

Styrene과 Acrylonitrile의 괴상 공중합을 위한 회분식 반응기의 모델링 및 모사

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Modeling and Simulation of a Batch Reactor for Bulk Copolymerization of Styrene and Acrylonitrile

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Abstract - A mathematical model is developed for a batch reactor in which the free radical bulk copolymerization of styrene and acrylonitrile takes place. In this model, we introduce the free volume theory to quantify the diffusion controlled termination and propagation reactions, and develop a model for the chain length dependent termination reaction in the context of the pseudo kinetic rate constant method (PKRCM). The simulation results from this model are found to be in good agreement with experimental data under different copolymerization conditions. The present model can predict both the copolymer composition and the number and weight average molecular weights. These kinetic approaches provide greater insight into the performance of the batch reactor used for the free radical bulk copolymerization of styrene and acrylonitrile.

INTRODUCTION

As monomer is converted into 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 at moderate conversion level. However, changes in

viscoelastic properties must have a strong influence on those kinetic events that are diffusion controlled. It has long been realized that termination reactions in the free radical polymerization are in the latter category. Therefore, any relevant model of polymerization must include these different mechanisms of termination.

The bulk free radical copolymerization of styrene and acrylonitrile exhibits an autoacceleration in the reaction rate and a limiting conversion that the rate of polymerization falls to zero prior to depletion of all the monomer. Also the chain length dependent termination takes place after the onset of chain entanglements. The autoacceleration in the rate is usually referred to as the 'gel' or 'Trommsdorff' effect, and is associated with diffusion controlled termination. The limiting conversion is due to diffusion controlled propagation reactions at very high conversions. In this work, the diffusion controlled reactions are quantified using the free volume theory used by Jones et al.[1]

It is well known that the free radical copolymerization involves various elementary reactions and that as the number of comonomers increases the kinetic expressions become

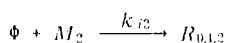
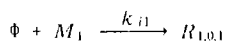
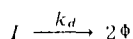
increasingly complicated. Therefore, the pseudo kinetic rate constant method developed by Tobita and Hamielec[2] is applied to a mathematical model for the bulk copolymerization of styrene and acrylonitrile in order to avoid the complications of the kinetic expressions. As far as the authors understand, the chain length dependent termination rate constants have not been treated explicitly. In this study, the model for the termination rate constant with chain length dependence[3] is extended to copolymerization system in the context of the pseudo kinetic rate constant method.

MODEL DEVELOPMENT

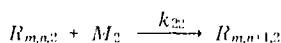
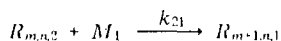
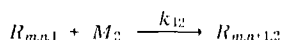
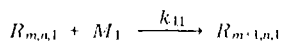
In the present study, the bulk copolymerization of styrene and acrylonitrile with AIBN initiator in a batch reactor is to be considered. A binary copolymerization producing linear chains is dealt with the terminal model[4]. In the terminal model the reactivities of two monomers, styrene and acrylonitrile, and those of the two types of polymeric radicals carrying each of the monomers at the growing chain end, respectively, are distinguished. This 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 . In the termination reaction, however, the end monomer unit of polymeric radicals need not be considered since then the termination rate constant is dependent upon the diffusion rate of the growing polymeric radicals in the reaction medium[5]. 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 this case, the kinetic scheme is represented by the following reactions.

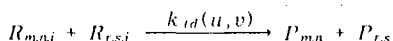
Initiation



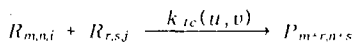
Propagation



Termination by disproportionation



Termination by combination



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 .

Pseudo Kinetic Rate Constant

We consider PKRCM with both chain length dependent and diffusion controlled termination in binary copolymerization. On the basis of the terminal model for copolymerization, the pseudo kinetic rate constants for propagation and termination reactions are defined by the following equations.

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

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

$$\overline{k_{tc}(u,v)} = k_{tc}(u,v) \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{ui} \Phi_{vj} \quad (3)$$

$$\overline{k_t(u,v)} = k_t(u,v) \sum_{i=1}^2 \sum_{j=1}^2 \Phi_{ui} \Phi_{vj} \quad (4)$$

where f_i is the mole fraction of monomer i and Φ_{*i} is the mole fraction of the polymeric radical with the i monomer end unit. To calculate the pseudo kinetic rate constants, the polymeric radical fraction Φ_{*i} needs to be evaluated. For a binary system, Φ_{*1} and Φ_{*2} are given as follows:

$$\Phi_{*1} = \frac{R_{*1}}{R_{*1} + R_{*2}} \approx \frac{k_{21}f_1}{k_{21}f_1 + k_{12}f_2} \quad (5)$$

$$\Phi_{*2} = \frac{R_{*2}}{R_{*1} + R_{*2}} \approx \frac{k_{12}f_2}{k_{21}f_1 + k_{12}f_2} \quad (6)$$

Chain-length Dependent Termination

The model of chain length dependent termination in binary copolymerization is based on the following two assumptions:

Assumption 1

The termination rate constant between two polymeric radicals of chain length u can be determined by $k_t(u,u) = k_{tof} f(u)$ and $k_t(u,v)$ is the arithmetic average of $k_t(u,u)$ and $k_t(v,v)$ [3]; i. e.,

$$k_t(u,v) = \frac{k_{tof}}{2} [f(u) + f(v)] \quad (7)$$

Assumption 2

The mole fraction of any polymeric radical type is essentially equal to the radical mole fraction of the same radical type at each chain length except for short chains[2]; i. e.,

$$\Phi_{*i} \approx \Phi_{ui} / \Phi_{u*} \quad (8)$$

Using Assumptions 1 and 2, the total termination rate constant is derived as follows

$$\overline{k_t} = k_{tof} \sum_{u=1}^{\infty} f(u) \Phi_{u*} = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} \overline{k_t(u,v)} \quad (9)$$

And the total termination rate constant can be calculated by the following scheme. If $P(u)$ is a probability that a primary radical will survive to become a polymeric radical of chain length u , Φ_{u*} can be expressed as

$$\Phi_{u*} = \frac{P(u)}{\sum_{u=1}^{\infty} P(u)} \quad (10)$$

By combining $\overline{k_t}$ and Eq. (10), we obtain

$$Z = \frac{\overline{k_t}}{k_{tof}} = \sum_{u=1}^{\infty} \left\{ f(u) \frac{P(u)}{\sum_{u=1}^{\infty} P(u)} \right\} \quad (11)$$

Because discrete summations makes computations tedious, we shall define the relative chain length $y = u / x_c$, where x_c denotes the chain length beyond which the chain length dependence begins to appear, and perform the continuous variable approximation. Then the ratio Z can be determined by the following equation

$$Z = \frac{\overline{k_t}}{k_{tof}} = \frac{\int_0^{\infty} f(y) P(y) dy}{\int_0^{\infty} P(y) dy} \quad (12)$$

where

$$P(y) = \exp\left[-\frac{\gamma}{2\sqrt{Z}} \int_0^y f(y) dy - \frac{\gamma\sqrt{Z}}{2} y\right] \quad (13)$$

$$\gamma = \frac{x_c (R_1 k_{tof})^{1/2}}{k_p M} \quad (14)$$

in which the chain length dependent function $f(u)$ is cast into the form of a continuous variable $f(y)$ as

$$f(y) = \begin{cases} 1 & y \leq 1 \\ y^{-2} & y > 1 \end{cases} \quad \text{when } \overline{M_w} \geq x_c M_{av} / \Phi \quad (15)$$

Equation (15) is justified by the facts that the self diffusion constant of a polymer molecule longer than the entanglement length is

proportional to M^{-2} after the onset of chain entanglements and that there is no chain length dependence before the onset of chain entanglements. To obtain the total termination rate constant, iteration procedure is needed to calculate Z with Eqs. (12) and (13).

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

$$\overline{k_{tu}} = \sum_{v=1}^{\infty} \overline{k_{tu}(u, v)} = \frac{1}{2} [k_{tu}(u, u) + \overline{k_{tu}}] \Phi_{u*} \quad (16)$$

$$\overline{k_{tdu}} = \sum_{v=1}^{\infty} \overline{k_{td}(u, v)} = \frac{1}{2} [k_{td}(u, u) + \overline{k_{td}}] \Phi_{u*} \quad (17)$$

$$\overline{k_{tcu}} = \sum_{v=1}^{u-1} \overline{k_{tc}(v, u-v)} = \sum_{v=1}^{u-1} k_{tc}(v, v) \Phi_{v*} \Phi_{u-v*} \quad (18)$$

Rate Equations

Considering the elementary reactions above, the rate expressions for initiator and monomer can be written as follows:

$$r_I = -k_d I \quad (19)$$

$$r_M = 2fk_d I - \overline{k_p} M G \quad (20)$$

The radical and dead polymer rate expressions using PKRCM are derived as follows: The rate expressions for radical and polymer with chain length unity are

$$r_{R_1} = R_I - \overline{k_p} M R_{1*} - \overline{k_{t1}} G^2 \quad (21)$$

$$r_{P_1} = \overline{k_{td1}} G^2 \quad (22)$$

And the rate expressions for radical and polymer with chain length u are

$$r_{R_u} = \overline{k_p} M R_{u-1*} - \overline{k_p} M R_{u*} - \overline{k_{tu}} G^2 \quad (23)$$

$$r_{P_u} = \frac{1}{2} \overline{k_{tcu}} G^2 + \overline{k_{tdu}} G^2 \quad (24)$$

Here the moments of living and dead polymer concentration are defined as

$$G_k = \sum_{u=1}^{\infty} u^k R_{u*}, \quad F_k = \sum_{u=1}^{\infty} u^k P_{u*} \quad (25)$$

Equations (21)~(24) can be treated as those for homopolymerization in molecular weight modeling. Using Eqs. (21) and (23), one can obtain the following moment equations of polymeric radical concentration.

$$r_{G_1} = R_I - \overline{k_t} G^2 \quad (26)$$

$$r_{G_2} = R_I + \overline{k_p} M G - \frac{1}{2} \overline{k_t} G G_1 - \frac{1}{2} k_{tof} \frac{B_1}{S_0} G^2 \quad (27)$$

$$r_{G_3} = R_I + \overline{k_p} M (2G_1 + G) - \frac{1}{2} \overline{k_t} G G_2 - \frac{1}{2} k_{tof} \frac{B_2}{S_0} G^2 \quad (28)$$

The moment equations of dead copolymer concentration are given as follows:

$$r_{F_1} = \frac{1}{2} \overline{k_{tc}} G^2 + \overline{k_{td}} G^2 \quad (29)$$

$$r_{F_2} = \frac{1}{2} \overline{k_{tc}} \frac{S_1}{S_0} G^2 + \frac{1}{2} \overline{k_{td}} G G_1 + \frac{1}{2} k_{tof} \frac{B_1}{S_0} G^2 \quad (30)$$

$$r_{F_3} = \frac{1}{2} \overline{k_{tc}} \frac{S_2}{S_0} G^2 + k_{tof} \frac{B_1}{S_0} \frac{S_1}{S_0} G^2 + \frac{1}{2} \overline{k_{td}} G G_2 + \frac{1}{2} k_{tof} \frac{B_2}{S_0} G^2 \quad (31)$$

where $S_i = \int_0^{\infty} y^i P(y) dy$

$$B_i = \int_0^{\infty} y^i f(y) P(y) dy$$

Batch Reactor Mass Balance Equations

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

$$\frac{1}{V} \frac{d(XV)}{dt} = r_X \quad (32)$$

where $X = [I \ M \ G \ G_1 \ G_2 \ F_0 \ F_1 \ F_2]$.

Since there is usually a change in density as monomers are converted to polymer, the reactor volume V of a batch reactor will shrink. These

changes in the reactor volume are accounted for by the following equations:

$$\frac{dV_{m,i}}{dt} = -\frac{1}{\rho_{m,i}} \left[Mw_i \frac{d(M_1V)}{dt} - V_{m,i} \frac{\partial \rho_{m,i}}{\partial T} \frac{dT}{dt} \right] \quad (33)$$

$$\frac{dV_r}{dt} = -\frac{1}{\rho_r} \left[\sum_{i=1}^2 Mw_i \frac{d(M_1V)}{dt} + V_r \frac{\partial \rho_r}{\partial T} \frac{dT}{dt} \right] \quad (34)$$

The number and weight average molecular weights of the accumulated copolymer are given by

$$\overline{M}_n(t) = \frac{\int_0^t \frac{d(F_1V)}{dt} M_{av}(t) dt}{\int_0^t \frac{d(F_0V)}{dt} dt} \quad (35)$$

$$\overline{M}_w(t) = \frac{\int_0^t \frac{d(F_2V)}{dt} M_{av}^2(t) dt}{\int_0^t \frac{d(F_1V)}{dt} M_{av}(t) dt} \quad (36)$$

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

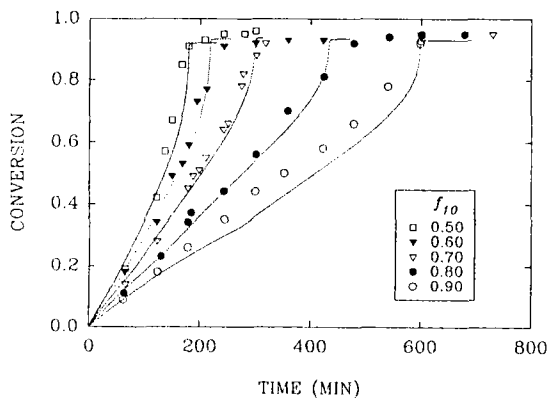
$$M_{av}(t) = Mw_1 \left(\frac{R_{p,1}}{R_p} \right) + Mw_2 \left(\frac{R_{p,2}}{R_p} \right) \quad (37)$$

The overall composition of a copolymer produced instantaneously can be expressed as

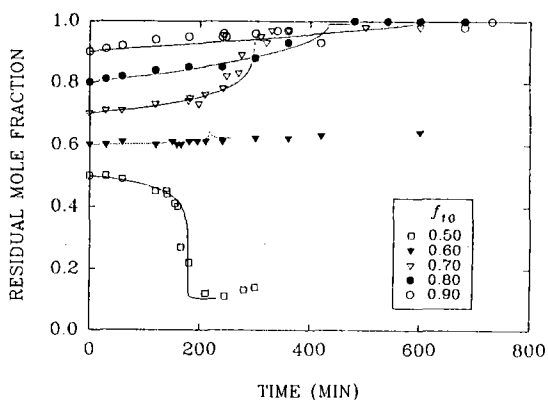
$$F_i = \frac{R_{p,i}}{R_p} \quad (38)$$

SIMULATION AND DISCUSSION

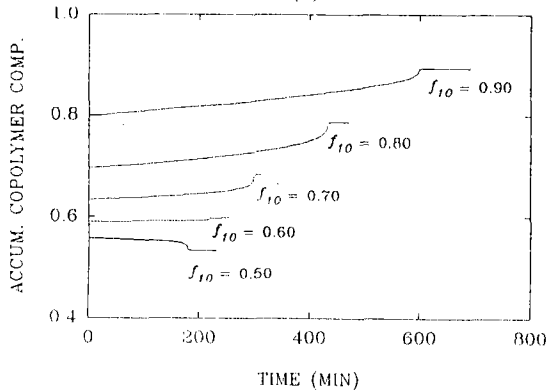
Model simulation results are compared with experimental data reported by Garcia et al. [5] on the bulk copolymerization of styrene and acrylonitrile over a range of initial mole fractions



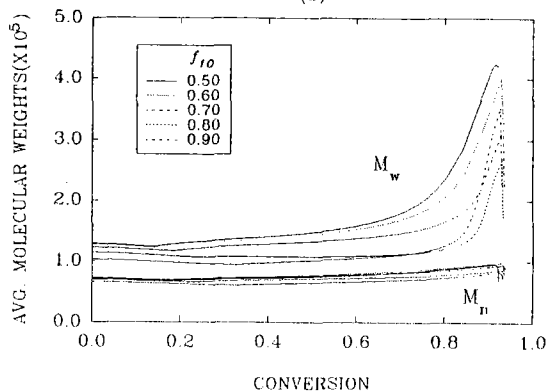
(a)



(b)



(c)



(d)

Fig. 1. Comparison between simulation results and experimental data by Garcia et al. [5] (a) conversion vs. time, (b) residual styrene mole fraction vs. time, (c) accumulated copolymer composition vs. time, (d) average molecular weight vs. conversion.

of styrene f_{10} (0.5, 0.6, 0.7, 0.8 and 0.9).

The conversion and residual styrene mole fraction vs. time are shown in Parts (a) and (b) of Fig. 1. The curves shown in the diagrams are predictions given by the developed model whereas the open and filled keys represent the experimental data. The noticeable consistency is observed between simulation results and the experimental data obtained under various reaction conditions.

The copolymer composition histories shown in Part (c) of Fig. 1 are predicted by this model. It is observed that the composition drift is appreciable as the conversion increases; however, the composition drift is slight near the azotropic monomer feed composition.

We also plot the number and weight average molecular weights of the copolymer in Part (d) of Fig. 1. The number average molecular weight is relatively independent of monomer composition and increases only slightly, the weight average molecular weight, however, increases rapidly with conversion and acrylonitrile content.

CONCLUSIONS

A simulation model is derived describing the bulk copolymerization of styrene and acrylonitrile in a batch reactor. This system exhibits complex kinetic events such as gel effect, chain length

dependent termination and limiting conversion. For rigorous modeling, the diffusion controlled termination and propagation rate constants based on the free volume theory are used. The pseudo kinetic rate constant method is extended to model the chain length dependent termination reaction. By application of this PKRCM, the moment equations of living and dead polymer concentrations are derived.

The simulation results are compared with the experimental data under different copolymerization conditions. As a result, the model is proven valid so that it may predict both the copolymer composition and the number and weight average molecular weights.

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