

Semicontinuous Thermal Bulk Copolymerization of Styrene and Maleic Anhydride: Experiments and Reactor Model

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ABSTRACT: Thermal bulk copolymerization of styrene (St) and maleic anhydride (MAH) has been carried out at 110–130°C and up to around 55 wt % conversion in a stirred tank reactor with an anchor impeller to prepare the random copolymer of St–MAH (R-SMA). A series of experiments in semicontinuous monomer adding process were done to investigate the effects of operating condition on monomer conversion, copolymer composition, and its uniformity. It has been shown that a random copolymer with constant composition can be obtained by semicontinuous copolymerization. A reactor model was developed to simulate the copolymerization processes. The numerical method in which the gel effect on the copolymerization is incorporated has exhibited excellent agreement between the model calculation and the experimental data. However, when using the assumption that (1) $k_{22} = 0$; (2) $k_{21}[M_1] \gg k_{12}[M_2]$; and (3) $(R_1/2k_t)^{1/2}$ is a constant, an analytical solution to the model was found to be available also. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1905–1912, 1998

Key words: thermal bulk polymerization; semicontinuous polymerization; St–MAH copolymerization

INTRODUCTION

Copolymerization of styrene (St) and maleic anhydride (MAH) is well known to have a very strong tendency towards alternation. However, it has been found that random copolymer can be obtained when the copolymerization is carried out in a relatively high temperature or in the presence of polar solvent.¹ The random copolymer product is widely accepted as being the most economical performance choice for structurally important automotive interior components, as well as for many commercial industrial applications since it exhibits better heat resistance, miscibility with other polymers, and compatibility with glass fiber than other St copolymers.² In our recent work, the thermal bulk random copolymerization of St and MAH was carried out at 110–130°C in a semicontinuous

and a continuous reactors. In order to develop an effective commercial process for production of the random copolymer of St–MAH (R-SMA) resin, a reactor model was developed to simulate the copolymerization processes. Model parameters were determined by fitting the data of monomer conversions and copolymer compositions versus reaction time of all semicontinuous tests. The transferability of kinetics from semicontinuous experiments to continuous copolymerization process was examined also. This article is to report the investigation of the semicontinuous copolymerization experiments and their modeling results.

EXPERIMENTAL

Experimental Materials

The St monomer was distilled under vacuum with the fraction 53–55°C/13 mm Hg being collected and stored at –5°C. MAH (analytical reagent grade) was dried under vacuum at room tempera-

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ture. The purified MAH was stored in a moisture-free desiccator.

Copolymerization Process

Semicontinuous bulk copolymerization of St and MAH was carried out in a 0.5-L tank reactor with an anchor impeller. The reactor was precharged with one-third of monomer mixture in which the amount of MAH was given as a operating condition. When the desired reaction temperature was reached, the residual monomer mixture with 10 wt % MAH was pumped into the reactor in a given rate, and the copolymerization was conducted under nitrogen atmosphere. After an appropriate interval, sampling was made. The amount of copolymer was determined by the method of dissolution (by pure dry acetone) and reprecipitation (by methanol), from which monomer-to-polymer conversion was obtained. For determining the fraction of MAH in SMA copolymers, the purified sample in amount of 0.1–0.2 g was dissolved in 150 mL acetone and 10 mL 0.1N NaOH solution was added. After 4–6 h, the solution was back-titrated with 0.05N H₂SO₄ solution.

REACTOR MODEL

Material Balance Equations

The bulk copolymerization is characterized by the fact that all reaction steps proceed in a single phase. A model for the semicontinuous reactor would consist of a set material balance describing the rates of accumulation, inflow, and disappearance or appearance by reaction of each monomer and polymer in the reactor, which are outlined as follows:

$$\frac{dN_1}{dt} = F_1 - R_1V \quad (1)$$

$$\frac{dN_2}{dt} = F_2 - R_2V \quad (2)$$

$$P_1 = F_1t + N_{1,0} - N_1 \quad (3)$$

$$P_2 = F_2t + N_{2,0} - N_2 \quad (4)$$

$$V = \frac{N_1M_{w1}}{\rho_1} + \frac{N_2M_{w2}}{\rho_2} + \frac{P_1M_{w1} + P_2M_{w2}}{\rho_P} \quad (5)$$

where N_1 and N_2 are the mol numbers of monomer St and MAH; F_1 and F_2 , their molar inlet flow rates; P_1 and P_2 , the molecular numbers of mono-

mer unit St and MAH in copolymer, respectively; M_{w1} and M_{w2} , the molecular weights of monomer St and MAH; ρ , density; and $N_{1,0}$ and $N_{2,0}$, the values of N_1 and N_2 at initial time.

The reaction rate terms of St and MAH in eqs. (1)–(2), R_1 and R_2 , are given by³

$$R_1 = \left(\frac{R_I}{2k_t} \right)^{1/2} \frac{k_{11}k_{21}[M_1]^2 + k_{21}k_{12}[M_1][M_2]}{k_{12}[M_2] + k_{21}[M_1]} \quad (6)$$

$$R_2 = \left(\frac{R_I}{2k_t} \right)^{1/2} \frac{k_{22}k_{12}[M_2]^2 + k_{21}k_{12}[M_1][M_2]}{k_{12}[M_2] + k_{21}[M_1]} \quad (7)$$

For the St–MAH copolymerization system, the propagation coefficient of MAH homopolymerization, k_{22} , can be taken as zero because the maleic free radical on the end of a growing chain is difficult to react with MAH monomer.⁴ Therefore, eq. (7) can be rewritten as

$$R_2 = \left(\frac{R_I}{2k_t} \right)^{1/2} \frac{k_{21}k_{12}[M_1][M_2]}{k_{12}[M_2] + k_{21}[M_1]} \quad (8)$$

In eqs. (6)–(8), $[M_1]$ and $[M_2]$ are molar concentration of St and MAH; k_t is the termination rate coefficient; k_{ij} , the coefficients for various of propagation reaction; and R_I , the thermal initiation rate of St, which is given by^{5,6}

$$R_I = 2k_I[M_1]^3 \quad (9)$$

where k_I is the initial rate coefficient.

Numerical Solutions

It is well known that both termination and propagation coefficients fall with increasing conversion due to strong diffusion limitations. Many semiempirical or theoretical models have been developed to describe this phenomena, among which the Soh and Sunderg model⁷ and the Marten and Hamielec model⁸ are frequently used in literature. The Marten and Hamielec model, which was based on the free-volume theory, has been extended to the copolymerization system.^{9,10} In this article, the Marten and Hamielec model is used to treat both termination and propagation coefficients; that is,

$$k_i = (k_i)_0 \quad V_F > V_{Fcr} \quad (10)$$

Table I Values of Model Parameters Used in Calculations

Model Parameter
$k_{11} = 1.05 \times 10^7 \exp(-3,557/T)^{11}$
$\alpha_1 = 1.0 \times 10^{-3\ 11}$
$\alpha_2 = 1.25 \times 10^{-3\ 13}$
$\alpha_P = 2.04 \times 10^{-4\ 14}$
$k_t = 2.19 \times 10^7 \exp(-13,810/T)^{12}$
$T_{g,1} = -88.2^\circ\text{C}^{11}$
$T_{g,2} = 10^\circ\text{C}^{13}$
$T_{g,P} = 120^\circ\text{C}^{14}$

$$k_t = (k_t)_0 \left(\frac{M_{wcr}}{M_w} \right)^\alpha \exp\left(\frac{A}{V_F} - \frac{A}{V_{Fcr}} \right) \quad V_F < V_{Fcr} \quad (11)$$

and

$$k_{ij} = (k_{ij})_0 \quad V_F > V_{Fcr ij} \quad (12)$$

$$k_{ij} = (k_{ij})_0 \exp\left(\frac{B}{V_F} - \frac{B}{V_{Fcr}} \right) \quad V_F < V_{Fcr ij}. \quad (13)$$

In the above equations, A , B , and α are model parameters, and \overline{M}_w is the weight-average molecular weight of copolymer.

V_F , the free volume fraction, is given by

$$V_F = [0.025 + \alpha_P(T - T_{gP})]\phi_P + [0.025 + \alpha_{M1}(T - T_{gM1})]\phi_{M1} + [0.025 + \alpha_{M2}(T - T_{gM2})]\phi_{M2} \quad (14)$$

where T_g is glass transition temperature; T , the reaction temperature; α , thermal expansion coefficient; and ϕ , the volume fraction. Subscripts M_1 , M_2 , and P denote St, MAH, and the copolymer, respectively; cr denotes critical case.

Using the fourth-order Runge–Kutta algorithm, the differential equations for material balance incorporated with other algebraic equations given above can be solved numerically, and the monomer-to-polymer conversion and the MAH weight fraction can be obtained from the following equations:

$$C \% = \frac{P_1 M_{w1} + P_2 M_{w2}}{(N_1 + P_1)M_{w1} + (N_2 + P_2)M_{w2}} \quad (15)$$

$$\text{MAH \%} = \frac{P_2 M_{w2}}{P_1 M_{w1} + P_2 M_{w2}} \quad (16)$$

There are a large number of parameters in above equations. In this work, some parameters were taken from the literature, as shown in Table I.

The critical free volume for termination reaction, V_{Fcr} , is taken to be that at zero conversion in consideration of that the termination is controlled by the diffusion of chain radicals right from the start of polymerization. On the other hand, it is assumed that the diffusion control for propagation reaction occurs later. Under the diffusion control state, it was expected that $k_{21} = k_{11}$ since the propagation rates depend on the diffusion coefficient of the monomer and no longer on the radical type. Therefore,

$$(k_{11})_0 = (k_{21})_0 \exp\left(\frac{B}{V_{Fcr11}} - \frac{B}{V_{Fcr21}} \right) \quad (17)$$

That is, V_{Fcr11} was obtained by V_{Fcr21} , $(k_{21})_0$ and $(k_{11})_0$. Except for the above parameters, the others including V_{Fcr12} , V_{Fcr21} , A , B , α ; the frequency factors A_t , A_{21} , A_{12} ; and the activation energies E_t , E_{21} , E_{12} were estimated from the experimental data of the semicontinuous tests by using the following nonlinear least-squares criterion:

$$\min \left\{ \sum_{i=1}^n ((C_i \% - \overline{C}_i \%)^2 + (\text{MAH}_i \% - \overline{\text{MAH}}_i \%)^2) \right\} \quad (18)$$

More than 500 observations (that is, $n > 500$) were involved in estimation. The variable matrix method was used to minimized this objective function, and the desired gradient can be computed by solving the sensitivity equation. The estimated parameters are listed in Table II.

Analytical Solutions

Assuming that (a) $(R_t/2k_t)^{1/2}$ is constant, signed as C , and (b) $k_{21}[M_1] \gg k_{12}[M_2]$, eqs. (6) and (8) were rewritten as

Table II Values of Model Parameters Estimated from Semicontinuous Tests

Model Parameter
$k_{12} = 3.60 \times 10^7 \exp(-2873/T)$
$k_t = 9.91 \times 10^{11} \exp(-2892/T)$
$A = -0.52$
$V_{Fcr12} = 0.128$
$k_{21} = 1.81 \times 10^{10} \exp(-4524/T)$
$\alpha = 2.00$
$B = -0.92$
$V_{Fcr21} = 0.192$

$$R_1 = C(k_{11}[M_1] + k_{12}[M_2]) \quad (19)$$

$$R_2 = Ck_{12}[M_2] \quad (20)$$

Using $N_1 = [M_1]V$ and $N_2 = [M_2]V$, the material balance equations for semicontinuous reactor become

$$\frac{dN_1}{dt} = F_1 - C(k_{11}N_1 + k_{12}N_2) \quad (21)$$

$$\frac{dN_2}{dt} = F_2 - Ck_{12}N_2 \quad (22)$$

When assuming that all propagation rate coefficients and inflow rate keep unchanged, the following analytical solutions were obtained:

$$N_1 = \left(N_{1,0} - \frac{b}{b-a} N_{2,0} + \frac{b}{(b-a)a} F_2 - \frac{F_1}{a} \right) \times \exp(-at) + \left(\frac{b}{b-a} N_{2,0} - \frac{F_2}{b-a} \right) \times \exp(-bt) + \frac{F_1 - F_2}{a} \quad (23)$$

$$N_2 = \left(N_{2,0} - \frac{F_2}{b} \right) \exp(-bt) + \frac{F_2}{b} \quad (24)$$

where a equals Ck_{11} and b equals Ck_{12} .

It should be noticed that only two parameters, a and b , are needed in either eqs. (23) and (24). In calculations for semicontinuous processes by the analytical method, parameters k_{11} and k_{12} are from Table I and II, so only C is estimated.

RESULTS AND DISCUSSION

In our previous article,¹⁵ evidence has been given to support that the products of the semicontinuous thermal bulk copolymerization have a random structural unit arrangement. Here, Figure 1 shows the conversion, C %, and the weight fraction of MAH in SMA copolymer, MAH %, as a function of reaction time at the temperature of 115°C, and the weight fraction of MAH in initial charge is 0.25%. Figure 2 is similar to Figure 1, except that the weight inflow rate of monomer mixture is slower. Figure 3 and 4 show the experimental and the calculated results from semicontinuous runs both carried out at 110°C, but the amount of MAH in initial charge is different. Fig-

ure 5 compares the conversion–time curves at different reaction temperatures. Their copolymer compositions curves are shown in Figure 6. These figures have shown that the copolymer composition is maintained constant during the polymerization process. The higher the polymerization temperature, the higher the monomer conversion, and the lower MAH fraction in the copolymer.

Besides experimental data, the calculated results from the numerical methods in which the Marten–Hamielec gel effect model is incorporated (dotted lines) and the analytical solution equations (solid lines), respectively, are all plotted in the figures. It has been found that the numerical results fit with the experimental data very well both in conversion and in copolymer composition when the gel effect model is incorporated. However, it is of interest to note that the analytical solution also appear to be in good agreement with the experimental data, although the gel effect is ignored. The reasons may be as follows.

1. In this work, the thermal initiation rate, R_I , is decreased with an increase of monomer conversion. This descent just corresponds to the decrease of k_t with conversion increase so that $(R_I/2k_t)^{1/2}$ is likely to keep constant.

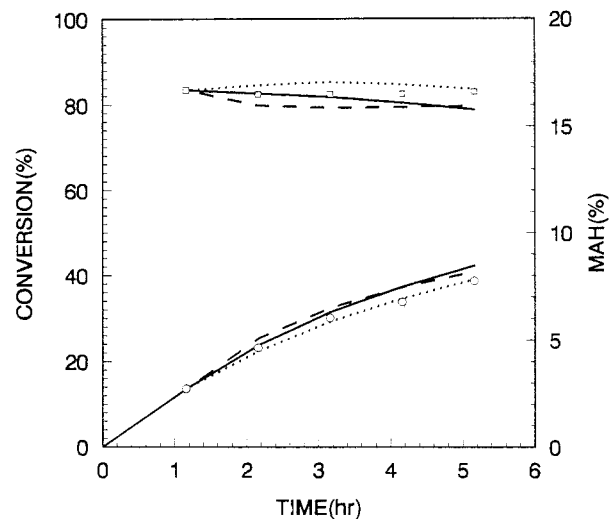


Figure 1 The time evolution of the conversion and copolymer composition for semicontinuous copolymerization carried out at $T = 115^\circ\text{C}$, $\text{MAH}_0 = 0.25$, and a flow rate of the monomer mixture = 38 g/h; (\cdots) numerical solution in which gel effect is incorporated; ($---$) numerical solution in which gel effect is not incorporated; ($—$) analytical solution; (\circ) experimental data for conversion; and (\square) experimental data for the weight percentage of MAH in the copolymer.

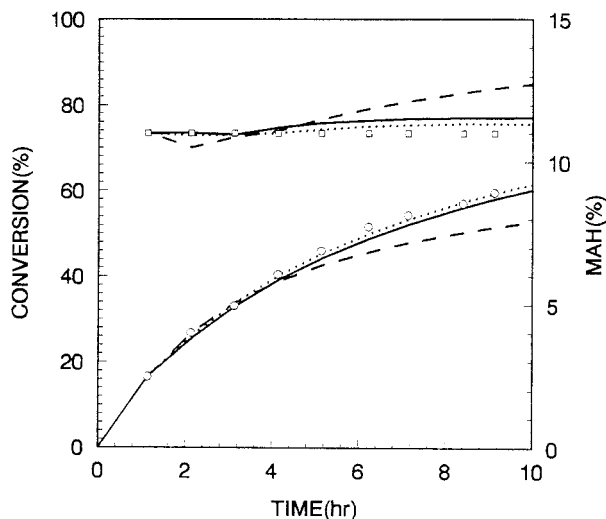


Figure 2 The time evolution of conversion and copolymer composition for semicontinuous copolymerization carried out at $T = 115^{\circ}\text{C}$, $\text{MAH}_0 = 0.25$, and a flow rate of monomer mixture = 19 g/h (curves and points as described in Fig. 1).

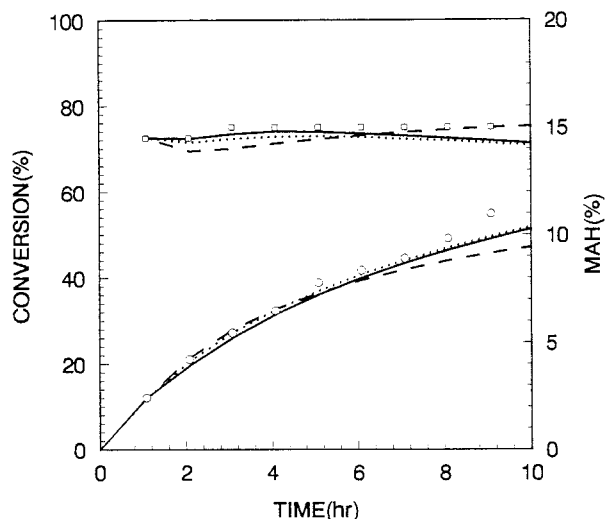


Figure 4 The time evolution of conversion and copolymer composition for semicontinuous copolymerization carried out at $T = 110^{\circ}\text{C}$, $\text{MAH}_0 = 0.5$, and a flow rate of the monomer mixture = 22.5 g/h (curves and points as described in Fig. 1).

Figure 7 shows C , that is, $(R_t/2k_t)^{1/2}$, as a function of conversion at different reaction temperature. It can be seen that C rises with increasing temperature but keeps almost constant for a fixed temperature.

- Comparing reaction activities of the MAH radical–St monomer with the St radical–MAH monomer, and considering $[M_1] \gg [M_2]$ in our experiments, it is appropriate to take

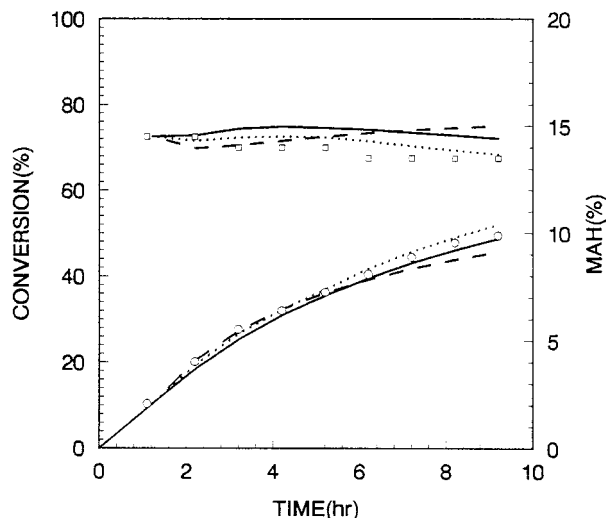


Figure 3 The time evolution of conversion and copolymer composition for semicontinuous copolymerization carried out at $T = 110^{\circ}\text{C}$, $\text{MAH}_0 = 0$, and a flow rate of the monomer mixture = 22.5 g/h (curves and points as described in Fig. 1).

$k_{21}[M_1] \gg k_{12}[M_2]$. As shown in Figure 8, although $k_{21}[M_1]/k_{12}[M_2]$ is decreased with an increase in monomer conversion, the value is usually greater than 100 when the conversion is lower than 60%.

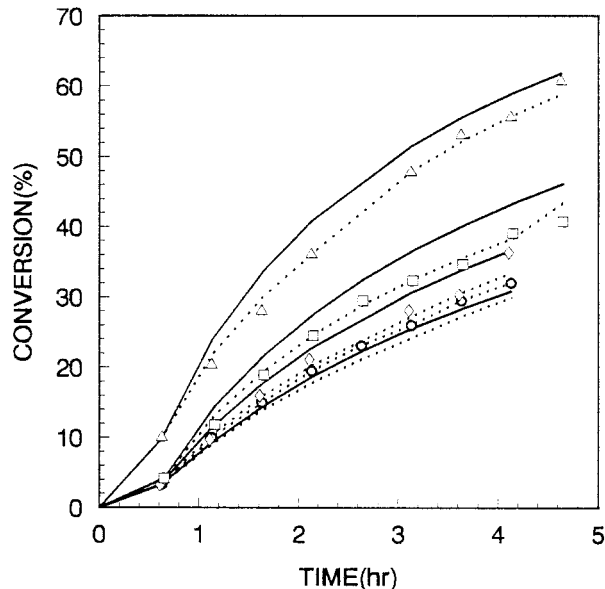


Figure 5 The time evolution of conversion for semicontinuous copolymerization carried out at $\text{MAH}_0 = 0.25$ and a flow rate of the monomer mixture = 22.5 g/h (curves as described in Fig. 1): (○) experimental data for $T = 110^{\circ}\text{C}$; (◇) experimental data for $T = 115^{\circ}\text{C}$; (□) experimental data for $T = 120^{\circ}\text{C}$; (△) experimental data for $T = 130^{\circ}\text{C}$.

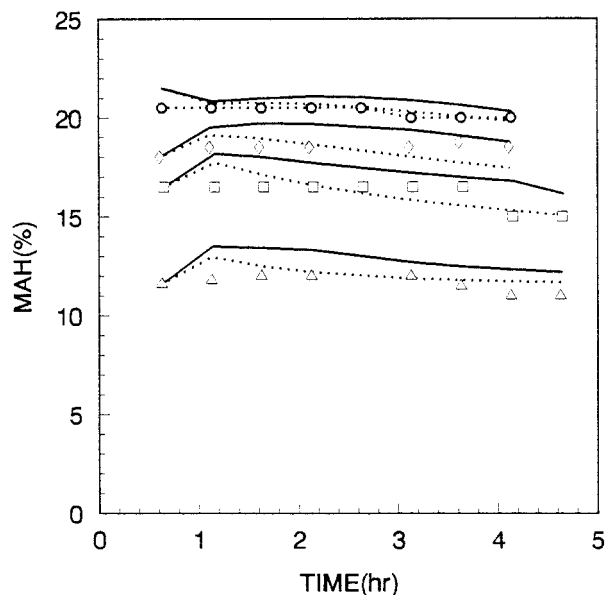


Figure 6 The time evolution of copolymer composition for semicontinuous copolymerization carried out at $MAH_0 = 0.25$ and a flow rate of the monomer mixture = 22.5 g/h (curves as described in Fig. 1; reaction temperature points as described in Fig. 5).

- In all runs, the monomer conversion usually did not exceed 55%, so the effect of diffusion on propagation rate is unimportant. Figure 9 shows the change of k_{11} and k_{12} with the conversion. It has been found both k_{11} and

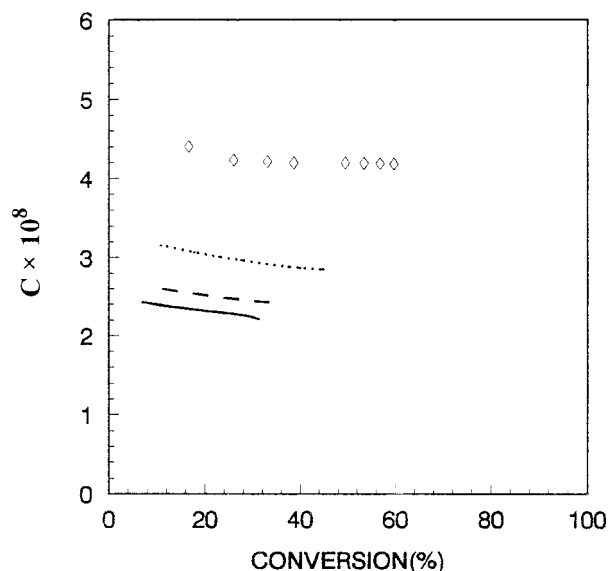


Figure 7 Changes of parameter C with monomer conversion and reaction temperature at $MAH_0 = 0.25$ and a flow rate of monomer mixture = 45 g/h: (—) $T = 110^\circ\text{C}$; (---) $T = 115^\circ\text{C}$; (\cdots) $T = 120^\circ\text{C}$; and (\diamond) $T = 130^\circ\text{C}$.

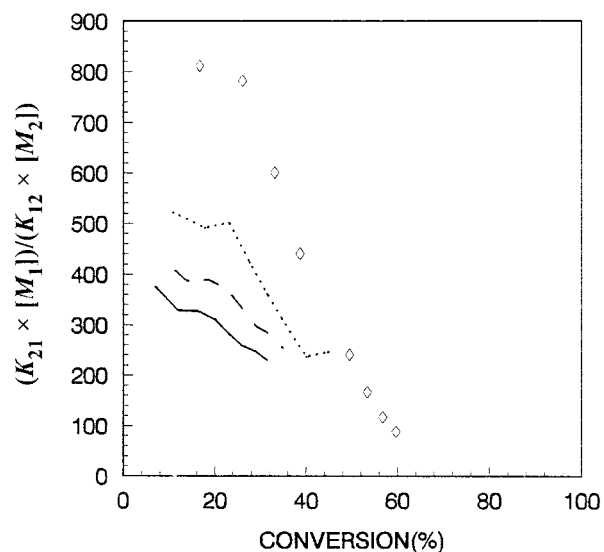


Figure 8 Changes of $k_{21}[M_1] \gg k_{12}[M_2]$ with monomer conversion and reaction temperature (the reaction conditions for curves and points as described in Fig. 7).

k_{12} keep constant, except that k_{12} begins to decrease as the conversion exceeds 55%, which occurs only at 130°C . The diffusion control for k_{12} may occur at a relative lower conversion, but k_{12} does not appear in the analytical solution.

When only the descent of R_f is considered without making allowance of the gel effect, using the Runge–Kutta algorithm to solve the material balance equations, the results are plotted in Figure

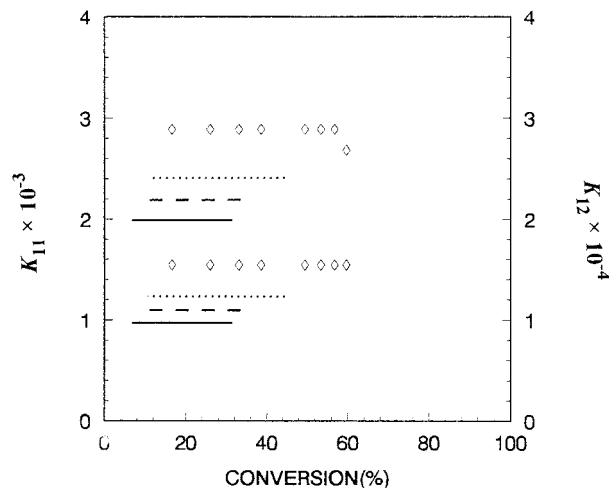


Figure 9 Changes of propagation rate coefficient with monomer conversion and reaction temperature (the reaction conditions for curves and points as described in Fig. 7).

1–4. It is obvious that these curves (broken lines) deviate from experimental data more than the other two curves, especially during the high conversion stage. This means the effect of diffusion on the termination rate is considerable.

CONCLUSIONS

The random copolymer of St and MAH with uniform composition can be prepared by the semicontinuous thermal bulk copolymerization process. A reactor model has been developed to simulate the bulk random copolymerization of St and MAH. Some parameters are estimated from experimental data for semicontinuous processes. The time evolution of monomer conversion and copolymer composition for semicontinuous processes are calculated, respectively, by the numerical method and analytical solution. It is found that the numerical results with consideration of the diffusion control effect on chain propagation and termination fit with the experimental data very well. It means that gel effect is significant for the bulk copolymerization processes. However, the descent of the termination rate coefficient due to the gel effect seems able to be counterbalanced by the decrease of the thermal initiation rate with an increase in monomer conversion. Otherwise, $k_{21}[M_1]$ and is much larger than $k_{21}[M_2]$, so the analytical solution agree with the actual process data also.

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NOMENCLATURE

a, b	parameters of eqs. (23) and (24)
A, B	parameters of the Marten–Hamielec gel effect model
$C \%$	weight conversion of monomers (model calculation)
$\bar{C} \%$	weight conversion of monomers (experimental data)
F_i	molar inlet flow rate of monomer i (mol/s)
k_{ij}	propagation rate coefficient ($\text{L mol}^{-1} \text{s}^{-1}$)
$(k_{ij})_0$	propagation rate coefficient (for $C \%$ = 0) ($\text{L mol}^{-1} \text{s}^{-1}$)

k_t	termination rate coefficient ($\text{L mol}^{-1} \text{s}^{-1}$)
$(k_t)_0$	termination rate coefficient (for $C \%$ = 0) ($\text{L mol}^{-1} \text{s}^{-1}$)
MAH ₀	weight fraction of MAH in initial charge of reactor
MAH %	weight fraction of MAH in copolymer (model calculation)
$\overline{\text{MAH}} \%$	weight fraction of MAH in copolymer (experimental data)
$[M_i]$	molar concentration of monomer i (mol/L)
\overline{M}_w	accumulated weight-average molecular weights of copolymer
M_{wi}	molecular weight of monomer i
M_{wcr}	critical molecular weights of copolymer in the Marten–Hamielec gel effect model
N_i	mol number of monomer i (mol)
P_i	molecular number of monomer unit i in copolymer (mol)
R_i	reaction rate of monomer I ($\text{mol l}^{-1} \text{s}^{-1}$)
R_I	initiation rate ($\text{mol l}^{-1} \text{s}^{-1}$)
T_g	glass transition temperature (K)
V	available volume of reactor (L)
V_F	free volume
$V_{Fcr ij}$	critical free volume in the Marten–Hamielec gel effect model
α	parameter of the Marten–Hamielec gel effect model
α_i, α_p	thermal expansion coefficient
ρ_i, ρ_p	density (g/L)
ϕ_i, ϕ_p	volume fraction

Subscripts

1, 2, and p St, MAH, and copolymer, respectively

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