A New Model of Mechanism and Treatment of Kinetics for Styrene/*N*-Phenylmaleimide Copolymerization

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Received June 19, 1996; Revised Manuscript Received December 4, 1996[⊗]

ABSTRACT: The copolymerization of styrene (St, M_1) and *N*-phenylmaleimide (PMI, M_2) in chloroform using 2,2′-azobis(isobutyronitrile) as an initiator was investigated. A new kinetic model with assumption of homopolymerization and cross-propagation and diffusion-controlled termination was proposed. The reactivity ratios of free monomers and the charge-transfer complex (CTC) in the copolymerization were determined by a new method, and the values were obtained to be $r_{12} = 0.03370$, $r_{21} = 0.01157$, $r_{1C} = 0.002972$, and $r_{2C} = 0.003379$, respectively. A kinetic treatment based on the model of mechanism was used to quantitatively estimate the ratio of the CTC rate to the total copolymerization rate in the St/PMI copolymerization. It was about 33.0−55.0% in a wide range of monomer feed.

Introduction

At present much interest has been taken not only in the synthesis of new types of plastic materials but also in the modification of commodity polymers in order to improve their properties to meet requirements for new applications. One of the modification methods to improve the polymer properties is copolymerization.

It was believed for a long time that some copolymerization systems, such as styrene (St)/maleic anhydride,[1] St/*N*-(4-bromophenyl)maleimide,[2] and St/*N*-(2-chlorophenyl)maleimide,[3] formed alternating copolymers over a wide range of monomer feeds. Early in 1946, Bartlett and Nozaki[4] prepared alternating copolymers of St and maleic anhydride, but did not derive a mathematical formulation to explain the copolymer compositions and the copolymerization kinetics. They proposed a simple terminal model and thought that electropositive and electronegative monomers could form a charge-transfer complex (CTC) with each other. In 1971, Seiner and Litt[5] first presented a mathematical formulation for alternating copolymerization systems in terms of the participation of a monomer−monomer complex in propagation. Considering the complexity of the mathematical expressions, they could be only used under certain conditions with some assumptions which did not represent the real situation in most cases. In 1976, Shirota et al.[6] presented a model and gave the kinetic treatment for 1:1 alternating radical copolymerization systems, in which 1:1 alternating copolymers were produced at both low and high monomer feed ratios. However, the radical copolymerization systems always deviated from 1:1 alternation at low and high monomer feed ratios. For these systems, homoreactions and cross-reactions should be considered in the kinetic model.

In this paper the copolymerization of St and PMI in chloroform using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator was investigated. A new determination method was presented to calculate the reactivity ratios of free monomers and CTC. A new kinetic model and treatment method were proposed and used to quantitatively estimate the participation of the CTC and the free monomers.

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

Experimental Section

Materials. Styrene was distilled under reduced pressure after removal of the inhibitor and stored in a refrigerator.

N-phenylmaleimide was prepared according to the method of Searle[7] and recrystallized at least six times from ethanol/water mixture (1:2 by volume). *N*-phenylmaleimide (PMI) was characterized by ^{1}H-NMR and IR to make sure that unreacted maleic anhydride and the uncyclized maleamic acid were removed. The purity of PMI was measured by elemental analysis.

Elemental Anal. Calcd for $C_{10}H_7O_2N$ (173.17): C, 69.359; H, 4.074; N, 8.088. Found: C, 69.335; H, 4.070; N, 8.102. IR spectrum (KBr) 3100 (=C−H, aromatics), 1775 and 1708 (−C=O, imide), 1600 (−C=C−), 1509 (−C=C−, aromatics), 1393 (=C−H), 1146 (=C−C−), 830 (=C−H), 755 and 697 (=C−H, aromatics) cm^{-1}. ^{1}H-NMR spectrum (δ) ($CDCl_3$) 6.85 (2H, −CH=CH−), 7.41 ppm (5H, aromatics).

AIBN was recrystallized from ethanol with melting point of 104 °C.

Chloroform was purified according to the usual chemical method and then distilled before use.

Copolymerization. All the glass vessels were washed with potassium dichromate/concentrated sulfuric acid solution, then with distilled water, and finally dried under vacuum at 100 °C for 24 h.

PMI, St ($[M]_T = 1.0$ mol/L), and AIBN ([AIBN] = 0.5, 1.0, 2.0, 3.0×10^{-2} mol/L) were accurately weighed and placed into a 100-mL volumetric flask, then chloroform was added. About 20 mL of the above solution was added to a polymerization tube which contained a magnetic stirrer. The tube was connected to a vacuum and nitrogen system, and after being sweeped of oxygen, the tube was sealed. Under stirring, copolymerization was carried out in a water bath thermostated at 40, 50, or 60 °C. The glass tube was removed at time intervals and cooled down immediately to stop the reaction, then the product was poured out and precipitated from ethanol. The copolymer was dissolved in dimethyl formamide again, precipitated from a large amount of ethanol, washed with ethanol, and dried under vacuum at 60 °C. The weight conversion of St/PMI copolymerization was obtained.

Copolymer Analysis. The compositions of copolymer were calculated on the basis of the nitrogen content in the copolymer, which determined by an elemental analyzer (CARLO ERBA-1106). The tendency to form an alternating copolymer can be seen from the copolymerization diagram, as shown in Figure 1.

Results and Discussion

Model and Kinetic Treatment. We proposed a detailed kinetic scheme, as follows.

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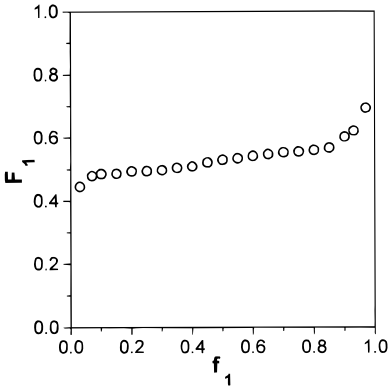


Figure 1. Copolymer composition curve for St/PMI copolymerization in $CHCl_3$ at 50 °C with AIBN as initiator.

Free monomers and CTC equilibrium:

$$M_1 + M_2 \overset{K}{\leftrightarrow} CTC \tag{1}$$

Initiation:

$$I \xrightarrow{k_d} 2R^{\bullet} \tag{2}$$

$$R^{\bullet} + M_1 \xrightarrow{k_{i1}} M_1^{\bullet} \tag{3}$$

$$R^{\bullet} + M_2 \xrightarrow{k_{i2}} M_2^{\bullet} \tag{4}$$

$$R^{\bullet} + CTC \xrightarrow{k_{iC}} M_1^{\bullet} \text{ or } M_2^{\bullet} \tag{5}$$

Propagation:

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1M_1^{\bullet} \tag{6}$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_1M_2^{\bullet} \tag{7}$$

$$\sim M_1^{\bullet} + CTC \xrightarrow{k_{1C}} \sim M_1M_2M_1^{\bullet} \tag{8}$$

$$\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim M_2M_2^{\bullet} \tag{9}$$

$$\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim M_2M_1^{\bullet} \tag{10}$$

$$\sim M_2^{\bullet} + CTC \xrightarrow{k_{2C}} \sim M_2M_1M_2^{\bullet} \tag{11}$$

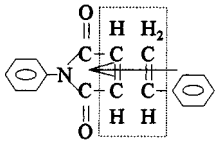
Termination:

$$\sim M_k^{\bullet} \xrightarrow{k_{td}} P \qquad (k = 1 \text{ or } 2) \tag{12}$$

$$\sim M_i^{\bullet} + \sim M_j^{\bullet} \xrightarrow{k_{tc}} P \qquad (i, j = 1 \text{ or } 2) \tag{13}$$

In the proposed propagation, the kinetic scheme is different from that of Shirota in the existence of homoreaction of two monomers, and different from that of Seiner and Litt in the possibility that the radical only cross-reacted with monomer units of CTC. The experimental results indicated that the copolymer composition deviated from 0.5 (F_1) when the concentration of either monomer was lower or higher. So, the homoreaction must exist in the propagation.

The CTC can be illustrated as



If CTC was attacked by a radical, the attacked site should be in the boxed area with three-dimensions. In the boxed area, the advantage of cross-propagation led to the radical connecting with the opposite monomer and giving the radical end again.

In termination, the radical termination steps (monomolecular or/and bimolecular termination) were controlled by diffusion and they could be described in terms of a single rate constant (k_{td} or k_{tc}). It is different from Shirota, Seiner, and Litt's kinetic scheme.

The overall copolymerization rate, R_p, is the sum of the rate of the free monomers, $R_p(f)$, and that of CTC, $R_p(CTC)$, and is expressed as

$$R_p = R_p(f) + R_p(CTC) = k_{11}[M_1^{\bullet}][M_1] + k_{12}[M_1^{\bullet}][M_2] + k_{21}[M_2^{\bullet}][M_1] + k_{22}[M_2^{\bullet}][M_2] + k_{1C}[M_1^{\bullet}][CTC] + k_{2C}[M_2^{\bullet}][CTC] \tag{14}$$

where $[M_1]$, $[M_2]$, and $[CTC]$ represent the concentrations of the free monomers M_1 and M_2, and CTC, respectively, $[M_1^{\bullet}]$ and $[M_2^{\bullet}]$ represent the concentrations of the growing chain radicals with an end of M_1 and M_2, respectively.

The steady-state approximation is

$$k_{12}[M_1^{\bullet}][M_2] = k_{21}[M_2^{\bullet}][M_1] \tag{15}$$

and the concentration of CTC is

$$[CTC] = K[M_1][M_2] \tag{16}$$

Here K is the CTC formation equilibrium constant.

Introducing eqs 15 and 16 into eq 14, we have

$$R_p = \left\{(k_{11}[M_1] + k_{12}[M_2])\frac{k_{21}[M_1]}{k_{12}[M_2]} + k_{21}[M_1] + k_{22}[M_2] + K\left(k_{1C}\frac{k_{21}}{k_{12}}[M_1]^2 + k_{2C}[M_1][M_2]\right)\right\}[M_2^{\bullet}] \tag{17}$$

Case I (Monomolecular Termination):

$$R_i = R_t = k_{td}([M_1^{\bullet}] + [M_2^{\bullet}]) \tag{18}$$

$$[M_2^{\bullet}] = k_{12}[M_2](R_i/k_{td})/(k_{12}[M_2] + k_{21}[M_1]) \tag{19}$$

thus,

$$R_p = (R_i/k_{td})\{(k_{11}k_{21}[M_1]^2 + 2k_{12}k_{21}[M_1][M_2] + k_{12}k_{22}[M_2]^2) + K(k_{1C}k_{21}[M_1]^2[M_2] + k_{2C}k_{12}[M_1][M_2]^2)\}/(k_{12}[M_2] + k_{21}[M_1]) = (R_i/k_{td})\{A([M_1],[M_2]) + KB([M_1],[M_2])\}/C([M_1],[M_2]) \tag{20}$$

Case II (Bimolecular Termination):

$$R_i = R_t = 2k_{tc}([M_1^{\bullet}] + [M_2^{\bullet}])^2 \tag{21}$$

$$[M_2^\bullet] = k_{12}[M_2](R_i/2k_{tc})^{1/2}/(k_{12}[M_2] + k_{21}[M_1]) \quad (22)$$

thus,

$$R_p = (R_i/2k_{tc})^{1/2}\{(k_{11}k_{21}[M_1]^2 + 2k_{12}k_{21}[M_1][M_2] + k_{12}k_{22}[M_2]^2) + K(k_{1C}k_{21}[M_1]^2[M_2] + k_{2C}k_{12}[M_1][M_2]^2)\}/(k_{12}[M_2] + k_{21}[M_1]) = (R_i/2k_{tc})^{1/2}\{A([M_1],[M_2]) + KB([M_1],[M_2])\}/C([M_1],[M_2]) \quad (23)$$

In eqs 20 and 23,

$$A([M_1],[M_2]) = k_{11}k_{21}[M_1]^2 + 2k_{12}k_{21}[M_1][M_2] + k_{12}k_{22}[M_2]^2 \quad (24)$$

$$B([M_1],[M_2]) = k_{1C}k_{21}[M_1]^2[M_2] + k_{2C}k_{12}[M_1][M_2]^2 \quad (25)$$

$$C([M_1],[M_2]) = k_{12}[M_2] + k_{21}[M_1] \quad (26)$$

The contribution of CTC in the copolymerization process can be written as

$$R_p(CTC)/R_p = KB([M_1],[M_2])/\{A([M_1],[M_2]) + KB([M_1],[M_2])\} \quad (27)$$

Thus, the contribution of CTC is a function of $[M_1]$ and $[M_2]$. It is different from that of Shirota.

The kinetic parameters k_{11}, k_{12}, k_{1C}, k_{22}, k_{21}, and k_{2C}, must be given in order to calculate the rates of CTC and free monomers. However, $R_p(CTC)/R_p$ could be estimated if the reactivity ratios r_{12} (k_{11}/k_{12}), r_{21} (k_{22}/k_{21}), r_{1C} (k_{11}/k_{1C}), and r_{2C} (k_{22}/k_{2C}) were known.

A New Determination Method of Reactivity Ratios. From the propagation equations, the ratio of disappearance rates of the monomers yield the compositions of the copolymers and are given by

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] + k_{1C}[M_1^\bullet][CTC] + k_{2C}[M_2^\bullet][CTC]}{k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2] + k_{1C}[M_1^\bullet][CTC] + k_{2C}[M_2^\bullet][CTC]} \quad (28)$$

Using the steady-state approximation (eq 15) and eq 16,

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}k_{21}[M_1]^2 + k_{21}k_{12}[M_1][M_2] + Kk_{1C}k_{21}[M_1]^2[M_2] + Kk_{2C}k_{12}[M_1][M_2]^2}{k_{22}k_{12}[M_2]^2 + k_{12}k_{21}[M_1][M_2] + Kk_{1C}k_{21}[M_1]^2[M_2] + Kk_{2C}k_{12}[M_1][M_2]^2} \quad (29)$$

Let $k_{11}/k_{12} = r_{12}$ and $k_{22}/k_{21} = r_{21}$; we obtain

$$y = \frac{d[M_1]}{d[M_2]} = \frac{1 + r_{12}\frac{[M_1]}{[M_2]} + K[M_1]\frac{k_{1C}}{k_{12}} + K[M_2]\frac{k_{2C}}{k_{21}}}{1 + r_{21}\frac{[M_2]}{[M_1]} + K[M_1]\frac{k_{1C}}{k_{12}} + K[M_2]\frac{k_{2C}}{k_{21}}} \quad (30)$$

and the Mayo−Lewis equation is

$$y = \left(1 + r_1\frac{[M_1]_0}{[M_2]_0}\right)\Big/\left(1 + r_2\frac{[M_2]_0}{[M_1]_0}\right) \quad (31)$$

Here $[M_1]_0$ and $[M_2]_0$ represent the M_1 and M_2 concentrations at the assumption of $[CTC] = 0$. The relationship among $[M_1]$, $[M_2]$, $[M_1]_0$, and $[M_2]_0$ is

$$[M_1] + K[M_1][M_2] = [M_1]_0 \quad (32)$$

$$[M_2] + K[M_1][M_2] = [M_2]_0 \quad (33)$$

Let $[M_1]_0 + [M_2]_0 = [M]_T$. Comparing eqs 30 and 31, we have

$$\frac{[M_1]_0[M_2]}{[M_1][M_2]_0}r_1 = r_{12} + K\frac{k_{1C}}{k_{12}}[M_2] + K\frac{k_{2C}}{k_{21}}\frac{[M_2]^2}{[M]_T - [M_2]} \quad (34)$$

$$\frac{[M_2]_0[M_1]}{[M_2][M_1]_0}r_2 = r_{21} + K\frac{k_{2C}}{k_{21}}[M_1] + K\frac{k_{1C}}{k_{12}}\frac{[M_1]^2}{[M]_T - [M_1]} \quad (35)$$

Introducing eqs 32 and 33 into eqs 34 and 35 and rearranging, we have

$$r_1 = \frac{1 + K[M_1]}{1 + K[M_2]}\left\{r_{12} + K\frac{k_{1C}}{k_{12}}[M_2] + K\frac{k_{2C}}{k_{21}}\frac{[M_2]^2}{[M]_T - [M_2]_0}\right\} \quad (36)$$

$$r_2 = \frac{1 + K[M_2]}{1 + K[M_1]}\left\{r_{21} + K\frac{k_{2C}}{k_{21}}[M_1] + K\frac{k_{1C}}{k_{12}}\frac{[M_1]^2}{[M]_T - [M_1]_0}\right\} \quad (37)$$

i.e.

$$\lim_{[M_2]\to 0} r_1 = (1 + K[M]_T)r_{12} \quad (38)$$

$$\lim_{[M_1]\to 0} r_2 = (1 + K[M]_T)r_{21} \quad (39)$$

where r_1 and r_2 are the reactivity ratios calculated by Mayo−Lewis equation.

In chloroform at 50 °C, the equilibrium constant of St−PMI complex formation is 0.2726.[8] The Mayo−Lewis equation was used to calculate the results when the concentration was as low as possible, and the data are listed in Table 1. From the curves of r_1 *vs* $[M_2]$ and r_2 *vs* $[M_1]$ (see Figures 2 and 3), it was simulated with a quadratic equation, and the reactivity rates were obtained:

$$r_{12} = 0.03370 \qquad r_{21} = 0.01157$$

Rearrangement in the form of eq 30 results in

$$D([M_1],[M_2]) = \frac{y(1 + r_{12}[M_2]/[M_1]) - 1 - r_{12}[M_1]/[M_2]}{K[M_1](1 - y)} = \frac{k_{2C}}{k_{21}}\frac{[M_2]}{[M_1]} + \frac{k_{1C}}{k_{12}} \quad (40)$$

The ratios of rate constants, k_{2C}/k_{21} and k_{1C}/k_{12}, were

Table 1. The Values of $[M_2]$ or $[M_1]$ and Its Corresponding r_1 or r_2 of St/PMI Copolymerization in Chloroform at 50 °C ($[M]_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L)

$[M_2]_0$	$[M_2]$	r_1	$[M_1]_0$	$[M_1]$	r_2
0.03	0.02376	0.04485	0.03	0.02376	0.01502
0.07	0.05600	0.04507	0.07	0.05600	0.01554
			0.10	0.08064	0.01592
0.15	0.1225	0.05375			
0.20	0.1655	0.06052	0.20	0.1655	0.01750
0.30	0.2546	0.07794	0.30	0.2546	0.01961

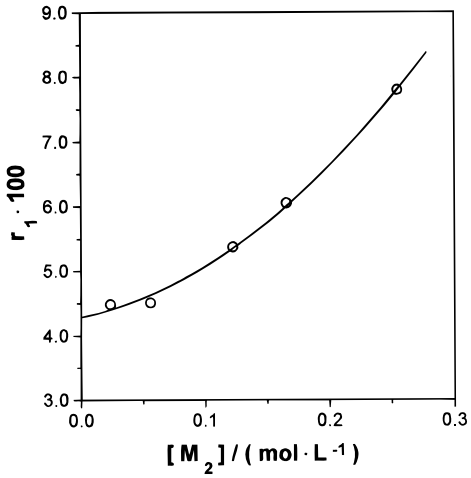


Figure 2. Plots of r_1 *vs* $[M_2]$ in the St/PMI copolymerization in chloroform at 50 °C ($[M]_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L).

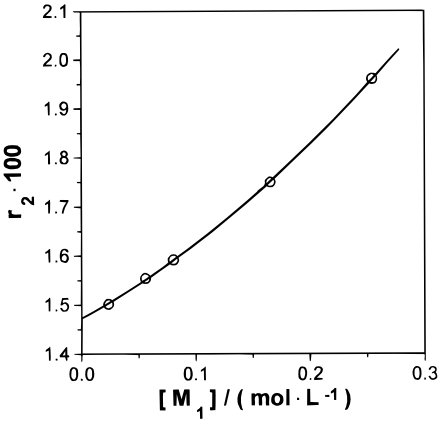


Figure 3. Plots of r_2 *vs* $[M_1]$ in the St/PMI copolymerization in chloroform at 50 °C ($[M]_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L).

determined from the slope and intercept of the straight line in a plot of $D([M_1],[M_2])$ versus $[M_2]/[M_1]$. Calculated from Figure 4, k_{2C}/k_{21} = 3.4238 and k_{1C}/k_{12} = 11.3375.

If the homopropagation rate constants, k_{11} and k_{22}, are given, it is possible to obtain the propagation rate constants, k_{12}, k_{1C}, k_{21}, and k_{2C}. In order to compare the values of the cross-propagation rate constants with the homopropagation rate constants, the ratios of the cross-propagation to homopropagation rate constants are listed in Table 2.

The results indicated that the propagation of radical reacting with the CTC was much faster than that reacting with the free monomers, and the rate constant of cross-propagation was much higher than that of homopropagation.

Determination of Termination Mode. Figure 5 illustrates the dependence of R_p on $[AIBN]^{0.5}$. A straight line passing through the origin demonstrates the bimolecular termination of the copolymerization process.

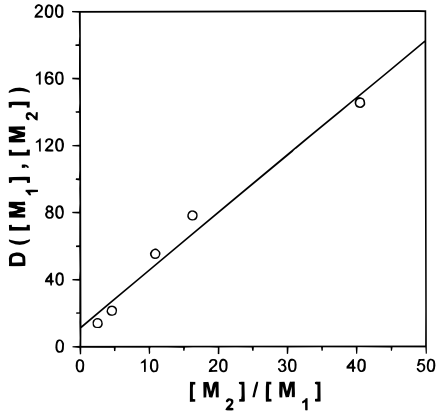


Figure 4. Plot of $D([M_1],[M_2])$ *vs* $[M_2]/[M_1]$ in the St/PMI copolymerization in chloroform at 50 °C ($[M]_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L).

Table 2. The Ratios of Cross-Propagation to Homopropagation Rate Constants in Chloroform at 50 °C ($[M]_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L)

r_{12}	0.03370	k_{12}/k_{11}	29.67
r_{21}	0.01157	k_{21}/k_{22}	86.42
r_{1C}	0.002972	k_{1C}/k_{11}	336.42
r_{2C}	0.003379	k_{2C}/k_{22}	295.95

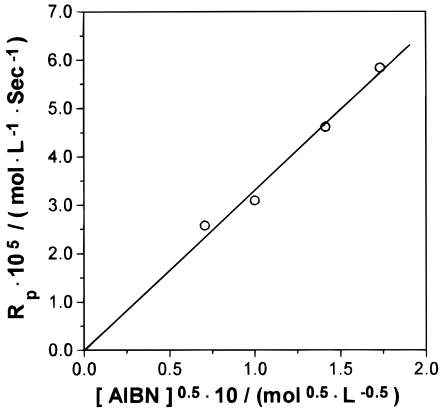


Figure 5. Initial rate of St/PMI copolymerization *vs* $[AIBN]^{0.5}$ at 50 °C in chloroform (f_1 = 0.9, $[M]_T$ = 1.0 mol/L).

Role of CTC in the St/PMI Copolymerization. In the copolymerization, it is assumed that there is only CTC and no free monomer participation. According to the equilibrium equation of CTC, we can get

$$K = \frac{[\mathrm{CTC}]}{([M_1]_0 - [\mathrm{CTC}])([M_2]_0 - [\mathrm{CTC}])} \quad (41)$$

Let $[\mathrm{CTC}] = z[M]_T$; we then have

$$K[M]_T z^2 - (K[M]_T + 1)z + K[M]_T(1 - f_2)f_2 = 0 \quad (42)$$

Let $\partial z/\partial f_2 = 0$; this leads to $f_2 = 0.5$.

The integrated molar conversion−time curves were calculated and are presented in Figures 6 and 7. It is clearly evident that the initial copolymerization rate increases with increasing of f_1 and reaches a maximum, then decreases. The highest initial copolymerization rate was found at f_1 = 0.3 (see Figure 6). The rate of St/PMI copolymerization was much faster than that of St or PMI homopolymerization (see Figure 7). It can only be explained by the participation of CTC in the St/PMI copolymerization process.

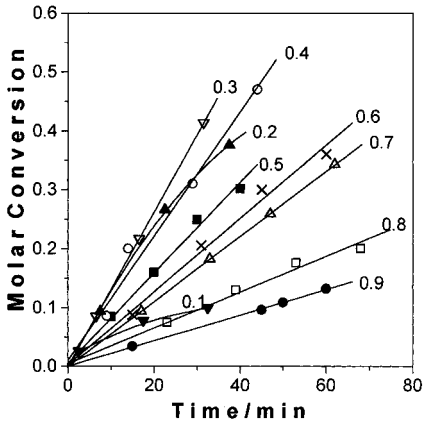


Figure 6. Effect of the initial molar fraction (f_1) on the molar conversion *vs* time in the St/PMI copolymerization at 50 °C in chloroform ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L; the numbers beside the curves are f_1).

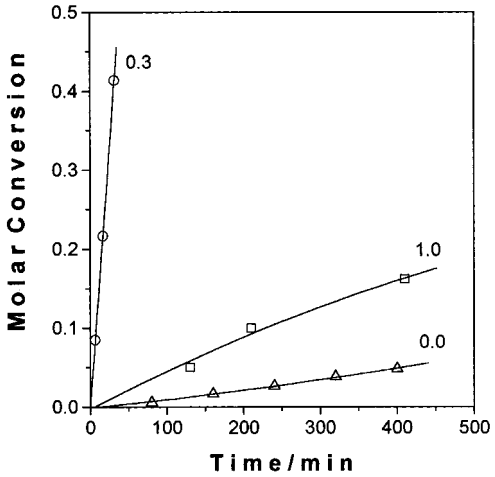


Figure 7. Comparison of the copolymerization rate at $f_1 = 0.3$ with the St or PMI polymerization at 50 °C in chloroform ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L; the numbers beside the curves are f_1).

Table 3. The Contribution of CTC and Free Monomers in the St/PMI Copolymerization at 50 °C ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L)

f_1	$R_p \times 10^5$	$R_p(CTC)/R_p$	$R_p(CTC) \times 10^5$	$R_p(f) \times 10^5$
0.0	0.6620	0.0	0.0	0.6620
0.1	9.8589	0.3347	3.2998	6.5591
0.2	19.6183	0.3730	7.3176	12.3007
0.3	21.9048	0.4063	8.8999	13.0049
0.4	17.5858	0.4376	7.6955	9.8903
0.5	13.3083	0.4673	6.2190	7.0893
0.6	11.2329	0.4949	5.5592	5.6737
0.7	9.2035	0.5195	4.7812	4.4223
0.8	5.5503	0.5387	2.9899	2.5604
0.9	3.6239	0.5414	1.9620	1.6619
1.0	0.2082	0.0	0.0	0.2082

In order to estimate the contribution of CTC and free monomers quantitatively, the proposed treatment method was used. In the case of a bimolecular termination, eq 27 was used to estimate the contribution of the CTC and free monomers in the copolymerization process; the results are given in Table 3.

To illustrate the contribution of CTC and free monomers in the copolymerization process, the rates R_p, R_p(CTC), and R_p(f) are shown in Figure 8 at various monomer feeds. The maximum rate of CTC copolymerization is located at approximately 0.35 molar fraction of St instead of the equimolar feed ratio ($f_1 = f_2 = 0.5$).

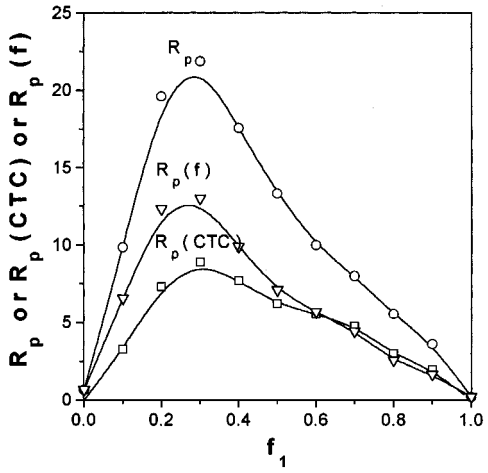


Figure 8. Dependence of the initial rate and f_1 in the St/PMI copolymerization at 50 °C in chloroform ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L).

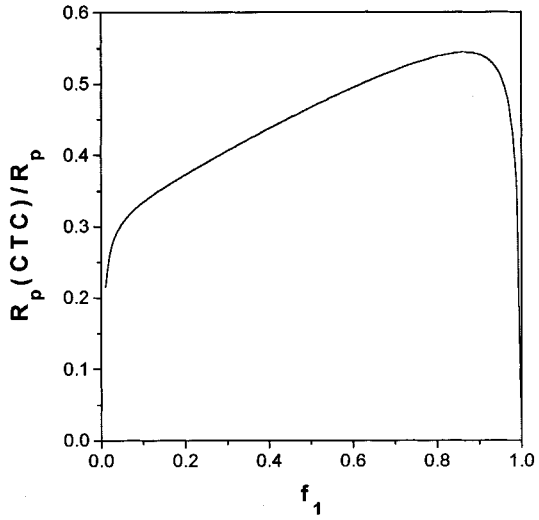


Figure 9. The effect of monomer feed on the contribution of CTC in the St/PMI copolymerization at 50 °C in chloroform ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L).

The maximum rate of R_p(f) is at approximately 0.25. It might be due to $k_{11} \neq k_{22}$, $r_{12} \neq r_{21}$, and $r_{1C} \neq r_{2C}$.

The contribution of CTC and $R_p(CTC)/R_p$, changed with the monomer feed as shown in Figure 9.

Conclusion

A new model of St/PMI copolymerization kinetics was proposed. The propagation reactions included homoreaction and cross-reaction, and its termination was controlled by diffusion. A new determination method based on the proposed kinetic model was presented to calculate the reactivity ratios of free monomers and CTC in the St/PMI copolymerization: $r_{12} = 0.03370$, $r_{21} = 0.01157$, $r_{1C} = 0.002972$, and $r_{2C} = 0.003379$. The results provided an evidence that the rate of radical reacting with the CTC was faster than that of radical reacting with free monomers, and the rate of cross-propagation was much higher than that of homopropagation. A kinetic treatment based on this mechanistic model was used to quantitatively estimate the participation of the CTC and the free monomers in the St/PMI copolymerization. The contribution of CTC changed from 33.0 to 55.0% in a wide range of monomer feed ($f_1 = 0.1-0.9$).

Acknowledgment. This work was supported by the Natural Science Foundation of Zhejiang Province and Doctoral Foundation of the Education Commission of China.

References and Notes

(1) Tsuchida, E.; Tomono, T. *Die Makromol. Chem.* **1971**, *141*, 265.
(2) Janovic, Z.; Matusinovic, T. T.; Ranogajec, F. *J. M. S.—Pure Appl. Chem.* **1992**, *A29* (9), 801.
(3) Mohamed, A. A.; Jebrael, F. H. *Macromolecules* **1986**, *19*, 32.
(4) Bartlett, P. D.; Nozaki, K. *J. Am. Chem. Soc.* **1946**, *68*, 1495.
(5) Seiner, J. A.; Litt, M. *Macromolecules* **1971**, *4* (3), 308.
(6) Yoshimura, M.; Nogami, T.; Yokoyama, M.; Mikawa, H.; Shirota, Y. *Macromolecules* **1976**, *9* (2), 211.
(7) Searle, N. E. U.S. Patent 2444536 (July 6, 1948).
(8) Shan, G. R.; Weng, Z. X.; Huang, Z. M.; Pan, Z. R. *Chem. React. Eng. Tech.* **1996**, *12* (3), 225.

MA9608885