Continuous Thermal Bulk Copolymerization of Styrene and Maleic Anhydride

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ABSTRACT: Thermal bulk copolymerization of styrene (monomer 1) and maleic anhydride (monomer 2) was carried out in a continuous stirred tank reactor (CSTR) with a double helical ribbon-anchor impeller. A series of experimental runs under different operating conditions (average residence time, reaction temperature, and the composition in the inflow stream) were done, which showed that steady states could be approached. The effect of operating conditions on monomer conversion and copolymer composition was discussed. A CSTR model was established and the model parameters from the semicontinuous tests were used to predict conversions and copolymer compositions of the continuous process under transient and steady states. Kinetics from the semicontinuous bulk copolymerization were transferable to the continuous process. The modeling work for the continuous process showed that the same result as in a semicontinuous process could be obtained; the numerical method in which the gel effect on the copolymerization was incorporated exhibited excellent agreement between the model calculation and the experimental data. However, when using the assumption that $k_{22} = 0$, $k_{21}[M_1] \gg k_{12}[M_2]$, $(R_I/2k_t)^{1/2}$ is a constant, and V is a constant, the predictions from the analytical solution to the model were in good agreement with the actual process data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 615-622, 1999

Key words: thermal bulk polymerization; continuous polymerization; St-MAH copolymerization

INTRODUCTION

Copolymerization of styrene (St) and maleic anhydride (MAH) carried out in a relatively high temperature or in the presence of polar solvent can reduce the tendency toward alteration to obtain high molecular weight random copolymer with a small fraction of MAH (R-SMA), which exhibits better heat resistance, miscibility with other polymers, and compatibility with glass fiber than other St copolymers.¹ To design a process to produce the copolymer resin, a reactor model is usually required, especially for a highly viscous polymerization process such as bulk polymerization. In our previous work² a reactor model for the semicontinuous process was developed to simulate the thermal bulk random copolymerization of St and MAH carried out at 110-130 °C. Model parameters were determined by fitting the data for monomer conversion and copolymer compositions versus reaction time for all semicontinuous tests. In this work, some experiments on continuous thermal bulk copolymerization of St and MAH were performed to develop a higher efficiency process to produce the resin. A continuous stirred tank reactor (CSTR) model was established and the transferability of kinetics from semicontinuous experiments to a continuous copolymerization process was examined.

EXPERIMENTAL

Monomer St and MAH were purified by the method mentioned in our former article.² The con-

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Run	RT (h)	Temp. (°C)	MAH ^a Content (wt %)	EB ^b Content (vol %)	Run	RT (h)	Temp. (°C)	MAH ^a Content (wt %)	EB ^b Content (vol %)
1	5	105	10	0	8	3	110	10	0
2	5	110	10	0	9	7	110	10	0
3	5	115	10	0	10	9	110	10	0
4	5	120	10	0	11	5	120	10	2
5	5	110	5	0	12	5	120	10	5
6	5	110	15	0	13	5	120	10	8
7	5	110	20	0	14	5	120	7	5

 Table I
 Reaction Conditions for Continuous Thermal Bulk Copolymerization

RT, residence time.

^a Weight fraction of MAH in inflow mixture.

^b Volume fraction of ethyl benzene (EB, AR grade) that was added to precharged and inflow mixtures.

tinuous copolymerization was carried out in a 1.4-L tank reactor with a double helical ribbon-anchor impeller. The reactor provides theoretical full mixing even if the conversion is up to 60%.

The starting process of the continuous bulk copolymerization is like a semicontinuous process. The reactor was precharged with one-third of the monomer mixture in which the amount of MAH was set as an operating condition. When the desired reaction temperature was reached, the monomer mixture with 5-20 wt % MAH was pumped into the reactor at a given rate; the copolymerization was conducted under nitrogen atmosphere. When the tank was full, the copolymer and residual monomer began to flow out. The polymerization conditions are listed in Table I.

After an appropriate interval, sampling was made. The instantaneous conversion was determined by the method of dissolution and reprecipitation. The fraction of MAH in the copolymer was determined by acid-base titration.

REACTOR MODEL

Material Balance Equations

A model for the CSTR in which the bulk random copolymerization was carried out would consist of a set of material balance equations describing the rates of accumulation, inflow, outflow, appearance, and disappearance by reaction of each monomer and polymer in the reactor. These are outlined as follows:

$$\frac{dN_1}{dt} = F_1 - \frac{N_1}{V}Q - R_1 V$$
(1)

$$\frac{dN_2}{dt} = F_2 - \frac{N_2}{V}Q - R_2V$$
(2)

$$\frac{dP_1}{dt} = -\frac{P_1}{V}Q + R_1 V \tag{3}$$

$$\frac{dP_2}{dt} = -\frac{P_2}{V}Q + R_2V \tag{4}$$

$$V = \frac{N_1 M_{w1}}{\rho_1} + \frac{N_2 M_{w2}}{\rho_2} + \frac{P_1 M_{w1} + P_2 M_{w2}}{\rho_P} \quad (5)$$

where N_1 and N_2 are the mole number of monomer St and MAH, F_1 and F_2 are their molar inlet flow rates, Q is the volumetric flow out of the reactor, V is the available volume of the reactor, P_1 and P_2 are the molecular number of monomer units of St and MAH in the copolymer, M_{W1} and M_{W2} are the molecular weight of St and MAH, and ρ is the density.

The reaction rate terms of St and MAH, R_1 and R_2 , in eqs. (1) and (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 so eq. (7) can be rewritten as

$$R_{2} = \left(\frac{R_{I}}{2k_{t}}\right)^{1/2} \frac{k_{21}k_{12}[M_{1}][M_{2}]}{k_{12}[M_{2}] + k_{21}[M_{1}]}$$
(8)

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

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

where k_I is the initial rate coefficient.

Analytical Solutions

Assuming that $(R_I/2k_t)^{1/2}$ was constant with symbol C and $k_{21}[M_1] \ge k_{12}[M_2]$, eqs. (6) and (8) were rewritten as

$$R_1 = C(k_{11}[M_1] + k_{12}[M_2])$$
(10)

$$R_2 = Ck_{12}[M_2] \tag{11}$$

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

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

$$\frac{dN_2}{dt} = F_2 - Ck_{12}N_2 - N_2\frac{Q}{V}$$
(13)

$$\frac{dP_1}{dt} = C(k_{11}N_1 + k_{12}N_2) - P_1\frac{Q}{V}$$
(14)

$$\frac{dP_2}{dt} = Ck_{12}N_2 - P_2\frac{Q}{V}$$
(15)

When assuming that all propagation rate coefficients, inflow rate, and the volume of the reaction system, V, remain unchanged (the last assumption means the reactor operates at full scale), the following analytical solutions were obtained:

$$N_{1} = \left[N_{1,0} - \frac{b}{b-a} N_{2,0} + \frac{1}{a+1/\tau} \left(\frac{b}{b-a} F_{2} - F_{1} \right) \right]$$

$$\times \exp\left[- \left(a + \frac{1}{\tau} \right) t \right] + \left[\frac{b}{b-a} N_{2,0} - \frac{F_{2}b}{(b-a)(b+1/\tau)} \right] \exp\left[- \left(b + \frac{1}{\tau} \right) t \right]$$

$$+ \frac{F_{1}}{a+1/\tau} - \frac{b}{b+1/\tau} \frac{F_{2}}{a+1/\tau} \quad (16)$$

Table IIValues of a, b, and C at DifferentReaction Temperatures

		Temperature (°C)				
	105	110	115	120		
$egin{array}{l} & imes 10^5 \ b imes 10^4 \ C imes 10^8 \end{array}$	$1.91 \\ 3.18 \\ 2.16$	$2.62 \\ 4.28 \\ 2.63$	$3.58 \\ 5.69 \\ 3.18$	4.83 7.52 3.83		

$$N_{2} = \left(N_{2,0} - \frac{F_{2}}{b+1/\tau}\right)$$

$$\times \exp\left[-\left(b+\frac{1}{\tau}\right)t\right] + \frac{F_{2}}{b+1/\tau} \quad (17)$$

$$P_1 = (N_{1,0} - F_1\tau)\exp(-t/\tau) + F_1\tau - N_1 \quad (18)$$

$$P_2 = (N_{2,0} - F_2 \tau) \exp(-t/\tau) + F_2 \tau - N_2 \quad (19)$$

Here $a = Ck_{11}$ and $b = Ck_{12}$, which are identified with those in the semicontinuous model's analytical solutions given in Table II; the $\tau = V/Q$ means the average residence time. When Q is zero, eqs. (16) and (17) become the solution of the semicontinuous reactor model.

Numerical Solutions

In this article the Marten and Hamielec model⁷ is used to treat the diffusion limitations on the termination and propagation coefficients, which is relative simple and has been extended to a copolymerization system.^{8,9} The gel effect model is based on the free-volume theory, that is,

$$k_t = (k_t)_0 \qquad \qquad \mathbf{V}_F > V_{F_{\mathrm{cr}}} \quad (20)$$

$$k_t = (k_t)_0 \left(\frac{M_{w_{\rm cr}}}{M_w}\right)^{\alpha} \exp\left(\frac{A}{V_F} - \frac{A}{V_{F_{\rm cr}}}\right) \quad V_F < V_{F_{\rm cr}} \quad (21)$$

and

$$k_{ij} = (k_{ij})_0$$
 $V_F > V_{F_{crij}}$ (22)

$$k_{ij} = (k_{ij})_0 \exp\left(\frac{B}{V_F} - \frac{B}{V_{F_{cr}}}\right) \quad V_F < V_{F_{crij}}$$
 (23)



Figure 1 The time evolution of conversion for continuous copolymerization carried out with different MAH weight fractions in the inflow. Experimental data for MAH weight fraction in inflow (wt %): (\bigcirc) 5, (\diamond) 10, (\square) 15, (\triangle) 20; *T* = 110°C, RT = 5 h EB = 0 vol %; (\cdots) numerical calculation result in which the gel effect is incorporated; (-) analytical solution.

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

 V_F , the free volume fraction is given by

$$V_F = (0.025 + \alpha_P (T - T_{gP}))\phi_P$$

+ (0.025 + \alpha_{M_1} (T - T_{gM_1}))\phi_{M_1}
+ (0.025 + \alpha_{M_2} (T - T_{eM_2}))\phi_{M_2} (24)

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

$$C\% = \frac{P_1 M_{w1} + P_2 M_{w2}}{(M_1 + P_1) M_{w1} + (M_2 + P_2) M_{w2}} \quad (25)$$

$$MAH\% = \frac{P_2 M_{W2}}{P_1 M_{w1} + P_2 M_{w2}}$$
(26)

The values of the model parameters are taken from those estimated from the semicontinuous tests in our previous article.²

RESULTS AND DISCUSSION

Figures 1–10 show the conversion, C% and the weight fraction of MAH in SMA copolymer, and MAH% as a function of reaction time at different polymerization conditions. Experimental data (points) and calculated results from the numerical methods in which the gel effect model is incorporated (dotted lines) and the analytical solution equations (solid lines) are all plotted in the figures. The figures show that the numerical results and analytical solutions are both in good agreement with the experimental data, except when the weight fraction of MAH in the inflow is 15 wt %. In this condition, repeated runs always show that the reaction system cannot reach a steady state (i.e., temperature runaway occurred).

The difference between Figures 5 and 7 (and Figures 6 and 8) is in the X axis, which in Figures 5 and 6 are actual polymerization times. For Figures 7 and 8 they are divided by corresponding residence time; hence, they are "dimensionless time." It is of interest to note that the actual transient time is increased with an increase of residence time, but the opposite situation occurs for



Figure 2 The time evolution of copolymer composition for continuous copolymerization carried out with different MAH weight fractions in the inflow. Reaction condition, calculated curves, and experimental points are as described in Figure 1.



Figure 3 The time evolution of conversion for continuous copolymerization carried out at different reaction temperatures (°C): (\bigcirc) 105, (\diamond) 110, (\Box) 115, (\triangle) 120; MAH weight fraction in the inflow = 10 wt %; RT = 5 h; EB = 0 vol %. Curves are as described in Figure 1.

the dimensionless transient time. In fact, eqs. (16) and (17) can both be devised into two parts: one is fixed, which could be taken as a steadystate component; the other decreases with time as an exponential function, which could be denoted as a transient component. The decreasing



Figure 4 The time evolution of copolymer composition for continuous copolymerization carried out at different reaction temperatures. Reaction conditions, calculated curves, and experimental points are as described in Figure 3.



Figure 5 The time evolution of conversion for continuous copolymerization carried out for different residence times (h): (\bigcirc) 3, (\diamond) 5, (\square) 7, (\triangle) 9; MAH weight fraction in the inflow = 10 wt %; $T = 110^{\circ}$ C; EB = 0 vol %. Curves are as described in Figure 1.

rate of the transient component is proportional to the time constant, $a + 1/\tau$ and $b + 1/\tau$. From Table I it is known that $b \ge a$, so the transient time is mainly dependent on $1/(a + 1/\tau)$, which is increased with residence time. But the dimensionless transient time is proportional to $1/(a\tau)$



Figure 6 The time evolution of copolymer composition for continuous copolymerization carried out for different residence times. Reaction conditions, calculated curves, and experimental points are as described in Figure 5.



Figure 7 Conversion versus dimensionless time for continuous copolymerization carried out for different residence times. Reaction conditions, calculated curves, and experimental points are as described in Figure 5.

+ 1), which is inversely proportional to residence time. Moreover, a increases with an increase in temperature, so the higher the polymerization temperature, the faster the system reaches steady state. The MAH weight fraction in inflow, F_2 , has nothing to do with transient time.



Figure 8 Copolymer composition versus dimensionless time for continuous copolymerization carried out for different residence times. Reaction conditions, calculated curves, and experimental points are as described in Figure 5.



Figure 9 The time evolution of conversion for continuous copolymerization in presence of EB (vol %): (\bigcirc) 0, (\diamond) %, (\Box) 5, (\triangle) 8; MAH weight fraction in the inflow = 10%; RT = 5 h; $T = 120^{\circ}$ C. Curves are as described in Figure 1.

The conversion, C%, and the weight fraction of MAH in the SMA copolymer MAH% at steady state are dependent on the steady-state component,



Figure 10 The time evolution of copolymer composition for continuous copolymerization in the presence of EB. Reaction condition, calculated curves, and experimental points are as described in Figure 9.

Operating Conditions				Conversion (wt %)			MAH Fraction (wt %)		
RT (h)	Temp. (°C)	MAH ^a Content (wt %)	EB ^b Content (vol %)	A Pred. ^c	N Pred. ^d	Exp. ^e	A Pred.	N Pred.	Exp.
5	110	10	0	45.5	46	46	19	19.5	19.5
5	110	20	0	57	56	55.5	30.5	30	28
5	110	5	0	39.5	40.5	40	11	11	11.5
5	105	10	0	39	43	41	21.7	21.5	21
5	115	10	0	52	52	52.5	17.5	18	18.5
3	110	10	0	35.5	36.5	39	23	23	24
7	110	10	0	52	53	51	17	17	16
5	110	10	2	57	56	58	15	15	14
5	110	10	8	57	57	59	16	15.5	14.5

^a Weight fraction of MAH in inflow mixture.

^b Volume fraction of ethyl benzene (EB, AR grade) that was added to the precharged and inflow mixtures.

^c Predicted values by analytical solution.

^d Predicted values by numerical method.

^e Experimental data.

C%

$$=\frac{F_{1}\tau + F_{2}\tau - \frac{F_{1}\tau}{a\tau + 1} - \frac{F_{2}\tau \times (a\tau - b\tau + 1)}{(a\tau + 1)(b\tau + 1)}}{F_{1}\tau + F_{2}\tau}$$
(27)

MAH%

$$=\frac{F_{2}\tau}{F_{1}\tau+F_{2}\tau-\frac{F_{1}\tau}{a\tau+1}-\frac{F_{2}\tau\times(a\tau-b\tau+1)}{(a\tau+1)(b\ \tau+1)}}$$
(28)

Note that the numerator of eq. (27) is the denominator of eq. (28), so raising the temperature and residual time can improve the C% but MAH% is decreased. Only increasing F_2 can improve C%and MAH% at the same time.

For the numerical method, the steady-state component can be obtained by simultaneous solution of the set of nonlinear algebraic equations generated by equating the right-hand side of eqs. (1)-(4) to zero. But the solutions of these nonlinear algebraic equations are difficult to obtain; integrating eqs. (1)-(4) to a long polymerization time is an appropriate way. As shown in Table III, we give the predicted results for CSTR under steady state in different operating conditions by the numerical method and analytical solution equations and their comparison with the experimental data.

Figures 9 and 10 show that the amount of ethyl benzene has little effect on the C% and MAH% under either the transient state or steady state. Adding ethyl benzene can sharply reduce the viscosity of the polymerization system.

CONCLUSIONS

It has been found that the CSTR runs that were carried out under different operation conditions to produce St-MAH random copolymer can usually reach the steady state except that when the weight fraction of MAH in the inflow is 15 wt %. The time required to approach the steady state varies with operating conditions.

A CSTR model is developed to predict the continuous bulk random copolymerization of St and MAH. The parameters, which are estimated from experimental data for semicontinuous processes in our previous work, are used in this model. The time evolution of monomer conversion and copolymer composition are calculated, respectively, by a numerical method and analytical solution. It is found that the numerical result, with consideration of the diffusion-control effect on chain propagation and termination, and the analytical solution, without the consideration of the diffusion-control effect, both fit the experimental data excellently. These demonstrate that the kinetic equations and data on bulk copolymerization established in semicontinuous tests can be applied to the continuous process.

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NOMENCLATURE

a, b	parameters in eqs. (16) and (17)
A, B	parameters of Marten-Hamielec
	gel effect model
C%	weight conversion of monomers
_	(model calculation)
C%	weight conversion of monomers (ex-
	perimental data)
F_i	inlet flow rate of monomer i , mol/s
k_{ii}	propagation rate coefficient, L/mol s
$(\check{k}_{ii})_0$	propagation rate coefficient (for $C\%$
5	= 0), L/mol s
k_t	termination rate coefficient, L/mol s
$(k_t)_0$	termination rate coefficient (for $C\%$
	= 0), L/mol s
MAH_0	weight fraction of MAH in the initial
	charge of reactor
MAH%	weight fraction of MAH in the copol-
	ymer (model calculation)
MAH%	weight fraction of MAH in the copol-
	ymer (experimental data)
$[M_i]$	molar concentration of monomers,
	mol/L
M_w	accumulated weight-average molec-
	ular weights of the copolymer
M_{wi}	molecular weight of monomer <i>i</i>
$M_{w_{ m cr}}$	critical molecular weights of copoly-
	mer in the Marten–Hamielec gel
	effect model
N_i	mole number of monomer i , mol

molecular number of monomer unit
<i>i</i> in the copolymer, mol
volumetric flow out of the reactor, L/s
polymerization rate of monomer i ,
mol/L s
initiation rate, mol/L s
glass transition temperature, K
available volume of the reactor, L
free volume
critical free volume in the Marten-
Hamielec gel effect model
parameter of the Marten-Hamielec
gel effect model
thermal expansion coefficient
density, g/L
volume fraction

Subscripts

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

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