two polymeric radicals of chain lengths  $u$  and  $v$ . The other symbols are defined in the nomenclature.

## MATHEMATICAL MODEL

By considering the elementary reactions above, the kinetic rate expressions for the radical and polymer in the copolymerization reaction can be derived as follows:

1. *Initiator and primary radical.* A certain fraction  $f$ , which is called the initiator efficiency, of such species reacts with monomer to form free radicals. The following equations represent the rates of formation for the initiator and primary radical.

$$r_I = -k_d I \quad (1)$$

$$r_\Phi = 2f k_d I - k_{i1} \Phi M_1 - k_{i2} \Phi M_2 \quad (2)$$

2. *Monomers.* The consumption rates of monomers 1 and 2 can be expressed, respectively, as follows:

$$r_{M_1} = -k_{i1} \Phi M_1 - (k_{11} R_{*,1} + k_{21} R_{*,2}) M_1 \quad (3)$$

$$r_{M_2} = -k_{i2} \Phi M_2 - (k_{12} R_{*,1} + k_{22} R_{*,2}) M_2 \quad (4)$$

3. *Radicals with chain length unity.*

$$r_{R_{1,0,1}} = k_{i1} \Phi M_1 - (k_{11} M_1 + k_{12} M_2) R_{1,0,1} - \left\{ \sum_{v=1}^{\infty} k_t(1, v) R_{v,*} \right\} R_{1,0,1} \quad (5)$$

$$r_{R_{0,1,2}} = k_{i2} \Phi M_2 - (k_{21} M_1 + k_{22} M_2) R_{0,1,2} - \left\{ \sum_{v=1}^{\infty} k_t(1, v) R_{v,*} \right\} R_{0,1,2} \quad (6)$$

4. *Radicals with chain length  $m + n$ .*

$$r_{R_{m,n,1}} = (k_{11} R_{m-1,n,1} + k_{21} R_{m-1,n,2}) M_1$$

$$- (k_{11} M_1 + k_{12} M_2) R_{m,n,1} - \left\{ \sum_{v=1}^{\infty} k_t(u, v) R_{v,*} \right\} R_{m,n,1} \quad (7)$$

$$r_{R_{m,n,2}} = (k_{12} R_{m,n-1,1} + k_{22} R_{m,n-1,2}) M_2 - (k_{21} M_1 + k_{22} M_2) R_{m,n,2} - \left\{ \sum_{v=1}^{\infty} k_t(u, v) R_{v,*} \right\} R_{m,n,2} \quad (8)$$

5. *Dead copolymer with chain length  $m + n$ .*

$$r_{P_{m,n}} = \frac{1}{2} \sum_{r=0}^m \sum_{s=0}^n \left\{ k_{tc}(v, u-v) \times \sum_{i=1}^2 \sum_{j=1}^2 R_{r,s,i} R_{m-r,n-s,j} \right\} + \left\{ \sum_{v=1}^{\infty} k_{td}(u, v) R_{v,*} \right\} \times \{R_{m,n,1} + R_{m,n,2}\} \quad (9)$$

where  $R_{i,0,1} = R_{0,i,2} = 0$  ( $i = 0 \sim \infty$ ). The first and second terms of eq. (9) represent the formation rates of dead copolymers by combination and disproportionation, respectively.

## Chain-Length-Dependent Pseudokinetic Rate Constant

Because the kinetics shown above are very complicated, one can reduce the complex rate expressions for the copolymerization reaction to those for the corresponding homopolymerization reaction by applying the PKRCM. The validity of the PKRCM has already been investigated in the context of the terminal model.<sup>6</sup> We shall extend the PKRCM of Xie and Hamielec<sup>7</sup> to the system with both the chain-length-dependent termination and the diffusion-controlled propagation and termination in copolymerization. On the basis of the terminal model for free radical copolymerization, the pseudo-kinetic rate constants for propagation and termination reactions can be expressed by the following equations:

$$\bar{k}_p = \sum_{i=1}^2 \sum_{j=1}^2 k_{ij} \Phi_{*,i} f_j \quad (10)$$

$$\overline{k_t(u, v)} = k_t(u, v) \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{u,i} \Phi_{v,j} \quad (11)$$

in which  $f_i$  is the mole fraction of monomer  $i$ . Termination rate constants by disproportionation and combination reactions are given by

$$\overline{k_{td}(u, v)} = k_{td}(u, v) \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{u,i} \Phi_{v,j} \quad (12)$$

$$\overline{k_{tc}(u, v)} = k_{tc}(u, v) \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{u,i} \Phi_{v,j} \quad (13)$$

To determine pseudo-kinetic rate constants, the polymeric radical fraction  $\Phi_{*,j}$  needs to be calculated. For a binary system,  $\Phi_{*,1}$  is defined as follows:

$$\begin{aligned} \Phi_{*,1} &= \frac{R_{*,1}}{R_{*,1} + R_{*,2}} \\ &= \frac{k_{21}M_1}{k_{21}M_1 + k_{12}M_2} \cong \frac{k_{21}f_1}{k_{21}f_1 + k_{12}f_2} \quad (14) \end{aligned}$$

As the monomer is converted to polymer, the viscoelastic properties of a polymerizing system change enormously. These changes will not affect the rates of chemically controlled reactions such as chain transfer and propagation, except at high conversion. However, changes in viscoelastic properties have a strong influence on those kinetic events that are diffusion-controlled. It has long been realized that termination reactions in free radical polymerization are in the latter category. Any accurate model of polymerization must not only take into account these different mechanisms of termination but also allow the dominant termination mechanism to change with conversion.

In the same manner, various termination pseudo-kinetic rate constants are derived as follows:

$$\begin{aligned} \overline{k_{t,u}} &= \sum_{v=1}^{\infty} \overline{k_t(u, v)} = \frac{1}{2}[k_t(u, u) + \overline{k_t}] \Phi_{u,*}; \\ \overline{k_t} &= \sum_{u=1}^{\infty} \overline{k_{t,u}} \quad (15) \end{aligned}$$

$$\begin{aligned} \overline{k_{td,u}} &= \sum_{v=1}^{\infty} \overline{k_{td}(u, v)} = \frac{1}{2}[k_{td}(u, u) + \overline{k_{td}}] \Phi_{u,*}; \\ \overline{k_{td}} &= \sum_{u=1}^{\infty} \overline{k_{td,u}} \quad (16) \end{aligned}$$

$$\begin{aligned} \overline{k_{tc,u}} &= \sum_{v=1}^{u-1} \overline{k_{tc}(v, u-v)} = \sum_{v=1}^{u-1} k_{tc}(v, v) \Phi_{v,*} \Phi_{u-v,*}; \\ \overline{k_{tc}} &= \sum_{u=1}^{\infty} \overline{k_{tc,u}} \quad (17) \end{aligned}$$

where  $\Phi_{u,*}$  is the polymeric radical fractions of type  $i$  and type  $j$  with chain length  $u$ .

Termination rate constant depends on the length of the growing chain undergoing termination because rates of center-of-mass diffusion of polymeric species vary dramatically with their degree of polymerization. The rate of termination of radicals with chain length  $u$  is described by

$$\begin{aligned} r_{t,u} &= \sum_{i=1}^2 \sum_{j=1}^2 R_{u,i} \sum_{v=1}^{\infty} k_t(u, v) R_{v,j} \\ &= R_{*,*}^2 \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{u,i} \sum_{v=1}^{\infty} k_t(u, v) \Phi_{v,j} \quad (18) \end{aligned}$$

where  $R_{*,*}$  represents the concentration of the polymeric radicals of type  $i$  and type  $j$  with any chain length, and  $\Phi_{u,i} = R_{u,i}/R_{*,*}$  is the polymeric radical fraction of type  $i$  with chain length  $u$ . The total termination rate  $r_t$  is given by

$$\begin{aligned} r_t &= \sum_{u=1}^{\infty} r_{t,u} \\ &= R_{*,*}^2 \sum_{i=1}^2 \sum_{j=1}^2 \sum_{u=1}^{\infty} \Phi_{u,i} \sum_{v=1}^{\infty} k_t(u, v) \Phi_{v,j} \quad (19) \end{aligned}$$

It is reasonable to assume that  $k_t(u, v)$  is the arithmetic average of  $k_t(u, u)$  and  $k_t(v, v)$ , and chain-length dependence may be expressed as  $k_t(u, u) = k_{tcf} f(u)$ , as Soh and Sundberg<sup>8</sup> proposed. Hence,

$$\begin{aligned} k_t(u, v) &= \frac{1}{2} [k_t(u, u) + k_t(v, v)] \\ &= \frac{k_{tcf}}{2} [f(u) + f(v)] \quad (20) \end{aligned}$$

The mole fraction of radicals is essentially independent of chain length provided  $u \geq 2$  and is equal to the total radical mole fraction of the same radical type except for short chains.<sup>2,9</sup> With this equation, eq. (19) can be further simplified as follows:

$$r_t = R_{*,*}^2 \left\{ \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{*,i} \Phi_{*,j} k_{tcf} \right\}$$

$$\times \left\{ \sum_{u=1}^{\infty} f(u) \Phi_{u,*} \right\} = \bar{k}_t R_{*}^2 \quad (21)$$

and  $\Phi_{u,*}$  can be expressed as

$$\Phi_{u,*} = P(u) / \sum_{u=1}^{\infty} P(u) \quad (22)$$

where  $P(u)$  represents the probability that a polymeric radical will survive to become a polymeric radical of chain length  $u$ , which is given by the ratio of propagation rate to propagation and termination rates.<sup>8</sup> By combining the overall termination rate constant and eq. (22), we obtain

$$\bar{k}_t = k_{t,f} \sum_{u=1}^{\infty} f(u) \Phi_{u,*} = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} \overline{k_t(u,v)} \quad (23)$$

Dealing with discrete summations makes computations tedious, so the relative chain length  $y = u/x_c$  is used, where  $x_c$  denotes the critical chain length. Then the ratio  $Z$  can be determined by the following equation<sup>8</sup>:

$$Z = \frac{\bar{k}_t}{k_{t,f}} = \int_0^{\infty} f(y) P(y) dy / \int_0^{\infty} P(y) dy \quad (24)$$

where  $Z$  accounts for the entanglement contribution to the termination rate constant. To calculate the chain-length-dependent termination rate constants, the continuous probability with chain length  $u$  is derived as

$$p(u) = \frac{\bar{k}_p M R_{u,*}}{\bar{k}_p M R_{u,*} + \bar{k}_{t,u} G^2} \quad (25)$$

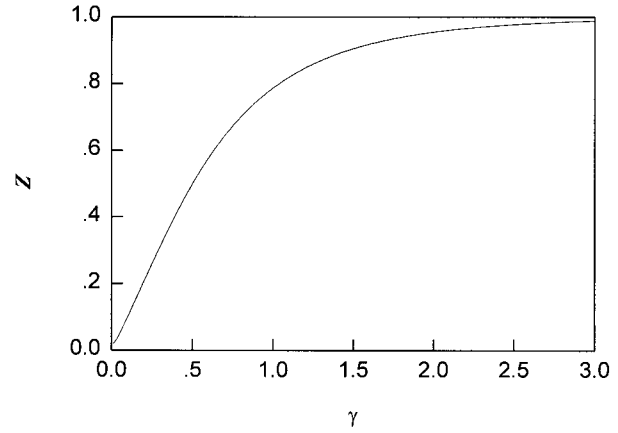
Using eqs. (15) and (25) and some algebra, we obtain the following equation:

$$\begin{aligned} -\ln p(u) &= \ln \left[ 1 + \frac{\gamma}{2x_c} \{f(u) + Z\} \right] \\ &\approx \ln \left[ \frac{\gamma}{2x_c} \{f(u) + Z\} \right] \end{aligned} \quad (26)$$

where

$$\gamma = \frac{x_c k_{t,f} G}{\bar{k}_p M} \quad (27)$$

It is to be pointed out that the pseudosteady-state



**Figure 1** Entanglement contribution to termination rate constant as a function of  $\gamma$  after the onset of chain entanglement.

assumption is not applied here in contrast to the formulation by Soh and Sundberg.<sup>8</sup> The continuous probability can be expressed now by the following relation:

$$\begin{aligned} P(y) &= \prod_{u=1}^y p(u) \\ &= \exp \left\{ -\frac{\gamma}{2} \left( \int_0^y f(y) dy + Zy \right) \right\} \end{aligned} \quad (28)$$

in which the chain length distribution function  $f(u)$  is cast into the continuous variable form  $f(y)$ <sup>10</sup>; that is,

$$f(y) = \begin{cases} 1 & y \leq 1 \\ y^{-2} & y > 1 \end{cases} \quad \text{if } \bar{M}_w \geq x_c M_{av} / \Phi_p \quad (29)$$

This equation is justified by the reptation theory,<sup>4</sup> which indicates that  $f(u)$  for polymer molecules longer than the critical length  $x_c$  is inversely proportional to  $y^2$  after the onset of chain entanglement and that there is no chain-length dependence before the entanglement. To obtain the total termination rate constant, the iteration procedure is needed to calculate  $Z$  with eqs. (24) and (28). This function is proportional to  $y^{-2}$ , which has been confirmed by computer simulation.<sup>10</sup> The relationship,  $Z$  versus  $\gamma$ , after chain entanglement is calculated by eq. (24) and shown in Figure 1.

### Rate and Moment Equations

The use of the PKRCM permits molecular weight average and, in fact, the full molecular weight

distribution to be easily calculated. The moments of live and dead polymers are defined as

$$G_k = \sum_{u=1}^{\infty} u^k R_{u,*}; \quad H_k = \sum_{u=1}^{\infty} u^k P_u$$

$$(k = 0, 1, 2, \dots) \quad (30)$$

Live and dead chain population balances using the PKRCM for a binary copolymerization have already been derived,<sup>9</sup> and, here, only modified key equations will be presented.

1. *Rate expressions for radical and polymer with chain length  $u$ .*

$$r_{R_{u,*}} = \bar{k}_p M (R_{u-1,*} - R_{u,*}) - \bar{k}_{t,u} G^2 \quad (31)$$

$$r_{P_{u,*}} = \left( \frac{1}{2} \bar{k}_{tc,u} + \bar{k}_{td,u} \right) G^2 \quad (32)$$

where pseudokinetic rate constants are defined by eqs. (10) and (15)–(17).

2. *Rate expressions for radical and polymer with chain length unity.* The concentrations of radical and polymer with chain length unity can be similarly written as follows:

$$r_{R_{1,*}} = 2f k_d I - \bar{k}_p M R_{1,*} - \bar{k}_{t,1} G^2 \quad (33)$$

$$r_{P_{1,*}} = \bar{k}_{td,1} G^2 \quad (34)$$

The appearance of eqs. (31)–(34) is the same as that for the homopolymerization reaction system except for the reaction rate constants. Therefore, we can treat these equations as those for homopolymerization during molecular weight modeling.

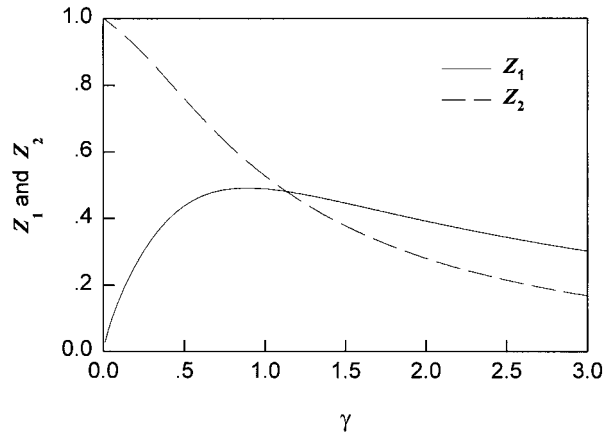
3. *Moment expressions of the polymeric radical concentration.* Using eqs. (31) and (33), one can obtain the following equations for zero, first, and second moments ( $G$ ,  $G_1$ , and  $G_2$ ) of the polymeric radical concentration, respectively.

$$r_G = 2f k_d I - \bar{k}_t G^2 \quad (35)$$

$$r_{G_1} = 2f k_d I + \bar{k}_p M G - \frac{1}{2} \bar{k}_t G G_1 - \frac{1}{2} \bar{k}_{tvf} Z_1 G^2 \quad (36)$$

$$r_{G_2} = 2f k_d I + \bar{k}_p M (2G_1 + G) - \frac{1}{2} \bar{k}_t G G_2 - \frac{1}{2} \bar{k}_{tvf} Z_2 G^2 \quad (37)$$

where



**Figure 2**  $Z_1$  and  $Z_2$  versus  $\gamma$  after the onset of chain entanglement.

$$Z_1 = \sum_{u=1}^{\infty} u f(u) \Phi_{u,*} \quad (38)$$

$$Z_2 = \sum_{u=1}^{\infty} u^2 f(u) \Phi_{u,*} \quad (39)$$

4. *Moment expressions of the dead copolymer concentration.* The moment equations of the dead copolymer concentration are given as follows:

$$r_H = \frac{1}{2} \bar{k}_{tc} G^2 + \bar{k}_{td} G^2 \quad (40)$$

$$r_{H_1} = \frac{1}{2} \bar{k}_{tc} Z_3 G^2 + \frac{1}{2} \bar{k}_{td} G G_1 + \frac{1}{2} \bar{k}_{tdvf} Z_1 G^2 \quad (41)$$

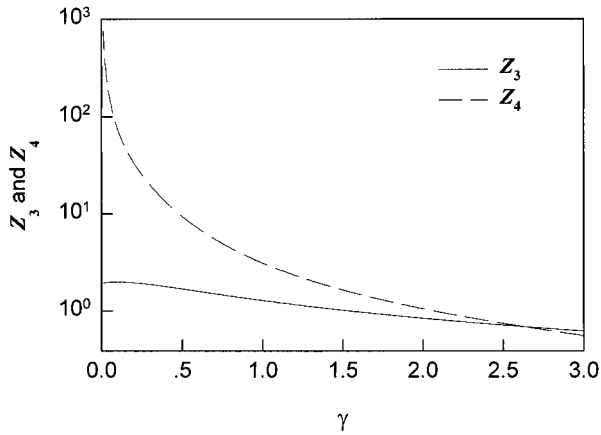
$$r_{H_2} = \frac{1}{2} \bar{k}_{tcvf} Z_4 G^2 + \bar{k}_{td} G G_2 + \frac{1}{2} \bar{k}_{tdvf} Z_2 G^2 \quad (42)$$

where

$$Z_3 = \left( \sum_{u=1}^{\infty} u \Phi_{u,*} \right) Z + Z_1 \quad (43)$$

$$Z_4 = \left( \sum_{u=1}^{\infty} u^2 \Phi_{u,*} \right) + 2 \left( \sum_{u=1}^{\infty} u^2 \Phi_{u,*} \right) Z_1 + Z_2 \quad (44)$$

By using eq. (29) in eqs. (38) and (39), we obtain the continuous variables  $Z_1$  and  $Z_2$ , as shown in Figure 2. The variables  $Z_3$



**Figure 3**  $Z_3$  and  $Z_4$  versus  $\gamma$  after the onset of chain entanglement.

and  $Z_4$  are determined by eqs. (43) and (44) and presented in Figure 3.

### Reference Chain Length

One method of estimating the critical chain length  $x_c$  is given by the following equation<sup>11</sup>:

$$x_c = \frac{x_{co}}{\Phi_p} \cong \frac{2M_e}{M_{av}\Phi_p} \quad (45)$$

where the entanglement molecular weight  $M_e$  is calculated by the equation  $M_e = \rho RT/G_N$ . Here,  $G_N$  denotes the rubbery plateau modulus and,  $\rho$  is the density of polymer. The value of  $M_e$  is an indication of the chain stiffness, being higher for stiffer macromolecules. A simple way to estimate  $G_N$  has been proposed by Tsenoglous.<sup>12</sup> In Tsenoglous's model, the plateau modulus versus composition is given by

$$\begin{aligned} \sqrt{G_N} = & F_1\sqrt{G_{N1}} \left[ 1 + \varepsilon \frac{F_2\sqrt{G_{N2}}}{F_1\sqrt{G_{N1}}} \right]^{-0.5} \\ & + F_2\sqrt{G_{N2}} \left[ 1 + \varepsilon \frac{F_1\sqrt{G_{N1}}}{F_2\sqrt{G_{N2}}} \right]^{-0.5} \end{aligned} \quad (46)$$

where  $\varepsilon$  is the parameter that represents the effect of the thermodynamic interaction on the entanglement probability. For the SAN copolymer, we find  $G_{N1} = 0.17$  and  $G_{N2} = 1.27$  MPa from the literature.<sup>13</sup> The entanglement molecular weight is calculated as a function of the copolymer compo-

sition at 40 and 60°C, respectively, by using the above expressions and is shown in Figure 4.

### Mass Balance and Copolymer Properties

With the above rate expressions, the following mass balance equations can be derived for initiator, monomer, living polymer, and dead polymer, respectively, as follows:

$$\frac{1}{V} \frac{d(XV)}{dt} = r_X \quad (47)$$

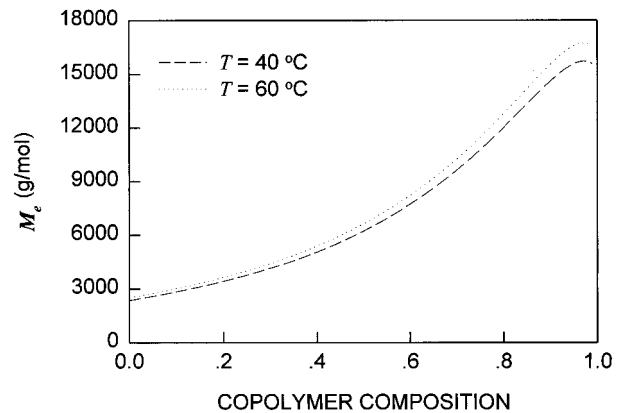
where  $X$  represents each of  $I$ ,  $M$ ,  $G$ ,  $G_1$ ,  $G_2$ ,  $H$ ,  $H_1$ , and  $H_2$ .

Since there is usually a change in density as monomers are converted to polymer, the volume  $V$  of the reaction mixture in a batch reactor shrinks as the reaction proceeds. The change in the volume of the reaction mixture can be calculated by the following equations.

$$V_{M_1} = (M_1V) \frac{Mw_1}{\rho_{M_1}}, \quad V_{M_2} = (M_2V) \frac{Mw_2}{\rho_{M_2}} \quad (48)$$

$$\frac{dV_p}{dt} = -\frac{1}{\rho_p} \left( \sum_{i=1}^2 Mw_i \frac{d(M_iV)}{dt} + V_p \frac{\partial \rho_p}{\partial T} \frac{\partial T}{\partial t} \right) \quad (49)$$

Equation (49) is a rearranged version of the total mass balance equation. In the case of the SAN batch reactor, the volume change amounts to 15–20%, depending on the initial mole fraction of styrene if calculated by eqs. (48) and (49) with 0.05M AIBN at 60°C. These results are presented



**Figure 4** Entanglement molecular weight versus copolymer composition.

in Figure 5 for various initial mole fractions of styrene  $f_0$ .

The physical and mechanical properties of copolymers are related to average molecular properties of the polymer, such as number- and weight-average molecular weights. These average molecular properties can be obtained from the moment equations of polymeric radical concentration. Based on the above equations, the molecular weight developments in a batch copolymerization reactor can be derived. The number- and weight-average molecular weights of the accumulated copolymer are given by

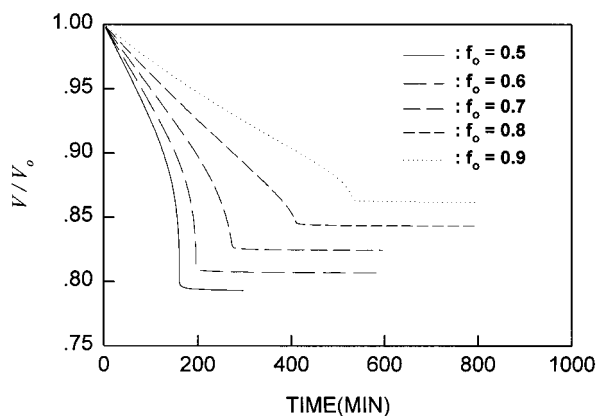
$$\overline{M}_n(t) = \frac{\int_0^t \{d(G_1V)/dt + d(H_1V)/dt\} M_{av}(t) dt}{\int_0^t \{d(GV)/dt + d(HV)/dt\} dt} \quad (50)$$

$$\overline{M}_w(t) = \frac{\int_0^t \{d(G_2V)/dt + d(H_2V)/dt\} M_{av}^2(t) dt}{\int_0^t \{d(G_1V)/dt + d(H_1V)/dt\} M_{av}(t) dt} \quad (51)$$

where  $M_{av}$  is the average molecular weights of styrene and acrylonitrile at any moment, which is defined by

$$M_{av}(t) = Mw_1F_1 + Mw_2F_2 \quad (52)$$

where  $F_i$  is the mole composition of monomer  $i$  in the copolymer produced instantaneously.



**Figure 5** Volume contraction during the course of copolymerization with 0.05M AIBN at 60°C.

**Table I** Parameters Used in the Model for SAN Copolymerization

Parameters	Values	Reference <sup>a</sup>
Physical Properties		
$A$	$92.0/\chi_c$	*
$B$	1.7	*
$\nu_{Fcr,21}$	0.033	*
$\nu_{Fcr,22}$	0.032	*
$T_{gM1}$ [K]	185.0	18
$T_{gM2}$ [K]	190.38	18
$T_{gp}$ [K]	378.2	18
$\alpha_{M1}$ [K <sup>-1</sup> ]	$1.00 \times 10^{-3}$	18
$\alpha_{M2}$ [K <sup>-1</sup> ]	$1.25 \times 10^{-3}$	18
$\alpha_p$ [K <sup>-1</sup> ]	$2.5 \times 10^{-4}$	18
$r_1$	0.331	19
$r_2$	0.053	19
Rate Constants		
$k_d$ [s <sup>-1</sup> ]	$1.5 \times 10^{15} \exp(-154500/T)$	20
$(k_{11})_0$ [l/mol/s]	$2.17 \times 10^7 \exp(-3905/T)$	20
$(k_{22})_0$ [l/mol/s]	$1.56 \times 10^{12} \exp(-7776/T)$	21
$k_{r1}$ [l/mol/s]	$8.20 \times 10^9 \exp(-1747/T)$	20
$k_{r2}$ [l/mol/s]	$1.71 \times 10^{14} \exp(-4648/T)$	*

<sup>a</sup> Parameters marked by an asterisk were estimated from the data in the confidence interval.<sup>5,14-17</sup>

## RESULTS AND DISCUSSION

In this work, a mathematical model is developed to describe the behavior of the batch reactor for the bulk copolymerization of SAN, and this model is used to calculate the conversion and residual styrene mole fraction and to predict copolymer compositions and molecular weights.

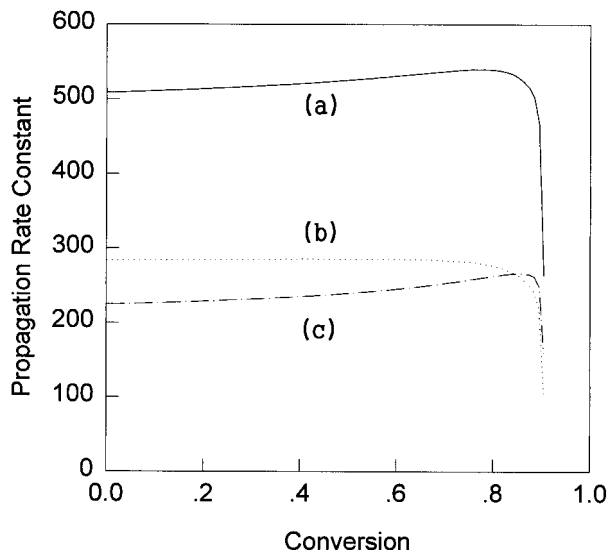
Experimental data for bulk copolymerization of styrene and acrylonitrile have been reported in the literature by Garcia-Rubio et al.<sup>5</sup> Batch runs in long glass ampoules were performed over a range of initial mole fractions of styrene  $f_0$  (0.5, 0.6, 0.7, 0.8, and 0.9) at two different levels of AIBN initiator concentration (0.01 and 0.05M) and at two different temperatures (40 and 60°C). The data are used in the following for comparison between experiment and modeling.

There are a large number of kinetic parameters used in the model for SAN copolymerization as listed in Table I.

### Propagation Rate Constant

In the diffusion-controlled region, the four propagation rate constants can be modeled by using the free volume theory proposed by Jones et al.<sup>3</sup>





**Figure 6** Variation in the propagation rate constant with respect to the conversion for bulk copolymerization of SAN: (a) overall  $k_p$ , (b)  $k_p$  for styrene, and (c)  $k_p$  for acrylonitrile.

$$k_{ij} = \frac{(k_{ij})_o (k_{jj})_o \exp[-B(1/v_F - 1/v_{Fcrij})]}{(k_{ij})_o + (k_{jj})_o \exp[-B(1/v_F - 1/v_{Fcrij})]} \quad (53)$$

where  $B$  is a parameter that determines the rate at which the  $k_{ij}$  falls off with decreasing free volume, and the  $v_{Fcrij}$ s are the critical free volume fractions at the onset of diffusion-controlled propagation for the  $i$ th radical type and the  $j$ th monomer type ( $i$  and  $j$  are 1 or 2). The free volume fraction of the mixture is determined by the weighted sum

$$v_F = 0.025 + \alpha_p(T - T_{gp})\Phi_p + \alpha_{M_1} \times (T - T_{gM_1})\Phi_{M_1} + \alpha_{M_2}(T - T_{gM_2})\Phi_{M_2} \quad (54)$$

where  $\alpha_i$  is the difference in the thermal expansion coefficient above and below the glass transition temperature  $T_{gi}$ , and  $\Phi_i$  is the volume fraction of the particular component in the solution. Subscript  $p$  and  $M_1$  and  $M_2$  denote SAN copolymer, styrene monomer, and acrylonitrile monomer, respectively.

As one can see in Figure 6, the propagation rate constant shows a relatively small change up to a very high conversion level (0.8) and then falls off dramatically because of the diffusion-controlled feature.

### Termination Rate Constant

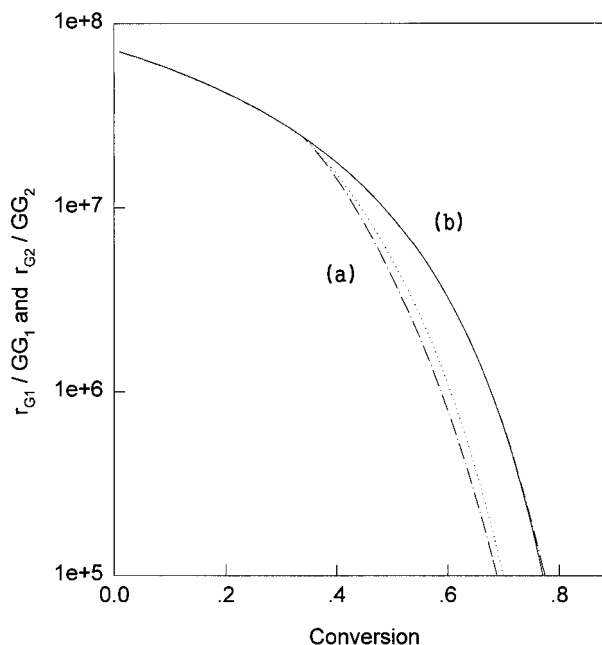
The chain-length dependence of termination reaction is simulated by the present model and pre-

sented as a function of the monomer conversion in Figure 7. As expected from eqs. (36) and (37), the curves for  $r_{G1}/GG_1$  and  $r_{G2}/GG_2$  turn out to be (a) distinct or (b) almost identical when the chain-length dependence (a) is or (b) is not taken into account. During the initial stages of polymerization, the chain-length dependence is negligible, as one can see in Figure 7, so only a single value is required to model the termination reaction. As the reaction proceeds and the polymer concentration increases, however, the values with chain-length dependency fall faster than the value without chain-length dependency. This indicates that the termination reaction in this system is chain-length dependent when polymer-monomer mixtures are entangled. In this region, the termination rate constant, which takes into account the chain-length dependency, could be modeled as

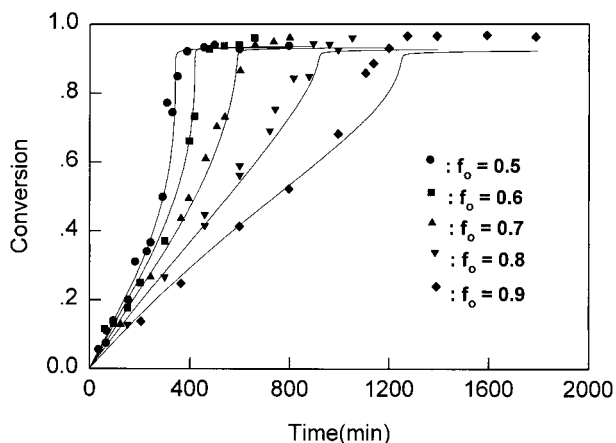
$$\bar{k}_t = \bar{k}_{t0} \frac{Z}{Z_e} \exp\left[-A\left(\frac{1}{v_F} - \frac{1}{v_{Fcr}}\right)\right] \quad \text{for } v_F \leq v_{Fcr} \quad (55)$$

where the  $Z_e$  is the value of  $Z$  at the onset of the entanglement, which may be determined by eq. (24).

If the polymer-monomer mixture is not entan-



**Figure 7**  $r_{G1}/GG_1$  (dot) and  $r_{G2}/GG_2$  (dash-dot) (a) with or (b) without the chain-length dependency for  $I_0 = 0.05M$  and  $f_0 = 0.5$  at  $T = 60^\circ C$ .



**Figure 8** Conversion history for SAN copolymerization in a batch reactor with 0.01M AIBN at 60°C. The curves represent the results of model calculation, whereas the filled keys denote the experimental data taken from the literature.<sup>5</sup>

gled,  $Z$  is equal to 1.0, and the initial termination rate constant may be calculated by the composition-weighted average of the homopolymerization termination rate constants; that is,

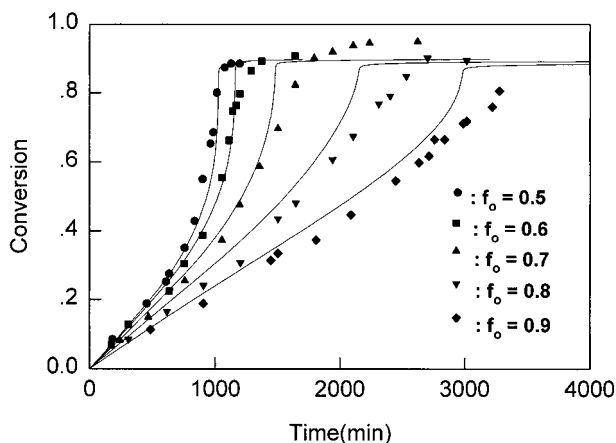
$$\overline{k_{t0}} = F_1 k_{t1} + F_2 k_{t2} \quad (56)$$

This seems to indicate that the termination is controlled by one or more units at the chain end. As the number of units of this “active” portion of the chain increases, its composition rapidly approaches that of the whole chain.

### Conversions and Residual Styrene Mole Fractions

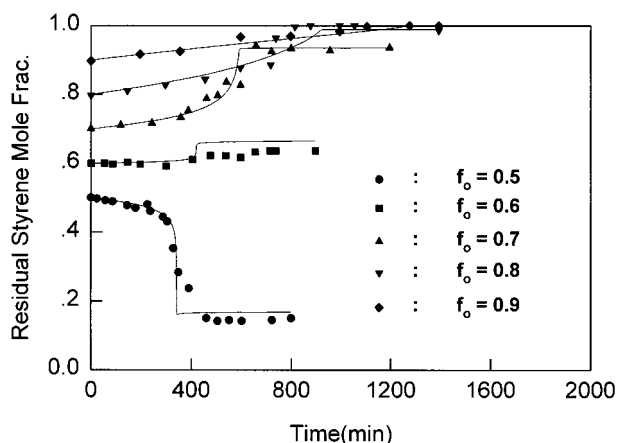
Numerical simulation of the mathematical model developed above is performed to determine the history of the monomer conversion in a batch copolymerization reactor. The results are presented in Figures 8 and 9, in which the curves represent the simulation results, and the filled keys represent the experimental data reported in the literature.<sup>5</sup> The figures show the dependence of the conversion history on the temperature (60 and 40°C), the initial initiator concentration (0.01 and 0.05M AIBN), and the initial monomer composition ( $f_o = 0.5$ –0.9). In all cases, the conversion history is found to be in good agreement with the experimental data. It is noticed that a limiting value of the monomer conversion exists because even the propagation reaction is controlled by diffusion of monomers at high conversion level.

For the residual styrene mole fraction, the

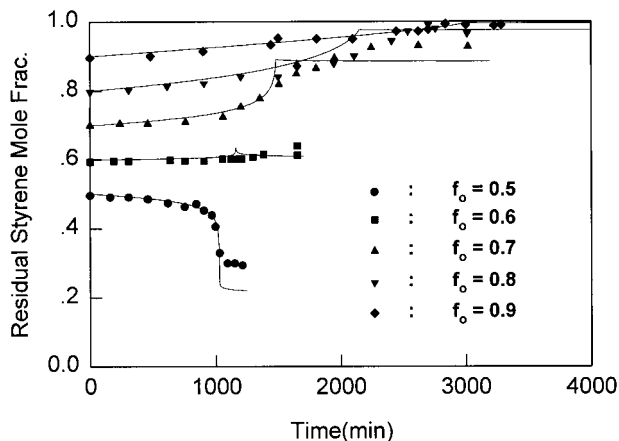


**Figure 9** Conversion history for SAN copolymerization in a batch reactor with 0.05M AIBN at 40°C. The curves represent the results of model calculation, whereas the filled keys denote the experimental data taken from the literature.<sup>5</sup>

curves shown in Figures 10 and 11 represent the results obtained by the present model under the same conditions as for Figures 8 and 9, respectively. Although the termination reaction becomes diffusion-controlled at high conversion, a noticeable consistency is observed between the simulation results and the experimental data in every case. Consequently, the simple model proposed in this study is proven valid over wide ranges of the reaction temperature and the initiator concentration and over the entire range of the initial mole fraction of styrene.



**Figure 10** The history of residual styrene mole fraction for SAN copolymerization in a batch reactor with 0.01M AIBN at 60°C. The curves represent the results of model calculation, whereas the filled keys denote the experimental data taken from the literature.<sup>5</sup>



**Figure 11** The history of residual styrene mole fraction for SAN copolymerization in a batch reactor with  $0.05M$  AIBN at  $40^\circ\text{C}$ . The curves represent the results of model calculation, whereas the filled keys denote the experimental data taken from the literature.<sup>5</sup>

### Copolymer Composition and Molecular Weight Predictions

The use of the accumulated copolymer compositions gives an accurate measure of the total number of monomer molecules of each type bound in the copolymer. The cumulative copolymer composition is calculated by integration of the corresponding instantaneous quantities. The copolymer composition histories are predicted by this model under the same conditions as in the previous cases. The azeotropic fraction of styrene is computed to be about 0.6, so the copolymer composition would remain fixed at 0.6 if the initial composition is set at this level. When the composition drift is appreciable, high molecular weight polymers of different composition will be produced. In most of the commercial copolymerizations, appreciable composition drift is not permitted.

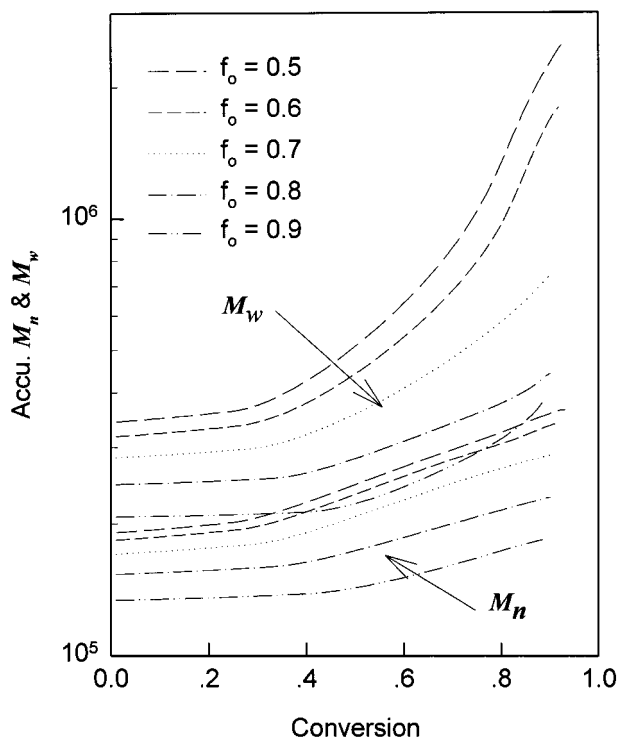
The number- and weight-average molecular weights of the copolymer are also predicted and plotted against the concentration in Figures 12 and 13. The number-average molecular weight is relatively independent of monomer composition and increases at a slower rate because SAN is a copolymer forming linear chains. The weight-average molecular weight, however, increases rather rapidly with the conversion as well as with the acrylonitrile content. As the monomer conversion increases, both the number- and weight-average molecular weights tend to grow. Since, however, the weight-average molecular weight increases at a faster rate, the molecular weight

distribution tends to become broader as the reaction proceeds.

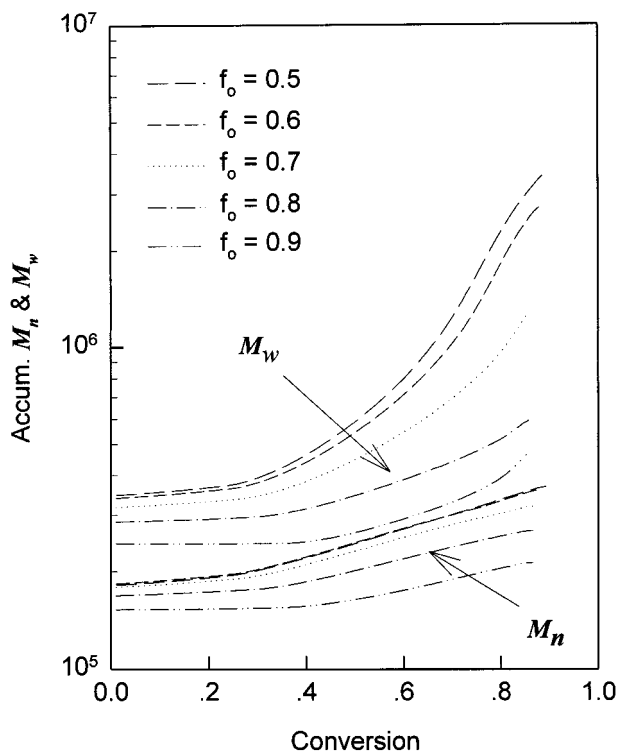
### CONCLUSIONS

The diffusion-controlled reactions are quantified by using the free volume theory proposed by Jones et al., while the chain-length dependency of the termination rate constant is taken into account by using the reptation theory. By applying the PKRCM and the terminal model, the complex rate expressions for the copolymerization reaction is reduced to those for the corresponding homopolymerization reaction. The mathematical model is proven adequate for a batch reactor in which bulk free radical copolymerization of SAN takes place.

The model can predict the monomer conversion, residual styrene mole fraction, the copolymer composition, and the number- and weight-average molecular weights for binary copolymerization. The results obtained from this model clearly shows that the propagation reaction is limited by the diffusion of monomers at higher con-



**Figure 12** Average molecular weights versus conversion for SAN copolymerization in a batch reactor with  $0.01M$  AIBN at  $60^\circ\text{C}$ . The curves represent the results of model calculations.



**Figure 13** Average molecular weights versus conversion for SAN copolymerization in a batch reactor with 0.05M AIBN at 40°C. The curves represent the results of model calculations.

version and that the copolymer composition drifts only slightly near the azeotropic monomer feed composition. Since the weight-average molecular weight increases at a faster rate than the number-average molecular weight, the molecular weight distribution would become broader as the conversion increases.

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## NOMENCLATURE

$F_i$	instantaneous copolymer composition ( $i = 1, 2$ )
$f_o$	initial styrene mole fraction
$f_i$	mole fraction of monomer $i$ ( $i = 1, 2$ )
$f(u)$	chain-length distribution function for polymer molecules with chain length $u$
$G_k$	$k$ th moment of living polymer concentration ( $k = 0, 1, 2$ )
$G_N$	rubbery plateau modulus

$H_k$	$k$ th moment of dead polymer concentration ( $k = 0, 1, 2$ )
$I$	initiator or initiator concentration
$k_{k1}, k_{k2}$	initiation rate constants
$k_{ij}$	diffusion-controlled propagation rate constant ( $i \& j = 1, 2$ )
$(k_{ij})_0$	chemically controlled propagation rate constants ( $i \& j = 1, 2$ )
$\bar{k}_p$	pseudokinetic rate constant for propagation
$\bar{k}_t$	pseudokinetic rate constant for termination
$k_{tc}(u, v)$	combination termination rate constant with chain length $u$ and $v$
$k_{td}(u, v)$	disproportionation termination rate constant with chain length $u$ and $v$
$k_{tvf}$	termination rate constant for the unentangled chain
$\bar{M}_{av}$	average monomer molecular weight in accumulated copolymer
$M_i$	monomer $i$ or concentration of monomer $i$ ( $i = 1, 2$ )
$\bar{M}_n$	accumulated number-average molecular weight
$\bar{M}_w$	accumulated weight-average molecular weight
$Mw_i$	molecular weight of monomer $i$ ( $i = 1, 2$ )
$P_{m,n}$	dead polymer with $m$ units of $M_1$ and $n$ units of $M_2$ or its concentration
$R_{u,i}$	polymeric radical of type $i$ with chain length $u$ or its concentration ( $i = 1, 2$ )
$R_{m,n,i}$	polymeric radical of type $i$ with $m$ units of $M_1$ and $n$ units of $M_2$ or its concentration ( $i = 1, 2$ )
$R_{*,*}$	concentration of polymeric radicals of type $i$ and $j$ with any chain length
$r_X$	rate of generation of species $X$
$\bar{V}$	volume of reaction mixture
$V_i$	volume of component $i$ ( $i = p, M_1, M_2$ )
$v_F$	free volume fraction of mixture
$x_c$	critical chain length
$Z$	parameter for chain-length dependence defined by eq. (24).
$Z_i$	parameter for chain-length dependence defined by eqs. (38), (39), (43), and (44) ( $i = 1, 2, 3, 4$ )

## Greek Letters

$\alpha_i$	difference in thermal expansion coefficient above and below $T_g$ ( $i = p, M_1, M_2$ )
$\Phi$	primary radical
$\Phi_i$	volume fraction of particular component in solution ( $i = p, M_1, M_2$ )
$\Phi_{u,i}$	polymeric radical fraction of type $i$ with chain length $u$ ( $i = 1, 2$ )

## Subscripts

$av$	average
$cr$	critical

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