

Modeling and Control of Continuous Stirred Tank Reactor for Thermal Copolymerization

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ABSTRACT: A mathematical model is developed for solution copolymerization in a continuous stirred tank reactor. For the thermal copolymerization of styrene and acrylonitrile (SAN), the kinetic rate expression for thermal initiation is derived by applying the pseudo-steady-state hypothesis to the intermediates, and the kinetic parameters are estimated by experimental investigation. The moment equations of living and dead polymer concentrations are derived by applying the pseudokinetic rate constant method. The model is used to calculate the conversion, the copolymer composition, the weight-average molecular weight, and the polydispersity. It is demonstrated that this model can predict the industrial data very well under various operating conditions. The dynamic analysis of the reaction system enables us to determine the polymer properties against the changes in the operation parameters. It is noticed that the monomer conversion is controlled to some extent by the reaction temperature and the feed monomer fraction. The monomer conversion control of a solution copolymerization reactor is treated with different control algorithms. The fuzzy/proportional–integral–derivative controller shows satisfactory performances for both setpoint tracking and disturbance rejection and can be easily applied to continuous polymerization processes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 921–931, 1998

Key words: continuous stirred tank reactor (CSTR); solution copolymerization; styrene and acrylonitrile (SAN); mathematical modeling; fuzzy control

INTRODUCTION

Synthetic polymers are produced in many types of reactors by different kinetic mechanisms, which result in complex and challenging control problems.¹ Free radical solution polymerization in a continuous stirred tank reactor (CSTR) is a very important method of polymer production.

Styrene (St) reacts with acrylonitrile (AN) thermally and spontaneously at high temperature. Many previous works have tried to deal with

the initiation mechanism for the copolymerization of St with AN,^{2,3} but a mathematical model for this system has not been established. This work proposes a kinetic model for the spontaneous thermal initiation reaction of St with AN in ethylbenzene (EB) under industrial operating conditions. With this, a simulation model for the continuous solution copolymerization of St and AN is developed. Dynamic behavior of the reaction system is investigated under various reaction conditions by numerical simulation—reactor temperature, feed flow rate, solvent fraction, and feed monomer composition.

The inadequacy of on-line sensors has mainly hindered the effective implementation of various control algorithms to polymerization reactors.⁴ In this study, a control system to produce the desired

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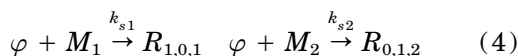
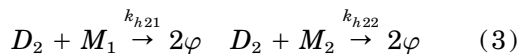
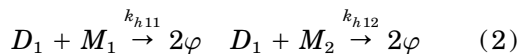
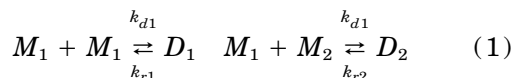
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monomer conversion is constructed by using proportional–integral–derivative (PID) and fuzzy controllers and is applied to continuous polymerization processes by numerical simulation.

KINETIC MODEL DEVELOPMENT

The kinetic scheme for free radical copolymerization of St and AN (SAN) includes initiation, chain transfers to monomer and solvent, propagation, and termination by combination and disproportionation. Thermal initiation mechanism for the St polymerization has been studied in the greatest detail.⁵ Flory⁶ and Mayo⁷ have proposed independent models to explain the thermal polymerization mechanism of St, and the Mayo mechanism has been generally accepted for the self-initiation of St after various studies.² In this study, we apply the Mayo mechanism to the copolymerization of St and AN and develop a mathematical model for the initiation mechanism.

Monomers M_1 (St) and M_2 (AN) combine and form D_1 and D_2 by Diels–Alder dimerization. These adducts react with either of the monomers and produce a pair of radicals (φ), which react with M_1 or M_2 and produce free radicals R_1 or R_2 .



Here, k_{hij} is the rate constant of the homolysis reaction, whereas k_{di} and k_{ri} correspond to the rate constants of the forward and reverse Diels–Alder dimerizations, respectively.

Assuming pseudosteady states for the reaction intermediates D_1 and D_2 , we obtain the initiation rate of the copolymerization R_I as follows: that is, R_I is proportional to the cube of the total monomer concentration, M and

$$R_I = (k_I f_1^3 + k_{II} f_1^2 f_2 + k_{III} f_1 f_2^2) M^3 \\ = \alpha(f_1, T) M^3 \quad (5)$$

in which f_i corresponds to the mole fraction of monomer i , and k_I , k_{II} , and k_{III} are the rate constants defined as

$$k_I = 2k_{d1}k_{h11}/k_{r1} \\ k_{II} = 2(k_{d1}k_{h12}/k_{r1} + k_{d2}k_{h21}/k_{r2}) \\ k_{III} = 2k_{d2}k_{h22}/k_{r2} \quad (6)$$

In eq. (5) α is a constant which is dependent on the temperature and the molar composition of the monomers.

Free radical R_i , which is formed by initiation reaction, combines with the monomer M_1 or M_2 and produces an activated free radical. During propagation reaction, the free radicals react with monomers and become living polymers with longer chain length. The living polymers may react with a monomer or a solvent to yield dead polymer and a free radical with unity chain length. Termination takes place by both disproportionation and combination reactions.

On the basis of the copolymerization mechanism described above, rate equations of monomer and living and dead polymer have already been derived by applying the pseudokinetic rate constant method⁸ and only modified key equations are presented here:

$$r_M = r_{M1} + r_{M2} = -R_I - \overline{k_p}MG - \overline{k_{fm}}MG_0 \\ r_{R_{1,*}} = R_I - \overline{k_p}MR_{1,*} - \overline{k_{fm}}MG_0 \\ \quad - \overline{k_{fs}}SG_0 - \overline{k_{t,1}}G_0^2 \\ r_{P_{1,*}} = \overline{k_{td,1}}G_0^2 \\ r_{R_{u,*}} = \overline{k_p}M(R_{u-1,*} - R_{u,*}) - \overline{k_{fm}}MG_0 \\ \quad - \overline{k_{fs}}SG_0 - \overline{k_{t,u}}G_0^2 \\ r_{P_{u,*}} = \overline{k_{fm}}MG_0 + \overline{k_{fs}}SG_0 + (\frac{1}{2}\overline{k_{tc,u}} + \overline{k_{td,u}})G_0^2 \quad (7)$$

where $\overline{k_p}$, $\overline{k_{fm}}$, $\overline{k_{fs}}$, $\overline{k_{td,u}}$, and $\overline{k_{tc,u}}$ are the pseudokinetic rate constants of propagation, chain transfers to monomer and solvent, termination by disproportionation, and combination for chain length u , respectively, and G_0 is the total concentration of the living polymer.

The copolymer properties are highly sensitive to the copolymer composition, the average molecular weight, and the molecular weight distribution. Average molecular weights of the copolymer can be calculated from the zero, first, and second moments of the polymer concentration. The k th mo-

ments of living and dead polymer concentrations with total monomer chain length u are defined as follows:

$$G_k = \sum_{u=1}^{\infty} u^k R_{u,*} \quad \text{and} \quad H_k = \sum_{u=1}^{\infty} u^k P_u \quad (8)$$

where $k = 0, 1$, and 2 .

The rate expressions for the zero, first, and second moments of living and dead polymer concentrations can be derived in a manner similar to those for the homopolymerization reaction system except for the reaction rate constants.

$$\begin{aligned} r_{G_0} &= R_I - \bar{k}_t G_0^2 \\ r_{G_1} &= R_I + \bar{k}_p M G_0 - (\bar{k}_{fm} M + \bar{k}_{fs} S + \bar{k}_t G_0) G_1 \\ r_{G_2} &= R_I + \bar{k}_p M (2G_1 + G_0) \\ &\quad - \bar{k}_{fm} M G_0 - (\bar{k}_{fm} M + \bar{k}_{fs} S + \bar{k}_t G_0) G_2 \\ r_{H_0} &= \frac{1}{2} (\bar{k}_{tc} + \bar{k}_{td}) G_0^2 + (\bar{k}_{fm} M + \bar{k}_{fs} S) G_0 \\ r_{H_1} &= (\bar{k}_t G_0 + \bar{k}_{fm} M + \bar{k}_{fs} S) G_1 \\ r_{H_2} &= (\bar{k}_t G_0 + \bar{k}_{fm} M + \bar{k}_{fs} S) G_2 + \bar{k}_{tc} G_1^2 \end{aligned} \quad (9)$$

MASS BALANCE AND COPOLYMER PROPERTIES

From the mass balances of various species in the CSTR for solution copolymerization, we obtain the following set of first-order ordinary differential equations:

$$\frac{d(YV)}{dt} = q_{in} Y_{in} - q_{out} Y + Vr_Y \quad (10)$$

where Y represents each of M , G_0 , G_1 , G_2 , H_0 , H_1 , and H_2 , V is the total volume of the reaction mixture, and q_{in} and q_{out} stand for the inlet and outlet volumetric flow rates, respectively.

Assuming that there is no polymer in the feed, one can derive equations to calculate the number- and weight-average molecular weights of the SAN copolymer produced in the reactor from the mass balance equations:

$$\bar{M}_n(t) = \frac{\int_0^t \{(r_{G_1} + r_{H_1})V(t)M_{av}(t) - q_{out}(G_1 + H_1)\bar{M}_{av}(t)\} dt}{\int_0^t \{(r_{G_0} + r_{H_0})V(t) - q_{out}(G_0 + H_0)\} dt}$$

$$\bar{M}_w(t) = \frac{\int_0^t \{(r_{G_2} + r_{H_2})V(t)M_{av}^2(t) - q_{out}(G_2 + H_2)\bar{M}_{av}^2(t)\} dt}{\int_0^t \{(r_{G_1} + r_{H_1})V(t)M_{av}(t) - q_{out}(G_1 + H_1)\bar{M}_{av}(t)\} dt} \quad (11)$$

in which M_{av} and \bar{M}_{av} are calculated from the molecular weight of the monomers and from the instantaneous and the accumulated average copolymer composition, respectively. In order to calculate the accumulated average composition of the copolymer in the reactor, the mass balance of each monomer contained in the copolymer should be taken into account.⁹

In a polymerization reactor, the total volume of the reaction mixture is continuously changing as the reaction proceeds. This is the result of the difference in densities of the monomers and the polymer. Especially in the case of solution polymerization, the volume change is significant. Therefore, the following equation for the volume change derived from the overall mass balance equation must be solved along with the mass balance equations of the individual species:

$$\begin{aligned} \frac{dV}{dt} &= \left[r_{M_1} M w_1 \left(\frac{1}{\rho_{M_1}} - \frac{1}{\rho_p} \right) \right. \\ &\quad \left. + r_{M_2} M w_2 \left(\frac{1}{\rho_{M_2}} - \frac{1}{\rho_p} \right) \right] V \\ &\quad + q_{in} \left(M_{1,in} \frac{M w_1}{\rho_{M_1}} + M_{2,in} \frac{M w_2}{\rho_{M_2}} + S \frac{M w_s}{\rho_s} \right) - q_{out} \\ V_{M_i} &= (M_i V) \frac{M w_i}{\rho_{M_i}} \end{aligned} \quad (12)$$

where V_{M_i} corresponds to the volume of the monomer i in the reactor. Equation (12) enables us to predict the volume change in the reactor quantitatively. In practice, however, the volume of the reaction mixture in the reactor is kept constant by manipulating the outlet volumetric flow rate as the reaction proceeds.

ESTIMATION OF INITIATION RATE CONSTANT

Rate Constants for Thermal Initiation

The rate constants for thermal initiation can be obtained if the rates of change in conversion for

various monomer compositions are measured. Thus, we express the monomer consumption rate in terms of the rate of change in conversion as follows:

$$r_M = \frac{dM}{dt} = -M_0 \frac{dX}{dt} \approx -R_I - \bar{k}_p M_0 G_0 \quad (13)$$

where M_0 is the initial monomer concentration.

In eq. (13), R_I is negligible compared with $\bar{k}_p M_0 G_0$ and one may assume that $M \approx M_0$ when the conversion is low. Applying the pseudo-steady-state hypothesis to the zero moment equation of the living polymer concentration, we obtain $G_0^2 = \alpha M^3 / \bar{k}_t$ from eq. (5) and the first equation of eq. (9), and thus

$$\frac{dX}{dt} = \frac{\bar{k}_p}{\sqrt{\bar{k}_t}} (\alpha M^3)^{1/2} \approx \frac{\bar{k}_p}{\sqrt{\bar{k}_t}} (\alpha M_0^3)^{1/2} \quad (14)$$

Experimental

St(Junsei) and AN(Yakuri) were used as monomers for thermal copolymerization. Because the monomers contain inhibitors to prevent polymerization during storage, St and AN were purified by passing through columns packed with activated aluminum oxide (acidic) and silica gel, respectively. Oxygen dissolved in the monomers was removed by bubbling nitrogen into the monomers for 1 h just before the reaction. EB (Junsei) was used as the solvent.

Purified St and AN were mixed in the weight

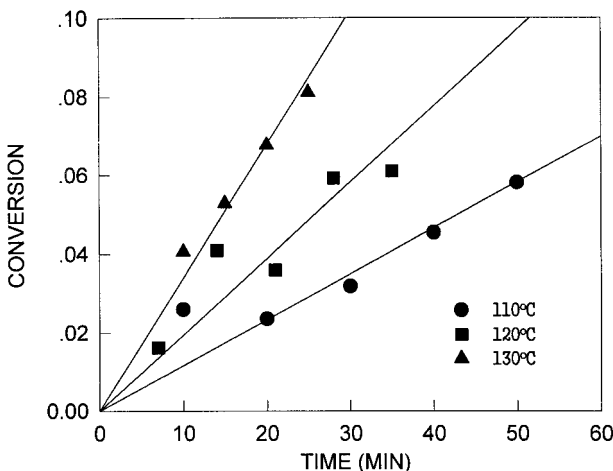


Figure 1 The monomer conversion histories for various reactor temperatures with $f_1 = 1.0$.

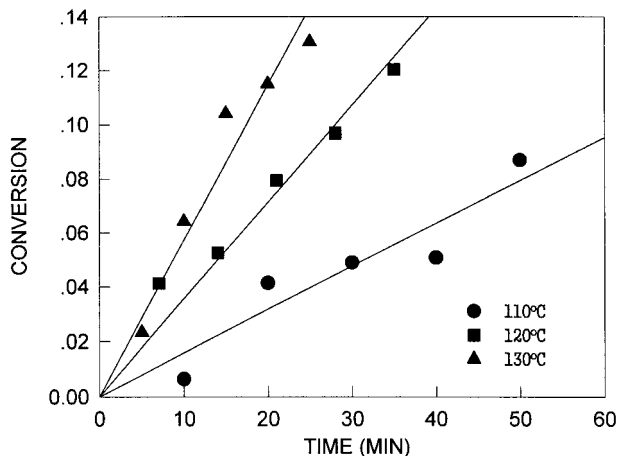


Figure 2 The monomer conversion histories for various reactor temperatures with $f_1 = 0.5$.

ratios of 100 : 0, 75 : 25, 50 : 50, and 25 : 75, and each mixture was diluted with EB so that the overall monomer weight fraction was 0.5. The mixtures were put in glass ampoules (outer diameter, 4 mm; inner diameter, 2 mm; length, 250 mm). The ampoules were sealed and placed in a hot oil bath. The reaction temperatures were 110, 120, and 130°C. At each sampling, one ampoule was taken out from the bath and the reaction mixture was poured into a test tube filled with methanol for quenching. The precipitated polymer product was removed by filtration. Conversion was determined by gravimetric methods and gas chromatographic (HP 5890 Series 2) analysis.

The experimental results are presented in Figures 1 and 2 for two different initial St weight fractions ($f_1 : 1.0$ and 0.5). Because the slope of the line in each plot corresponds to the rate of change in conversion, we can calculate the three initiation rate constants by using eq. (14). Figure 3 is the Arrhenius plot of the rate constants estimated from the experimental results. Activation energies are calculated from the slopes. The rate constants of thermal initiation of St and AN are listed in Table I.

NUMERICAL SIMULATION

The detailed nonlinear model of the reactor is derived from the material balance in order to simulate a CSTR for solution copolymerization of SAN. Considering the industrial operating conditions, we choose the following as the reference reaction

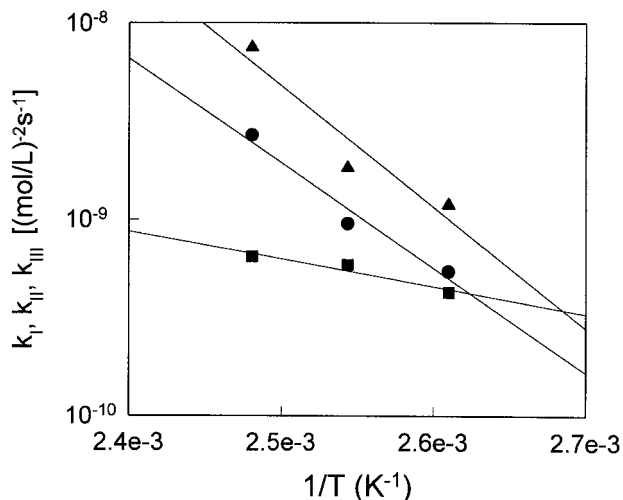


Figure 3 Arrhenius plot of initiation rate constants obtained by experiment.

system: the reactor temperature is 160°C and the initial weight fraction of St is 0.7, whereas the feed flow rate is kept constant at 1.0 L/s. Step tests for each choice of input variables are performed with the polymerization model to select the manipulated variable.

The model equations form a set of nonlinear coupled algebraic and differential equations given in eqs. (7)–(12). A computer program for simulation has been developed to calculate the conversion, the copolymer composition, and the average molecular weights. The equations were integrated using a fifth-order Cash–Karp Runge–Kutta algorithm. We apply the free volume theory¹⁰ to describe quantitatively the diffusion-controlled propagation and termination reactions. The values of other rate constants and physical properties used are mostly taken from the previous work.⁸

REACTOR BEHAVIOR

In a CSTR, the properties of the reaction mixture change until a steady-state operating point is

reached, and then they remain constant regardless of the reaction time. The time to reach a steady state varies with different reactor sizes, feed flow rates, and reaction rates.

Various factors such as reactor temperature, feed flow rate, solvent fraction, and AN content may affect the conversion and the average molecular weights in solution polymerization of SAN. As the AN content is increased, the properties of SAN would get better, but there are also some undesirable features: (1) temperature control becomes more difficult because of the increased viscosity; (2) the copolymer composition gets nonuniform as it drifts from the azeotropic composition; and (3) the copolymer yellowness becomes bad as a result of the increased melt temperature. Therefore, processes with little deviation from the azeotropic composition are favored.

The reactor temperature is an important factor to control the conversion of monomers and the average molecular weights of the polymer product, because it is directly related to the reaction rate. As shown in Figure 4(a), the conversion gets higher as the reactor temperature increases from 150 to 165°C. When the reactor temperature is 150°C, the final conversion at steady state is about 0.40, whereas at 165°C, it is 0.51. No significant gel effect is observed in solution polymerization as there is in bulk or suspension polymerization. It takes approximately 10 h to reach steady state in terms of conversion when fixed amounts of monomer (of azeotropic composition) and solvent (EB; 25%) are added at the initial stage and the feed flow rate is kept constant at 1.0 L/s. At the reference temperature of 160°C, the steady-state conversion is calculated to be 0.49 when the industrial operating data show 0.50.

The average molecular weights are strongly dependent on the reactor temperature and the concentration of chain transfer agents. Figure 4(b) shows the effect of reactor temperature on the weight-average molecular weight. It takes much longer to reach steady state in terms of average

Table I The Kinetic Parameters for Initiation Reaction

Parameter	Unit	Arrhenius Expression
k_I	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$	$4.14 \times 10^4 \exp(-12,278/T)$
k_{II}	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$	$2.03 \times 10^{-6} \exp(-3,231/T)$
k_{III}	$L^2 \text{ mol}^{-2} \text{ s}^{-1}$	$1.14 \times 10^7 \exp(-14,164/T)$

T , absolute temperature in K.

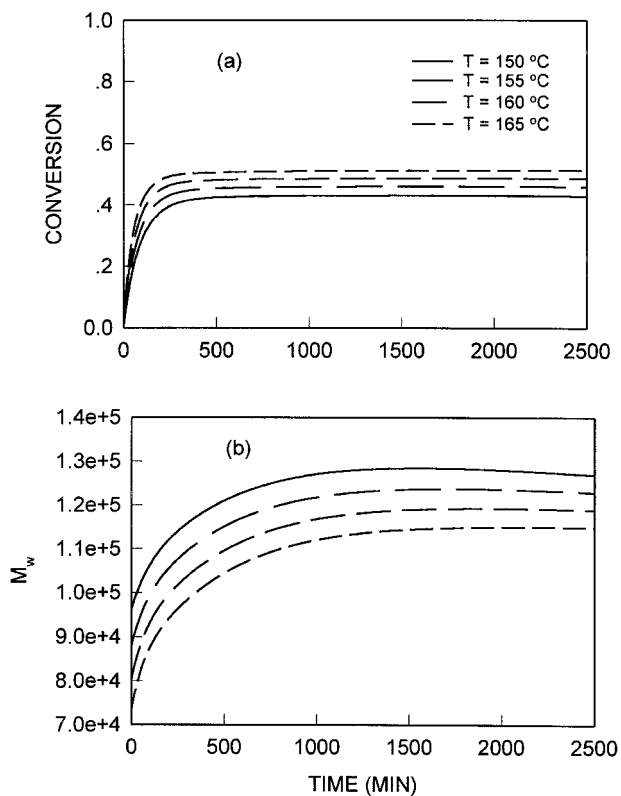


Figure 4 The histories of the monomer conversion and the weight-average molecular weight at various reactor temperatures.

molecular weight than in terms of conversion because the former is dependent on both the monomer concentration and the copolymer composition. The weight-average molecular weight decreases as the steady-state temperature changes from 150 to 165°C. This is due to the increased rate of radical formation and greater chances for the combination termination.

For the case of 150°C, the weight-average molecular weight does not reach a constant value in 2500 min because of the low temperature. If the simulation is performed for a longer period of time, a steady state would be reached. The time of 2500 min is sufficient for simulations at higher temperatures to show steady states. The industrial data operated under the reference conditions show 11.02×10^4 for the weight-average molecular weight, whereas the simulation result yields 11.82×10^4 . It is understood that the difference arises from the facts that the mixing is imperfect in the CSTR and that the molecular weight from

the industrial data is that of the final product which is measured after devolatilization.

Polydispersity increases slightly as the reactor temperature rises, and it remains constant after about 20 h of the reaction time. In the case of bulk polymerization, when the conversion is about 0.7, the number-average molecular weight decreases at a fast rate although the weight-average molecular weight and the polydispersity increase because of the diffusion-controlled features. Because of the relatively low conversion and the decreased diffusion-controlled feature by solvent, there is no glass effect in solution polymerization as in bulk polymerization.

Lower reactor temperature is favored in order to produce polymers with narrow molecular weight distribution and high weight-average molecular weight. However, lower temperature results in lower conversion. Therefore, the final conversion of monomer and the properties of the polymer product should be taken into account in the selection of reactor temperature.

Among various kinds of polymerization processes, the solution process is often the method of choice because of low viscosity of the system. Solvent effects in free radical reactions are manifested in reactions involving formation of free radicals. Figure 5 shows that both the conversion and the weight-average molecular weight decrease as the solvent fraction increases. Solvent fraction is found to have little effect on the copolymer composition.

Figure 6 shows the responses of the monomer conversion and weight-average molecular weight to a step change in the feed flow rate. The feed flow rate is observed to be the operating condition that is the least influential on the properties of the polymer product.

In addition to the average molecular weight and the molecular weight distribution, the composition of the copolymer is another important property in the solution copolymerization of SAN. Conditions such as reactor temperature, solvent fraction, and inlet flow rate do not affect the copolymer composition. The composition of the monomer feed, however, influences the composition of the copolymer product, as shown in Figure 7. In order to keep the copolymer composition constant, the composition of the monomer feed should be controlled. The SAN product is the most transparent when its composition is near the azeotropic value.

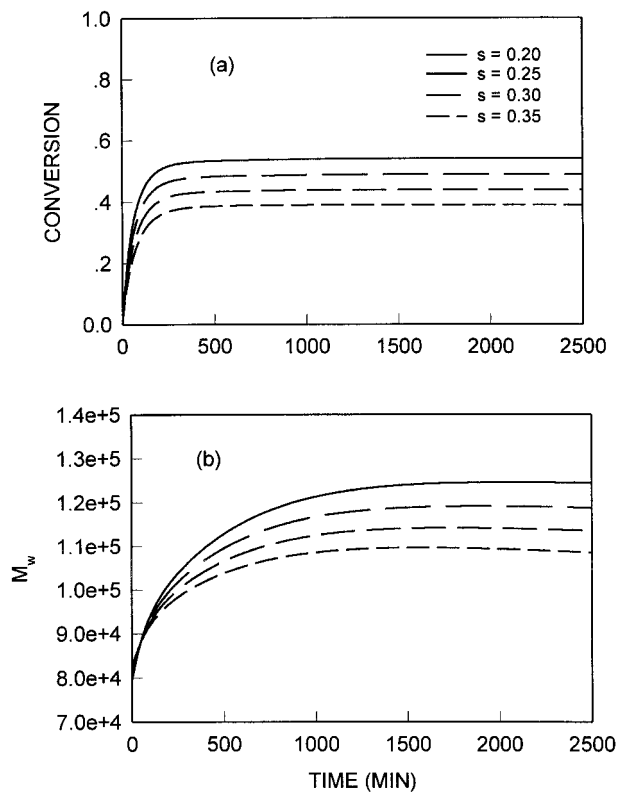


Figure 5 The histories of the monomer conversion and the weight-average molecular weight with various solvent weight fractions in the feed.

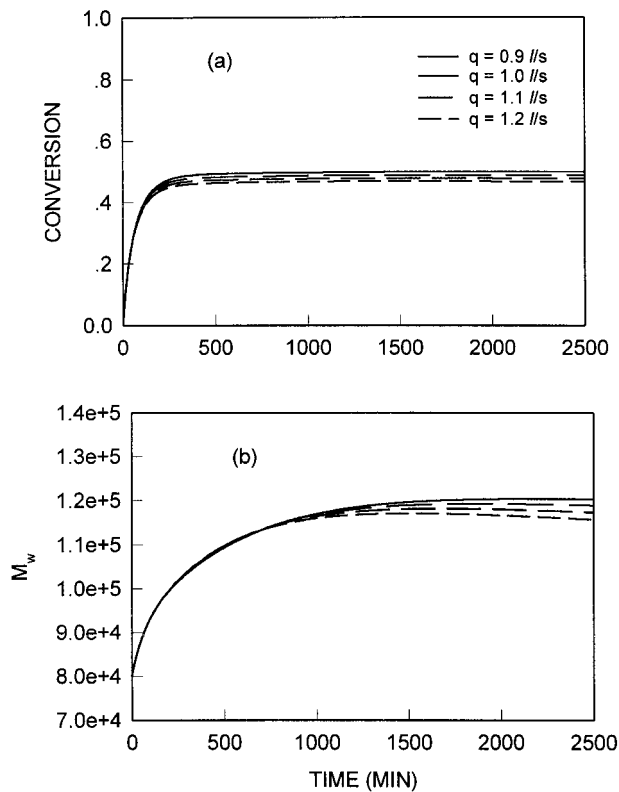


Figure 6 The histories of the monomer conversion and the weight-average molecular weight for various feed flow rates.

POLYMER PROPERTY CONTROL

The measuring instruments are often the weakest link in the polymerization reactor control circuit. Traditionally, conversion has been measured by gravimetric methods and molecular weight by off-line analysis using gel permeation chromatography (GPC). There have been a few attempts in recent years to develop on-line sensors for measuring such variables. Pinto and Ray¹¹ used an on-line refractometer to measure conversion in solution polymerization process and reported reliable results. Although GPC is widely used to measure molecular weight, only a few applications for on-line measurement have been reported.¹² For control purposes, the measurements of the output variables such as average molecular weight or polydispersity should be continuously available, but it is difficult to measure the properties in real time. In this work, therefore, the main controlled variable considered is the monomer conversion. Because change in the reactor temperature strongly affects the conversion, the control of con-

version is achieved by manipulating the reactor temperature.

Fractional deviation variables are defined for all manipulated and output variables. For example, the fractional deviation variable for the reaction temperature is

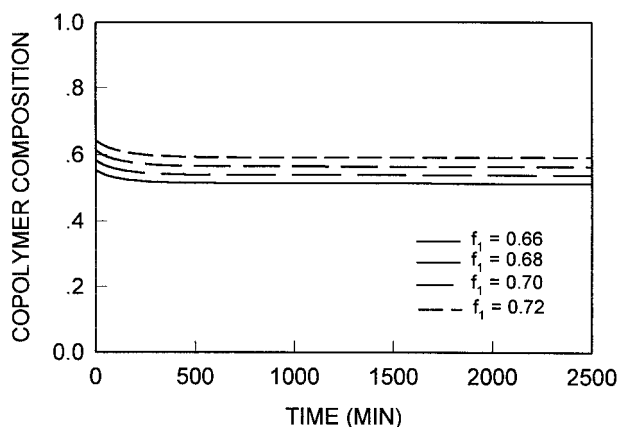


Figure 7 The copolymer composition histories with various monomer weight fractions in the feed.

$$T'_r = \frac{T_r - T_{rs}}{T_{rs}} \quad (15)$$

where T_{rs} is the steady-state value of the reaction temperature.

The closed-loop behavior of the continuous copolymerization reactor has been examined by simulation with the following control algorithms.

PID Controller

Although there are various kinds of controllers, the PID controller was chosen because of its simplicity and wide application in chemical industries. The PID controllers are tuned to give satisfactory performance by observing the output response to setpoint changes in the reaction parameters. It is not possible to find a single set of controller parameters which give good closed-loop behavior for all situations. This is the reason why it is difficult to tune the real plant controller.

Fuzzy Controller

The nonlinear behavior of a polymerization process may pose serious control problems if a PID controller with constant parameters is used to keep the reactor temperature under control. It has been recognized that fuzzy control is quite effective in coping with uncertain dynamics associated with polymerization processes. It is especially suitable for complex and nonlinear processes.¹³

We designed a simple fuzzy controller with position error (E), change of error (CE), and output (U) for closed-loop control. In this controller, the error between the process conversion and its setpoint is one of the input variables and can be partitioned into the fuzzy linguistic variables, i.e., NB (negative big), NS (negative small), ZO (zero), PS (positive small), and PB (positive big). Similarly, the change in error can be classified as NS, ZO, and PS, and the output variables can be classified as NB, NS, ZO, PS, and PB. Here, the fuzzy controller uses bell-type membership functions, shown in Figure 8.

The inference is performed in accordance with only seven fuzzy linguistic rules as follows:

- R_1 : If E is NB and CE is ZO, then U is NB.
- R_2 : If E is NS and CE is ZO, then U is NS.
- R_3 : If E is ZO and CE is ZO, then U is ZO.
- R_4 : If E is ZO and CE is NS, then U is PB.

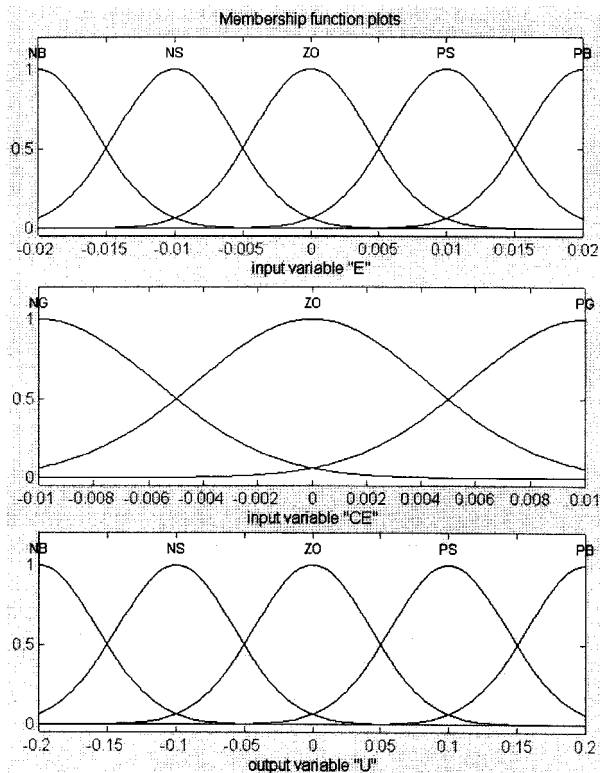


Figure 8 Membership functions for the fuzzy controller applied to the control of the monomer conversion.

- R_5 : If E is ZO and CE is PS, then U is NB.
- R_6 : If E is PS and CE is ZO, then U is PS.
- R_7 : If E is PB and CE is ZO, then U is PB.

The fuzzy inference is executed on the basis of the fuzzy linguistic rules listed above. The “defuzzification” technique used is the Centroid method.

Controller Performance

A disadvantage of the conventional feedback control is that the corrective action for disturbances does not begin until the controlled variable deviates from the setpoint. Therefore, a cascade control strategy is introduced to improve the dynamic response to load changes, so that the output signal of the master controller serves as the setpoint for the slave controller.

The control algorithms for the master controller are PID, fuzzy, and fuzzy/PID control. The configuration of the fuzzy/PID controller is shown

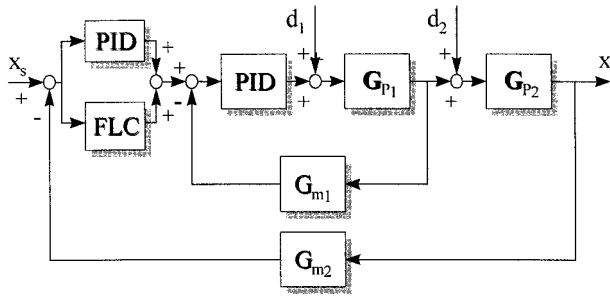


Figure 9 Configuration of parallel fuzzy/PID controller to control the monomer conversion.

in Figure 9. The master controller calculates the setpoint of the reactor temperature, and then the slave controller manipulates the jacket temperature. After the selection of the control structure is made, a feedback control of the output is implemented.

Figures 10 and 11 show a closed-loop response of the output and manipulated variables to 10% change in the setpoint for the monomer conversion. As one can see from Figure 10, the monomer conversion increases rather slowly because SAN is a copolymer forming linear chains. Clearly, the PID and fuzzy controller would not allow the proper reactor control, while the fuzzy/PID controller would lead to adequate process operation. The corresponding profiles of the reactor temperature (T_r) and the jacket temperature (T_j) obtained by using the fuzzy/PID controller are presented in Figure 11. It is noticed that the controller initially requests maximum jacket temperature to bring the reactor temperature up.

In practical operation, robustness to unexpected disturbance is of great importance. The regulatory performance to reject the influence of

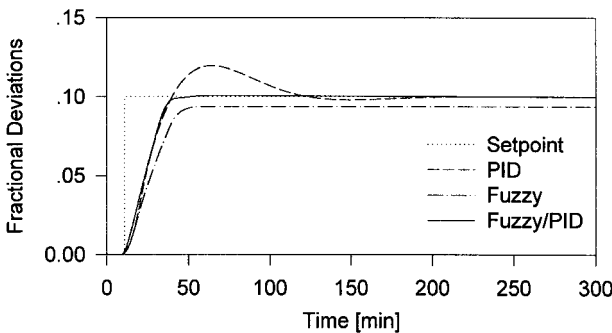


Figure 10 Fractional deviation of the monomer conversion for 10% change in the setpoint when three different control algorithms are applied.

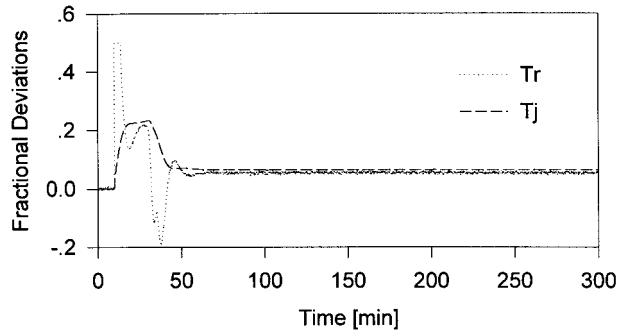


Figure 11 Fractional deviations of the reactor and jacket temperatures for 10% change in the setpoint for the conversion when the fuzzy/PID control algorithm is applied.

disturbance is examined by introducing a 10% change in the feed temperature; the result is shown in Figure 12. Here again, the fuzzy/PID controller shows the best and satisfactory performance in eliminating the influence of disturbance and regulating the monomer conversion, respectively.

CONCLUSIONS

A mathematical model is developed for free radical reaction mechanism with thermal initiation. The rate constants of the thermal initiation are estimated experimentally by measuring the changes in conversion with various monomer compositions at different temperatures. The model is proved to be adequate for a CSTR in which the

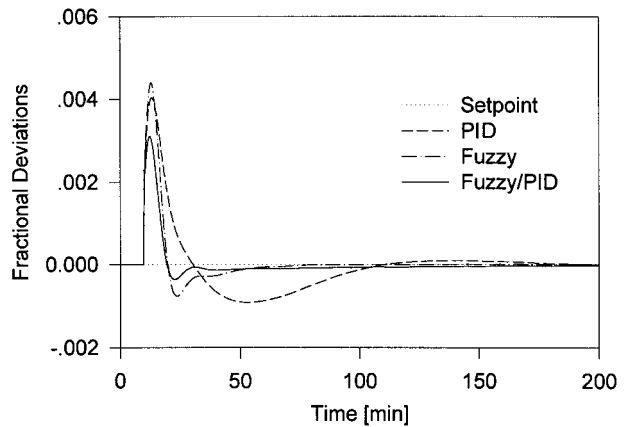


Figure 12 Fractional deviation of the monomer conversion for 10% change in the feed temperature (load) when three different control algorithms are applied.

free radical solution copolymerization of SAN takes place. While the reactor temperature is an important factor affecting the monomer conversion in solution copolymerization of SAN, the parameter that may affect the properties of the SAN copolymer is the weight fraction of the monomers fed into the reactor.

To control the monomer conversion in the solution copolymerization reactor, three different control algorithms are considered. We attempted to overcome the difficulty associated with the conventional PID control with the aid of fuzzy control, so that advantages of both control algorithms are combined to give more efficient control. The simulation results show that the performance of the fuzzy/PID controller is much better than that of the PID or fuzzy controller for setpoint tracking as well as disturbance rejection.

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NOMENCLATURE

F_i	instantaneous copolymer composition ($i = 1, 2$)
f_i	mole fraction of monomer i in feed ($i = 1, 2$)
G_k	k th moment of living polymer concentration ($k = 0, 1, 2$)
H_k	k th moment of dead polymer concentration ($k = 0, 1, 2$)
k_{hij}	rate constants for homolysis reaction (i and $j = 1, 2$)
k_{ij}	diffusion-controlled propagation rate constant (i and $j = 1, 2$)
\bar{k}_p	pseudokinetic rate constant for propagation
\bar{k}_{fm}	pseudokinetic rate constant for chain transfer to monomer
\bar{k}_{fs}	pseudokinetic rate constant for chain transfer to solvent
\bar{k}_t	pseudokinetic rate constant for termination
$\bar{k}_{t,u}$	pseudokinetic rate constant for termination with chain length u
$\bar{k}_{tc,u}$	pseudokinetic rate constant for termination by combination with chain length u
$\bar{k}_{td,u}$	pseudokinetic rate constant for termination by disproportionation with chain length u

k_{di}	rate constant for the forward Diels–Alder dimerization ($i = 1, 2$)
k_{ri}	rate constant for the reverse Diels–Alder dimerization ($i = 1, 2$)
k_{si}	rate constant of free radical formation ($i = 1, 2$)
\bar{M}_{av}	average molecular weight of monomers 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
q_{in}	inlet volumetric flow rate of the reactant
q_{out}	outlet volumetric flow rate of the product
R_I	initiation rate of copolymerization
$R_{u,i}$	polymeric radical of type i with chain length u or its concentration ($i = 1, 2$)
r_Y	rate of generation of species Y
S	solvent or concentration of solvent
V	volume of the reaction mixture in the reactor
V_{Mi}	volume of the monomer i in the reactor
X	conversion of monomer

Greek letters

α	constant dependent on temperature and the molar composition of the monomers
Φ	primary radical
ρ_{Mi}	density of monomer i ($i = 1, 2$)
ρ_p	density of polymer

Subscripts

av	average
s	steady-state value

Abbreviation

AN	acrylonitrile
CSTR	continuous stirred tank reactor
EB	ethylbenzene
FLC	fuzzy logic controller
PID	proportional–integral–derivative
SAN	styrene and acrylonitrile
St	styrene

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