Free Radical Copolymerization and Kinetic Treatment of Styrene with *N*-Phenylmaleimide

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ABSTRACT: The copolymerization of styrene (M_1) with *N*-phenylmaleimide (M_2) in chloroform with 2,2′-azobis(isobutyronitrile) as an initiator was investigated. The kinetic parameters, such as reactivity ratios, overall activity energy, and the effect of molar fraction of monomers on the initial copolymerization rate, were determined. The bimolecular termination of the copolymerization was proved. The treatment method proposed by Yoshimura and colleagues was used to estimate quantitatively the contribution of the charge–transfer complex (CTC) and the free monomers in the copolymerization process. The propagation reactivity ratios of CTC and free monomers were calculated by a new method. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1535–1542, 1997

Key words: styrene; *N*-phenylmaleimide; kinetic treatment

INTRODUCTION

At present there is considerable interest 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 existing methods of improving polymer properties is copolymerization.

Free radical copolymerizations of styrene with various *N*-substituted maleimides have been reported in many papers,[1–6] and a nearly alternating copolymer was obtained. Literature has reported that a few of these have been used to treat the kinetic data of systems with the anticipated participation of a charge–transfer complex (CTC) in the copolymerization process.[7,8] However, some model reactions against the complex addition mechanism have been reported.[9,10] The penultimate group effect model of Alfrey and Goldfinger[11] seems to fail for giving four reactivity ratios from the compositional data of such copolymerization systems. The treatment proposed by Yoshimura and colleagues[12] has the view that alternation in the resulting copolymers is brought about by the transition state in cross reactions between the free monomers and the complex. This treatment has been adopted in the present study.

In this paper the copolymerization of styrene (St) and *N*-phenylmaleimide (PMI) in chloroform with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator was investigated to determine the kinetic parameters. The treatment proposed by Yoshimura and associates[12] was used to estimate quantitatively the participation of the CTC and the free monomers.

EXPERIMENTAL

Materials

St was distilled under reduced pressure after removal of the inhibitor by the usual method. It was kept cold before use.

PMI was prepared by the method of Searle[13] and recrystallized several times from the ethanol/

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water mixture (volume ratio 1 : 2). PMI was characterized by nuclear magnetic resonance and infrared (IR) spectra in order to make sure that it was free from unreacted maleic anhydride and uncyclized maleamic acid. The purity of PMI was measured by elemental analysis.

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, 1708, 1600, 1509, 1393, 1146, 830, 755, and 697 cm^{-1}. ^{1}H-NMR spectrum (δ), CDCl$_3$, 6.85 ppm (2H, —CH=CH—), 7.41 ppm (5H, aromatics).

The initiator, AIBN, was recrystallized from ethanol. Its melting point was determined with a Perkin–Elmer DSC-7 differential scanning calorimeter and found to be 104.2°C.

The solvent, chloroform, was purified by the usual chemical method, then distilled before use.

Copolymerization

All the glass vessels employed were washed before use with potassium dichromate/concentrated sulphuric acid solution and distilled water, and dried under vacuum at 100°C for 24 h.

Accurately weighed PMI, St, and AIBN were placed in a 100-mL volumetric flask which was then filled with chloroform. A long, fine, glass tube was filled with a small polytetrafluoroethylene-covered magnet and about 20 ml solution, connected to a high-vacuum line, nitrogenized alternatively several times to sweep oxygen, then sealed off. Copolymerization was carried out in a water bath thermostatted at 40, 50, or 60°C. In the meantime, the magnet was raised and lowered to obtain an equal system. The glass tube was removed after an appropriate time interval; copolymerization was stopped by decreasing the temperature immediately; and the contents were poured out and weighed. The weighed mixture was poured into a large amount of ethanol and the copolymer was isolated by filtration, dissolved in dimethyl formamide, reprecipitated, and dried under vacuum at 60°C. Weighing the obtained copolymer provided the weight conversion of St/PMI copolymerization.

Copolymer Analysis

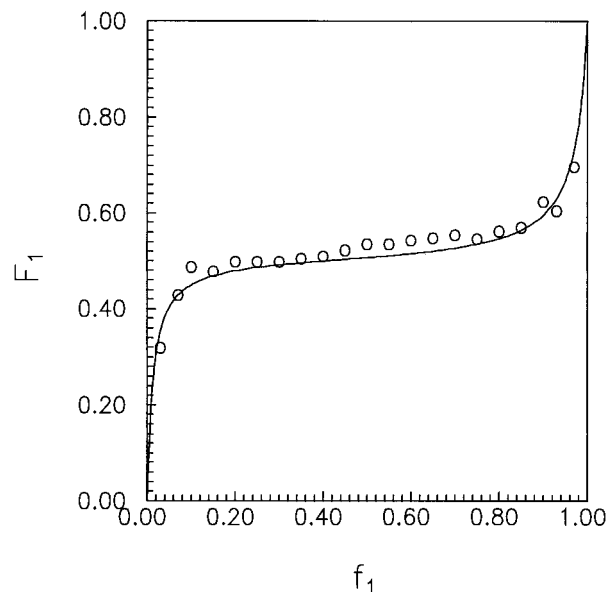The composition of copolymer was calculated on the basis of the nitrogen content in the copolymer

Figure 1 Copolymer composition curve for St/PMI copolymerization in CHCl$_3$ at 50°C with AIBN as initiator. (——) Calculated by r_1 and r_2; (○) experimental data.

measured by an elemental analyzer (CARLO ERBA-1106).

RESULTS AND DISCUSSION

Kinetics of St/PMI Copolymerization in Chloroform

The free radical copolymerization of St (M_1) with PMI (M_2) was performed in chloroform by using AIBN as initiator. The effects of the initial molar fraction of St in the monomer feed (f_1) on the molar composition of St unit in the copolymer (F_1) is shown in Figure 1. By using the Mayo–Lewis equation and the nonlinear least-square procedure, the monomer reactivity ratios $r_1 = 0.0530$ and $r_2 = 0.0256$ were obtained and were related to the polarity (e_2) and the resonance effect (Q_2) in the Alfrey–Price equation for PMI as follows: $e_2 = 1.77$ and $Q_2 = 5.01$ ($e_1 = -0.80$ and $Q_1 = 1.00$). The 95% and 99% confidence intervals are plotted in Figure 2 and the ratio of the elliptic large axis to the short one is about 1.67. Such a large e value indicates that CTC must form from the two monomers of St and PMI. In spite of large changes in the initial molar fraction, small difference in the composition of copolymers was found. The tendency to form an alternating copolymer is evident from the copolymerization diagram in
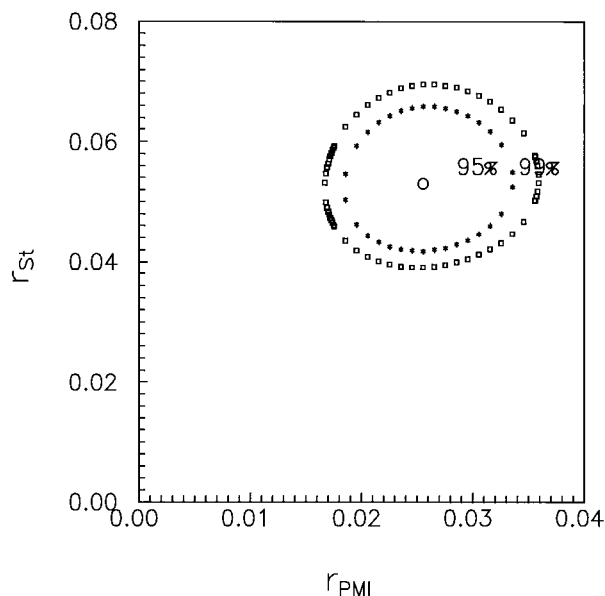
Figure 2 The 95% and 99% confidence intervals of reactivity ratios for St/PMI copolymerization in CHCl₃ at 50°C with AIBN as initiator.

Figure 1. It is sure that the St/PMI copolymerization is nearly alternating.

The molar conversion of copolymerization was calculated using the data of weight conversion and copolymer composition. The initial copolymerization rate, R_p, was determined by numerical differential of the molar conversion and reaction time data.

Because the propagation energy of the radical reacted with CTC is different from that reacted with free monomers, the overall energy of activation will change with increasing CTC concentration if the CTC participates in the copolymerization, and there will be a minimum value at $f_1 = 0.5$.

In order to establish the overall energy of activation and its decreasing effect by CTC, the temperature dependence of molar conversion was investigated in chloroform at 40, 50, and 60°C for five molar ratios of the initial monomer feed with a total concentration of 1.0 mol/L. Overall rate constants, k, were determined as the slopes of straight lines from a plot of $\ln([M]_0/[M]_t)$ against time. From Figure 3, the overall energies of activation were calculated; they are given in Table I.

The minimum value of overall energy of activation is 82.91 kJ/mol at $f_1 = 0.3$, showing that not only CTC but also free monomers participate in the copolymerization process.

Figure 4 illustrates the dependence of R_p on $[AIBN]^{0.5}$. A straight line passing through the ori-

gin demonstrates the bimolecular termination of the copolymerization process.

The integrated molar conversion-time curves were calculated and are presented in Figures 5 and 6. It is clearly evident that the initial copolymerization rate increases with increasing f_1, then decreases with increasing f_1. The highest initial copolymerization rate was found at $f_1 = 0.3$ (see Fig. 5). The St/PMI copolymerization was much faster than that of St or PMI homopolymerization (see Fig. 6). This can be explained only by the participation of CTC in the St/PMI copolymerization process.

In the copolymerization, assuming that there is only CTC and no free monomer participation, according to the equilibrium equation of CTC, we get

$$K = \frac{[CTC]}{([St]_0 - [CTC]) \times ([PMI]_0 - [CTC])} \quad (1)$$

Let

$$[St]_0 + [PMI]_0 = [M]_T; \quad [CTC] = y \times [M]_T$$

Thus we have

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

Let

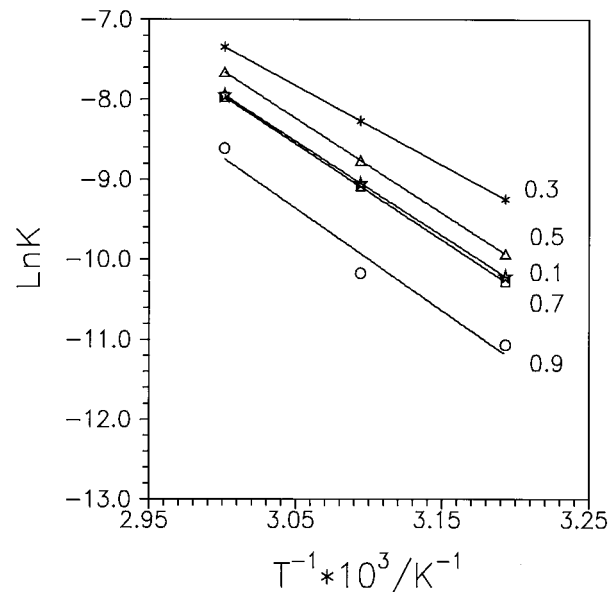$$\frac{\partial y}{\partial f_2} = 0$$

Figure 3 Arrhenius plots of St/PMI copolymerization 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 I   Overall Activation Energies at Various f_1

			f_1		
	0.9	0.7	0.5	0.3	0.1
E_a (kJ/mol)	106.02	100.06	98.68	82.91	98.18

This leads to

$$f_2 = 0.5$$

To illustrate the contribution of CTC and free monomers in the copolymerization process, the initial copolymerization rates were measured for various monomer feeds as shown in Figure 7. The initial copolymerization rate does not maximize at the equimolar feed ratio ($f_1 = f_2 = 0.5$) but at approximately 0.3 molar fraction of St.

This means that both the CTC and free monomers participate in the copolymerization process.

Kinetic Treatment of St/PMI Copolymerization

In order to estimate quantitatively the contribution of CTC and free monomers, the treatment method proposed by Yoshimura and coworkers[12] was used. In the case of a bimolecular termination, the following equations were derived by Yoshimura and colleagues to quantify the degree of participation of the CTC and free monomers in the copolymerization process.

$$R_p = A(x)K(k_{1C}/k_{12} + xk_{2C}/k_{21})[M_1]^2$$
$$+ A(x)[M_1] \quad (3)$$

$$R_p(\text{CTC}) = A(x)K(k_{1C}/k_{12} + xk_{2C}/k_{21})[M_1]^2 \quad (4)$$

$$R_p(f) = A(x)[M_1] \quad (5)$$

$$A(x) = 2k_{21}k_{12}R_i^{1/2}x/$$
$$(k_{t11}k_{21}^2 + 2k_{t12}k_{12}k_{21}x + k_{t22}k_{12}^2x^2)^{1/2} \quad (6)$$

$$R_i = 2k_d f[I] \quad (7)$$

$$x = [M_2]/[M_1] \quad (8)$$

$$R_p/[M_1] = A(x)K(k_{1C}/k_{12} + xk_{2C}/k_{21})[M_1]$$
$$+ A(x) \quad (9)$$
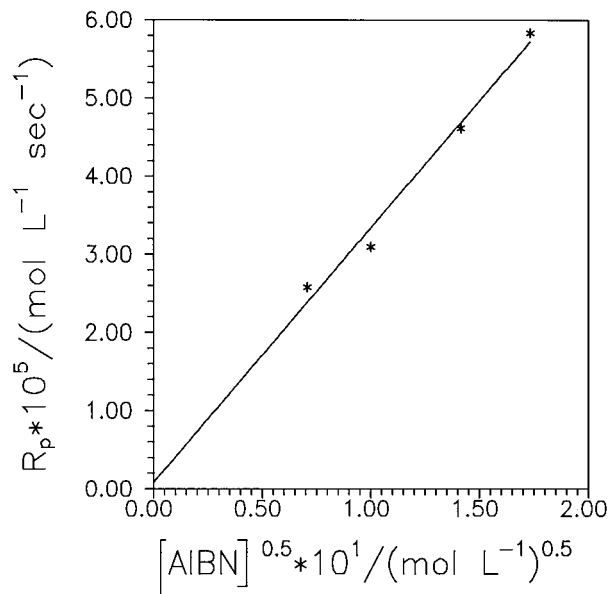
$$F(x) = K(k_{1C}/k_{12} + xk_{2C}/k_{21}) \quad (10)$$

Figure 4   Initial rate of St/PMI copolymerization versus $[AIBN]^{0.5}$ at 50°C in chloroform ($f_1 = 0.9$, $[M]_T = 1.0$ mol/L).
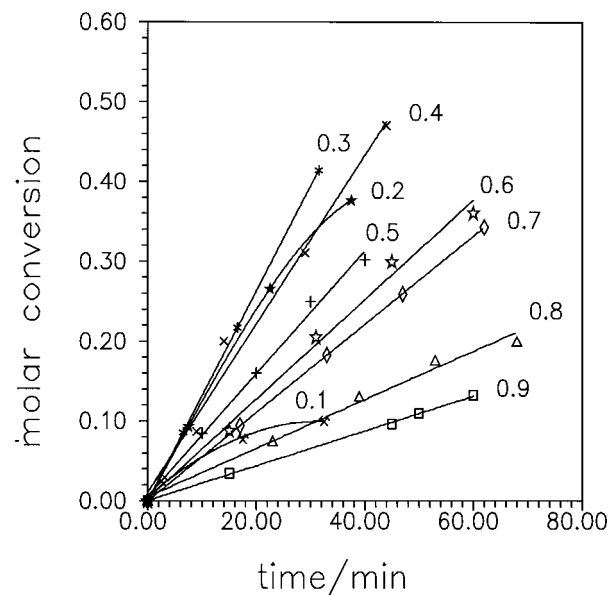

Figure 5   Effect of the initial molar fraction f_1 on the molar conversion versus time in St/PMI copolymerization at 50°C in chloroform ($[M]_T = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L; the numbers beside the curves are f_1).
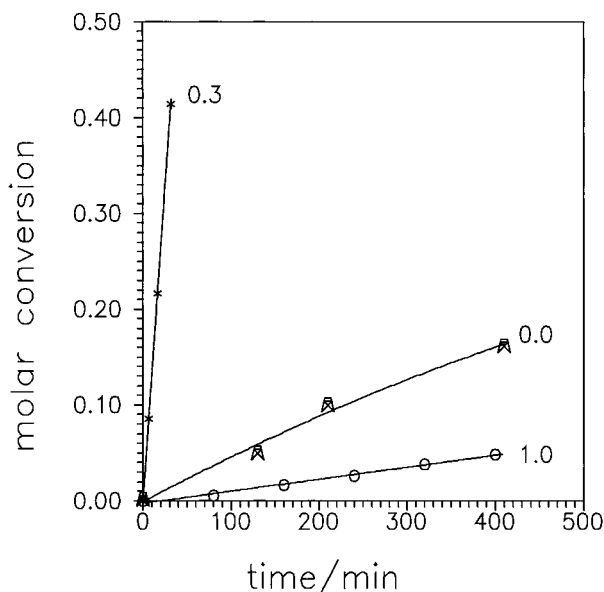
Figure 6 Comparison of the copolymerization rate at $f_1 = 0.3$ with the St or PMI polymerization at 50°C in chloroform ([M]$_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L; the numbers beside the curves are f_1).

Figure 8 Dependence of the $R_p/[M_1]$ on $[M_1]$ at various monomer feed ratios in chloroform at 50°C ([AIBN] = 1.0 × 10^{-2} mol/L).

Here x is the monomer feed molar ratio; K is the equilibrium constant for the formation of the CTC; k_{12}, k_{21}, k_{1C}, and k_{2C} are the corresponding propagation rate constants; and k_{t11}, k_{t22}, and k_{t12} are the rate constants for the bimolecular homo- and cross-termination reactions of radicals. The
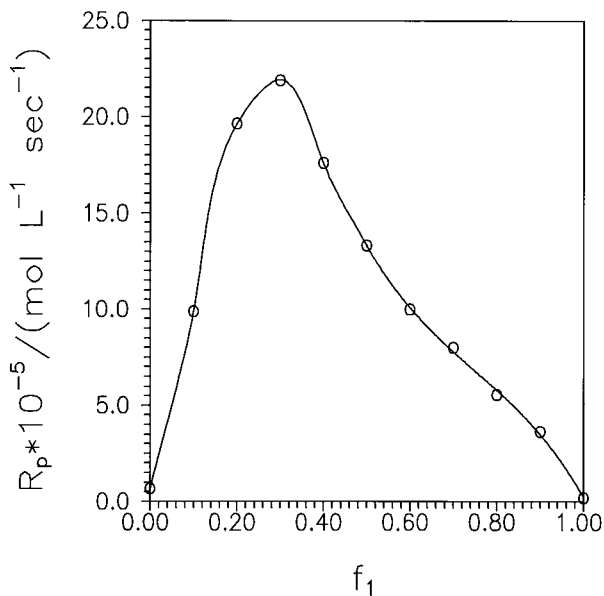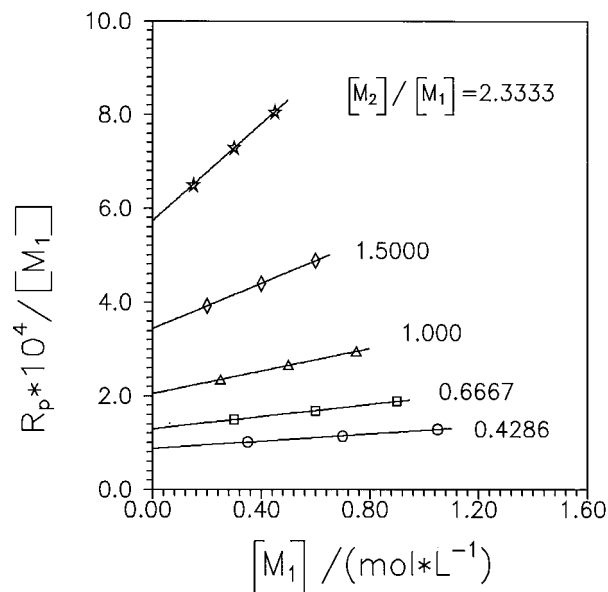

Figure 7 Dependence of the initial rate and f_1 in St/PMI copolymerization at 50°C in chloroform ([M]$_T$ = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L).

overall initial copolymerization rate R_p is the superposition of the reaction rates of the free monomers $R_p(f)$ and CTC R_p(CTC).

The application of this kinetic treatment to St/PMI copolymerization has been tested. The degree of participation of CTC can be estimated in the copolymerization process without the equilibrium constant of CTC formation. If the exact value is given, the individual rate constants can be calculated.

As shown in Figure 8, the plots of $R_p/[M_1]$ versus $[M_1]$ according to eq. (9) showed a good straight line for each x. The slope of the lines is $A(x)K(k_{1c}/k_{12} + xk_{2c}/k_{21}) = A(x)F(x)$ and the intercept is $A(x)$. The introduction of these obtained values into eqs. (4) and (5) allows calculation of the values of R_p(CTC) and $R_p(f)$. The data in Table II list the overall initial copolymerization rate and the slope and intercept, and also clearly indicate the role of the CTC in the St/PMI copolymerization process. The average contribution of R_p(CTC) is 12.8% (0.5 mol/L), 22.6% (1.0 mol/L), and 30.5% (1.5 mol/L). Thus the degree of the CTC participation depends on the initial monomer feed molar fraction as well as on the total monomer concentration.

It is possible to get a quantitative estimation of the relative reactivity between the CTC and the free monomers. The numerical values of the reactivity ratios determined from the intercept

Table II   Contribution of CTC in St/PMI Copolymerization at 50°C in Chloroform

f_1	$[M_1]$	$R_p \times 10^5$	$A(x) \times 10^5$	$A(x) \times F(x) \times 10^5$	$R_p(f) \times 10^5$	$R_p(CTC) \times 10^5$	$\dfrac{R_p(CTC)}{R_p}$
	0.15	9.5313			8.6008	1.1625	0.122
0.3	0.30	21.9048	57.3387	51.6667	17.2016	4.6500	0.212
	0.45	36.2574			25.8024	10.4625	0.289
	0.20	7.8360			6.8719	0.9623	0.123
0.4	0.40	17.5860	34.3597	24.0575	13.7439	3.8492	0.219
	0.60	29.2818			20.6158	8.6607	0.296
	0.25	5.8625			5.1259	0.7504	0.128
0.5	0.50	13.3085	20.5037	12.0060	10.2519	3.0015	0.226
	0.75	22.0898			15.3778	6.7534	0.306
	0.30	4.4808			3.8825	0.5883	0.131
0.6	0.60	10.0782	12.9417	6.5367	7.7650	2.3532	0.233
	0.90	16.9722			11.6475	5.2947	0.312
	0.35	3.5308			3.0499	0.4809	0.136
0.7	0.70	8.0234	8.7140	3.9257	6.0998	1.9236	0.240
	1.05	13.4778			9.1497	4.3281	0.321

$[AIBN] = 1.0 \times 10^{-2}$ mol/L.

and slope of the straight line in Figure 9 are $K(k_{1C}/k_{12}) = 0.3473$ and $K(k_{2C}/k_{21}) = 0.2371$, respectively. From Shan and associates,[14] the equilibrium constant K for the CTC formation in the St-PMI system at 50°C in chloroform is 0.2726. Thus
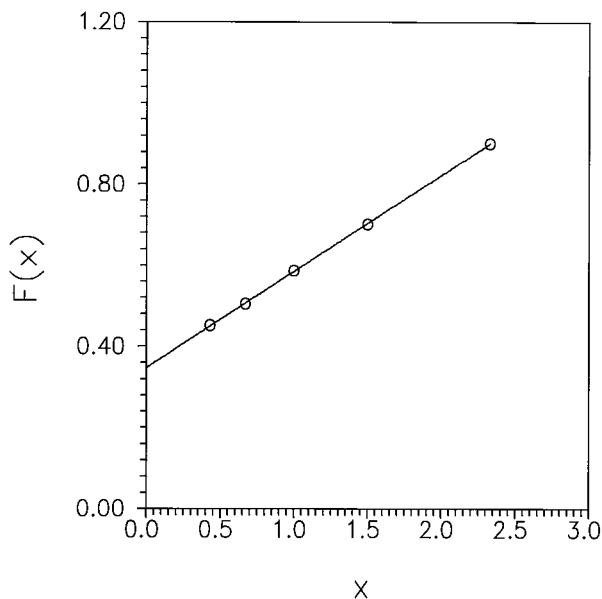
$$k_{1C}/k_{12} = 1.2740 \qquad (11)$$

Figure 9   Plot of $F(x)$ versus x in St/PMI copolymerization in chloroform at 50°C. ($[AIBN] = 1.0 \times 10^{-2}$ mol/L).

$$k_{2C}/k_{21} = 0.8698 \qquad (12)$$

indicating that the propagation of St radical reacted with CTC is somewhat faster than that reacted with the free monomer of PMI, and the propagation of PMI radical reacted with CTC is somewhat slower than that reacted with the free monomer of St. This fact demonstrates that not all the CTC reacted with radical would promote the copolymerization.

The copolymer composition equation can be derived as follows:

$$y = \frac{1 + r_{12}\dfrac{[M_1]}{[M_2]} + K[M_1]\dfrac{k_{1C}}{k_{12}} + K[M_2]\dfrac{k_{2C}}{k_{21}}}{1 + r_{21}\dfrac{[M_2]}{[M_1]} + K[M_1]\dfrac{k_{1C}}{k_{12}} + K[M_2]\dfrac{k_{2C}}{k_{21}}}$$

$$(13)$$

and the Mayo−Lewis equation is

$$y = \frac{1 + r_1\dfrac{[M_1]}{[M_2]}}{1 + r_2\dfrac{[M_2]}{[M_1]}} \qquad (14)$$

Comparing eq. (13) with eq. (14), we have

$$r_1 = r_{12} + K\frac{k_{1C}}{k_{12}}[M_2]$$

Table III Values of $[M_2]$ and $[M_1]$ with Their Corresponding r_1 or r_2

$[M_2]$	r_1	$[M_1]$	r_2
0.03	0.04485	0.03	0.01502
0.07	0.04507	0.07	0.01554
—	—	0.10	0.01592
0.15	0.05375	—	—
0.20	0.06052	0.20	0.01750
0.30	0.07794	0.30	0.01961

$$+ K \frac{k_{2C}}{k_{12}} \frac{[M_2]^2}{[M]_T - [M_2]} \quad (15)$$

$$r_2 = r_{21} + K \frac{k_{2C}}{k_{21}} [M_1]$$

$$+ K \frac{k_{1C}}{k_{12}} \frac{[M_1]^2}{[M]_T - [M_1]} \quad (16)$$

i.e.,

$$\lim_{[M_2] \mapsto 0} r_1 = r_{12} \quad (17)$$

$$\lim_{[M_1] \mapsto 0} r_2 = r_{21} \quad (18)$$

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

The Mayo–Lewis equation is used to calculate the values of r_1 or r_2 at the various $[M_2]$ or $[M_1]$ (the concentration is as small as possible). Table III lists the values of $[M_2]$ and $[M_1]$ with their corresponding r_1 or r_2. Plotting the curves of r_1 or r_2 versus $[M_2]$ or $[M_1]$ (see Fig. 10) and simulating with quadratic equation results in the reactivity ratios:

$$r_{12} = k_{11}/k_{12} = 0.0432 \quad (19)$$

$$r_{21} = k_{22}/k_{21} = 0.0147 \quad (20)$$

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} from eqs. (11), (12), (19), and (20). In order to compare the quantity of the cross-propagation rate constants with the homo-propagation rate constants, the ratios of the cross- to homo-propagation rate constants are listed in Table IV.
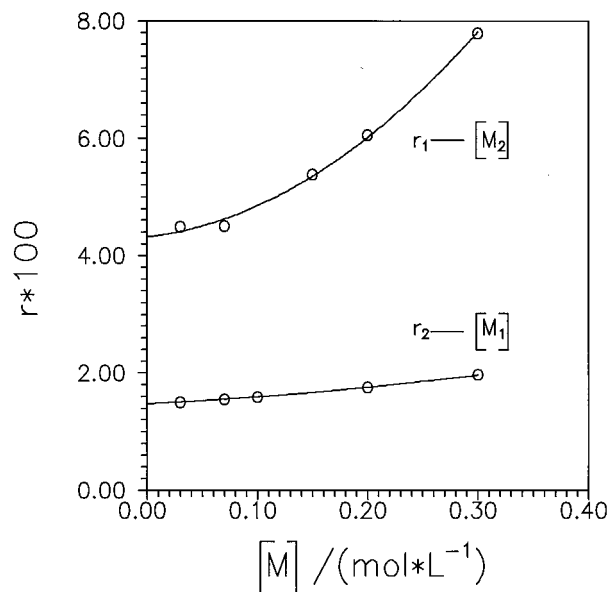
Figure 10   Plots of r versus $[M]$ in St/PMI copolymerization in chloroform at 50°C ([AIBN] = 1.0×10^{-2} mol/L).

CONCLUSION

The free radical copolymerization of St with PMI showed a strong tendency toward alternation. The monomer reactivity ratios were found to be r_1 = 0.0530 and r_2 = 0.0256, and 95% and 99% confidence intervals were given. The overall activation energy of the copolymerization for five feed ratios was obtained. The bimolecular termination was proved. Both the CTC and free monomers participated in the copolymerization process, and the average contributions of the CTC copolymerization rate in the overall copolymerization rate are 12.8% (0.5 mol/L), 22.6% (1.0 mol/L), and 30.5% (1.5 mol/L). Kinetic analysis provides evidence that not all the CTC reacted with radical would promote the copolymerization. In comparison of the rate constant ratios of cross- with homo-propagation, Yoshimura and colleagues' kinetic treatment method is no longer valid at a lower or higher St content. The reactivity ratios of radical

Table IV Ratios of Cross- to Homopropagation Rate Constants in Chloroform at 50°C

r_{12}	0.0432	k_{12}/k_{11}	23.15
r_{21}	0.0147	k_{21}/k_{11}	68.03
r_{1C}	0.0339	k_{1C}/k_{22}	29.50
r_{2C}	0.0169	k_{2C}/k_{22}	59.17

[AIBN] = 1.0×10^{-2} mol/L.

reacted with free monomers and CTC are given as $r_{12} = 0.0432$, $r_{21} = 0.0147$, $r_{1C} = 0.0339$, and $r_{2C} = 0.0169$.

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