

REACTIVITY RATIOS FOR COPOLYMERIZATION WITH THE PARTICIPATION OF A CHARGE-TRANSFER COMPLEX

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Abstract The complexation between styrene (St) and *N*-phenylmaleimide (PMI) was investigated by ¹H-NMR spectroscopy, and the existence of a complex was proved. The equilibrium constant of St/PMI in chloroform at 50°C was determined to be 0.27. New elementary propagation reactions were proposed. On the basis of the propagation elementary reactions for copolymerization with the participation of a charge-transfer complex (CTC), a method for measuring the reactivity ratios is presented. Four reactivity ratios and relative reactivities of free monomer and CTC were obtained. They are $r_{12} = 0.034$, $r_{21} = 0.012$, $r_{1C} = 0.0030$, $r_{2C} = 0.0034$, and $k_{1C}/k_{12} = 11.34$, $k_{2C}/k_{21} = 3.42$.

Keywords Charge-transfer complex, Copolymerization, Reactivity ratio

INTRODUCTION

Reactivity ratios are important parameters for the estimation and control of copolymer composition. They are dependent on the end, penultimate or even antepenultimate group effects, from which different theories and kinetics of copolymerization are derived. The first equation of copolymer composition in terms of monomer feed fraction was derived by Mayo-Lewis^[1] in 1944. They thought that the radical reactivity was related to the end group, so there are two reactivity ratios, r_1 and r_2 . Merz, Alfrey and Goldfinger^[2] considered that the radical reactivity was not only related to the end group, but also to the penultimate group, and there are four reactivity ratios, r_{11} , r_{12} , r_{22} and r_{21} . Furthermore, more reactivity ratios would appear after considering the more group effects^[3], but all of them are more difficult to solve.

The reactivities of free radical and comonomer can be recognized from the reactivity ratios. However, it was believed for a long time that electropositive and electronegative monomers could form a CTC with each other^[4-7]. The reactivities of CTC and free monomers can not be obtained from the Mayo-Lewis or Merz-Alfrey-Goldfinger theories for copolymerization with the participation of CTC, because these reactivity ratios are apparent, and the reactivities of CTC and free monomer are combined with each other, and can not be distinguished. The copolymer composition is contributed by both the CTC and free monomers.

In 1971, Seiner and Litt^[8] first presented a mathematical formulation for alternating copolymerization system in terms of the participation of monomer-monomer complex in propagation. There are six reactivity ratios, r_{11} , r_{12} , r_{1C} , r_{22} , r_{21} and r_{2C} . Without making any assumptions that do not represent the real situation in most cases, the reactivity ratios can not be solved. In 1976, Shirota *et al.*^[9] presented a model and gave the kinetic treatment for 1:1 alternating radical copolymerization systems. There are only cross-propagation constants, k_{12} , k_{1C} , k_{21} and k_{2C} , and no reactivity ratio.

In this paper, new elementary propagation reactions and a new determination method to calculate the reactivity ratios are proposed for the copolymerization with the participation of CTC. This method is applied to

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the St/PMI copolymerization to calculate the reactivity ratios and compare the reactivities of CTC and free monomers.

EXPERIMENTAL

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^[10] and recrystallized from ethanol/water mixture (1:2 by volume). 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol with a melting point of 104°C. Chloroform was purified according to the usual chemical method, and then distilled before use.

Complexation Analysis

¹H-NMR spectra were recorded with a JEOL FX 90Q spectrometer with Me₄Si as internal standard. For the determination of the equilibrium constant of complex formation, NMR spectroscopy was used. The concentrations of PMI were kept at the same value (0.014 mol/L) when the concentrations of styrene varied from 0.00 to 0.53 mol/L.

Copolymerization

PMI, St ([M]_T = 1.0 mol/L, total monomer concentration) and AIBN ([AIBN] = 1.0 × 10⁻² mol/L) were accurately weighed and placed in a 100 mL volumetric flask, then chloroform was added. About 20mL of the above solution was filled into a polymerization tube together with a magnetic stirrer. The tube was evacuated to remove the oxygen and then filled with nitrogen. The tube was sealed. Under stirring, copolymerization was carried out in a water bath thermostatted at 50°C. The glass tube was taken out after a definite time interval, and cooled immediately to stop the reaction, then the content was poured out and precipitated from ethanol. The copolymer was dissolved in tetrahydrofuran again, precipitated from a large amount of ethanol, washed with ethanol, and dried under vacuum at 60°C. St/PMI copolymerization was controlled, at lower conversion (< 10%).

Analysis of Copolymer

The compositions of copolymer were calculated on the basis of the nitrogen content in the copolymer which was determined by an elemental analyzer (Carlo Erba-1106).

RESULTS AND DISCUSSION

Existence Evidence and Formation Constant of Complex

The existence of St-PMI CTC has been proved by Abayasekara and coworkers^[11] from spectra at 360 nm. Although the enhancement of St-PMI complex absorption with the PMI mole fraction was not stronger than that of the St-maleic anhydride system, they also found that there was a maximum absorption at the equimolar ratio of St and PMI. The ¹H-NMR method was used to determine the formation constant of complex (*K*) which was found to be 0.0127 ± 0.0004 at 33°C. However, the temperature will greatly affect the formation and formation constant of CTC. The existence evidence and formation constant of the complex should be studied at the copolymerization temperature.

The ¹H-NMR spectra of St/PMI mixtures with fixed PMI concentration and various St concentrations in CDCl₃ at 50°C are shown in Fig. 1. On increasing the concentration of St, the peak height of St's vinyl protons (δ = 6.58, 6.69, 6.75 and 6.89) increases and the chemical shifts of those protons do not move. However, the peak height of PMI's vinyl protons decreases and the chemical shift of those protons moves to low field. The movement of this peak is attributed to the formation of St-PMI complex.

The ¹H-NMR spectra of St/PMI mixture in CDCl₃ at various temperatures are shown in Fig. 2. A single peak of PMI's vinyl protons is appears at δ = 6.85 at 30°C, while the quartet of St's vinyl protons appears at δ = 6.58, 6.69, 6.75 and 6.89. As the temperature increases, the singlet moves and approaches one of the quartet signals (δ = 6.75), and is covered by and separated from it. It may be considered sure that there is CTC formation between St and PMI. The formation equation from St and PMI is

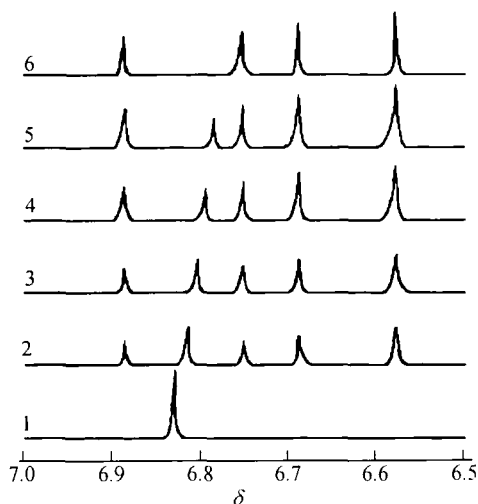


Fig. 1 ^1H -NMR spectra of St/PMI in CDCl_3 at various concentration of St
 $[\text{St}] = 0, 0.11, 0.17, 0.24, 0.30$ and 0.53 mol/L
 Corresponding to the numbers 1 to 6 at 50°C

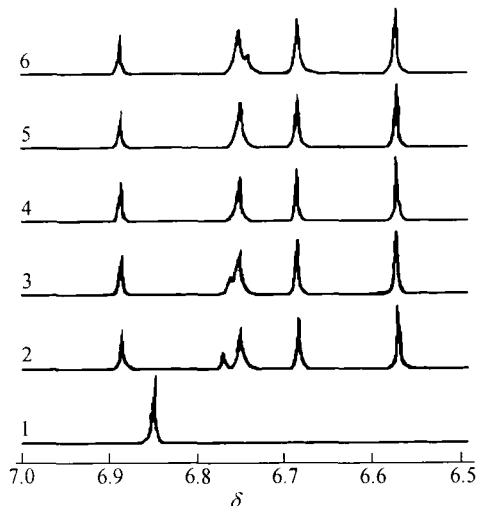


Fig. 2 ^1H -NMR spectra of St/PMI in CDCl_3 at various temperatures
 Curve 1 is the ^1H -NMR spectrum of PMI at 30°C , the temperature is $30, 40, 50, 60$ and 70°C corresponding to the numbers 2 to 6 at $[\text{St}] = 0.53$ mol/L

Using the following equations, the equilibrium constant of the weak charge-transfer complex can be determined by means of the ^1H -NMR spectra.

$$1/[\text{St}] = (1/\Delta_{\text{obsd}})K\Delta_{\text{com}} - K \quad (2)$$

$$K = [\text{CTC}]/([\text{St}] + [\text{PMI}]) \quad (3)$$

$$\Delta_{\text{obsd}} = \delta_{\text{fr}}^{\text{A}} - \delta_{\text{obsd}}^{\text{A}} \quad (4)$$

$$\Delta_{\text{com}} = \delta_{\text{fr}}^{\text{A}} - \delta_{\text{com}}^{\text{A}} \quad (5)$$

$$\delta_{\text{obsd}}^{\text{A}} = \delta_{\text{fr}}^{\text{A}} \frac{[\text{PMI}]}{[\text{PMI}] + [\text{CTC}]} + \delta_{\text{com}}^{\text{A}} \frac{[\text{CTC}]}{[\text{PMI}] + [\text{CTC}]} \quad (6)$$

where $\delta_{\text{fr}}^{\text{A}}$ is the chemical shift of the free PMI, $\delta_{\text{obsd}}^{\text{A}}$ is the chemical shift based on the PMI, and $\delta_{\text{com}}^{\text{A}}$ is the chemical shift of the complexed PMI.

Equation (2) can be derived from Eqs. (3)~(6) by assuming $[\text{St}] \gg [\text{PMI}]$ and $[\text{CTC}]$, and 1:1 type complex formation.

The result is shown in Fig. 3. The line of $1/[\text{St}]$ versus $1/\Delta_{\text{com}}$ is plotted according to Eq. (2). The equilibrium constant (K) obtained from the intercept by the least-squares method is 0.27 in CDCl_3 at 50°C . It indicates that there are considerable amounts of complexes in the St/PMI system. Since Eq. (2) is applicable to the 1:1 type complex, the St-PMI complex is also proved to have a 1:1 composition of St and PMI.

Elementary Propagation Reactions

The formation of CTC between the two reacting monomers will increase the number of elementary propagation reactions. The free radical attacks not only the two free monomers, it reacts with CTC, too.

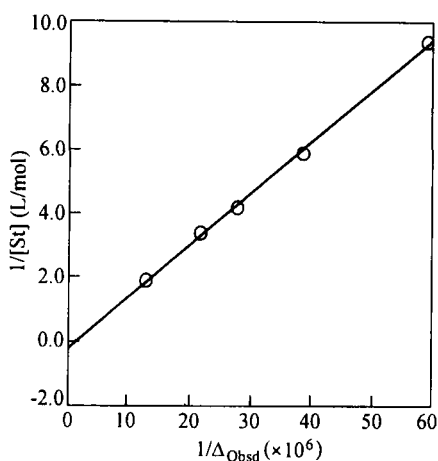
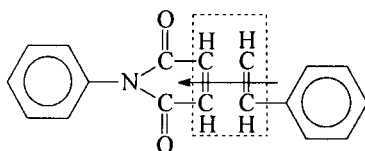


Fig. 3 Plot of $1/[\text{St}]$ versus $1/\Delta_{\text{obsd}}$ for the $^1\text{H-NMR}$ chemical shifts of PMI vinylene protons using styrene as donor in CDCl_3 at 50°C

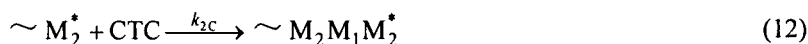
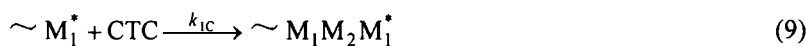
Many experimental results indicated that the copolymer composition deviated from 0.5 (F_1) when the concentration of either monomer was lower or higher. So, homopolymerization must exist in the propagation.

The CTC can be depicted as



If CTC was attacked by a free radical, the attacked site should be within the three-dimensional region indicated by the boxed area. In the boxed area, the advantage of cross-propagation leads to the radical connecting with the opposite monomer and giving the same radical end again.

So the elemental propagation reactions are proposed, as follows



The kinetic scheme is different from that of Shirota in the existence of homopolymerization of two monomers, and different from that of Seiner and Litt in the possibility that the radical only cross-reacted with the monomer units of CTC.

Calculation of Free Monomer Concentration

In the case of CTC formation in a copolymerization system, $[\text{CTC}] \neq 0$, thus the free monomer concentrations will not equal to the initial monomer concentrations, i.e. $[M_1] \neq [M_1]_0$ and $[M_2] \neq [M_2]_0$, where $[M_1]$ and $[M_2]$ represent the free monomer concentrations of M_1 and M_2 , $[M_1]_0$ and $[M_2]_0$ are the concentration of M_1 and M_2

assuming $[CTC] = 0$, respectively.

Using the mass balance and CTC equilibrium equation, we have

$$[M_1] + K[M_1][M_2] = [M_1]_0 \quad (13)$$

$$[M_2] + K[M_1][M_2] = [M_2]_0 \quad (14)$$

At the same total monomer concentration, the differences between $[M_1]$ and $[M_1]_0$ are shown in Fig. 4 with various equilibrium constants (K). The calculated results indicate that the deviation may become notable. The difference between $[M_1]$ and $[M_1]_0$ can not be neglected in the usual value ranges of K from 0.01 to 3.2 collected by Hill and coworkers^[12].

If $[M_1] = [M_1]_0$ and $[M_2] = [M_2]_0$, $[M_2]/[M_1]$ must be a constant at the same feed fraction, and it will not change with the total monomer concentration. However, according to Eqs. (13) and (14) with the participation of CTC, $[M_2]/[M_1]$ will not be a constant at the same feed fraction and usual value of K ($K = 0.5$) as the total monomer concentration changes (see Fig. 5). The deviation becomes obvious at lower total monomer concentrations.

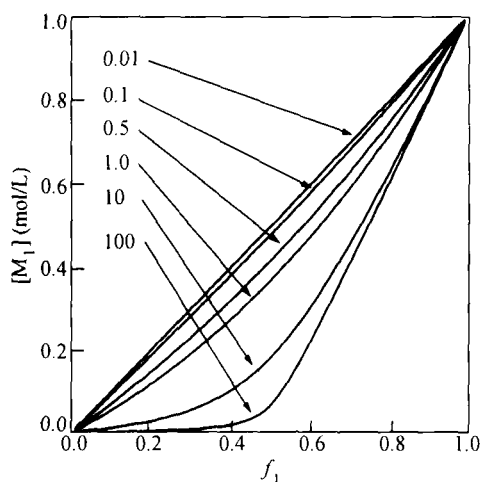


Fig. 4 Effect of equilibrium constant on concentration of free monomer
 $[M]_T = 1.0$ mol/L, the numbers beside the curves are values of K

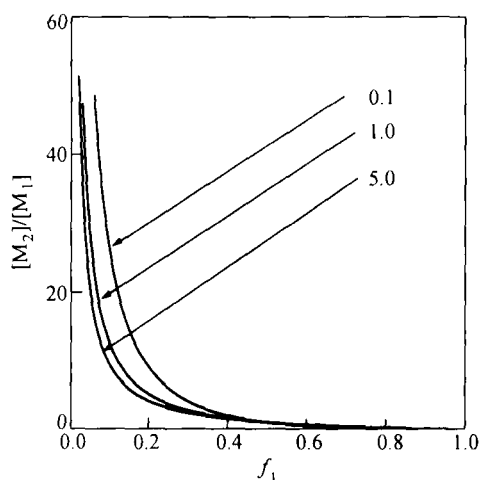


Fig. 5 Effect of total monomer concentration on concentration ratio of two free monomers
 $K = 0.5$, the numbers beside the curves are values of $[M]_T$

Determination of Reactivity Ratios

From the elemental propagation reactions, the ratio of disappearance rates of the monomers yields the composition of the copolymers and is given by:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] + k_{1C}[M_1^*][CTC] + k_{2C}[M_2^*][CTC]}{k_{22}[M_2^*][M_2] + k_{12}[M_1^*][M_2] + k_{1C}[M_1^*][CTC] + k_{2C}[M_2^*][CTC]} \quad (15)$$

The steady-state approximation is:

$$k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1] \quad (16)$$

The concentration of CTC is:

$$[CTC] = K[M_1][M_2] \quad (17)$$

Introducing Eqs. (16) and (17) into Eq. (15), we have:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}k_{21}[M_1]^2 + k_{21}k_{12}[M_1][M_2] + Kk_{1C}k_{21}[M_1]^2[M_2] + Kk_{2C}k_{12}[M_1][M_2]^2}{k_{22}k_{12}[M_2]^2 + k_{12}k_{21}[M_1][M_2] + Kk_{1C}k_{21}[M_1]^2[M_2] + Kk_{2C}k_{12}[M_1][M_2]^2} \quad (18)$$

For $r_{12} = k_{11}/k_{12}$ and $r_{21} = k_{22}/k_{21}$, we obtain:

$$y = \frac{d[M_1]}{d[M_2]} = \frac{1 + r_{12} \frac{[M_1]}{[M_2]} + K[M_1] \frac{k_{1C}}{k_{12}} + K[M_2] \frac{k_{2C}}{k_{21}}}{1 + r_{21} \frac{[M_2]}{[M_1]} + K[M_1] \frac{k_{1C}}{k_{12}} + K[M_2] \frac{k_{2C}}{k_{21}}} \quad (19)$$

The Mayo-Lewis equation is:

$$y = \left(1 + r_1 \frac{[M_1]_0}{[M_2]_0} \right) / \left(1 + r_2 \frac{[M_2]_0}{[M_1]_0} \right) \quad (20)$$

Let $[M_1]_0 + [M_2]_0 = [M]_T$. Comparing Eqs. (19) and (20), we have:

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

$$\frac{[M_2]_0}{[M_2]} \frac{[M_1]}{[M_1]_0} r_2 = r_{21} + K \frac{k_{2C}}{k_{21}} [M_1] + K \frac{k_{1C}}{k_{12}} \frac{[M_1]^2}{[M]_T - [M_1]} \quad (22)$$

Introducing Eqs. (13) and (14) into Eqs. (21) and (22), and rearranging, we have:

$$r_1 = \frac{1 + K[M_1]}{1 + K[M_2]} \left\{ r_{12} + K \frac{k_{1C}}{k_{12}} [M_2] + K \frac{k_{2C}}{k_{21}} \frac{[M_2]^2}{[M]_T - [M_2]_0} \right\} \quad (23)$$

$$r_2 = \frac{1 + K[M_2]}{1 + K[M_1]} \left\{ r_{21} + K \frac{k_{2C}}{k_{21}} [M_1] + K \frac{k_{1C}}{k_{12}} \frac{[M_1]^2}{[M]_T - [M_1]_0} \right\} \quad (24)$$

that is:

$$\lim_{[M_2] \rightarrow 0} r_1 = (1 + K[M]_T) r_{12} \quad (25)$$

$$\lim_{[M_1] \rightarrow 0} r_2 = (1 + K[M]_T) r_{21} \quad (26)$$

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

Rearranging Eq. (19), the following results will be obtained.

$$D([M_1], [M_2]) = \frac{y(1 + r_{21}[M_2]/[M_1]) - 1 - r_{12}[M_1]/[M_2]}{K[M_1](1 - y)} = \frac{k_{2C}}{k_{21}} \frac{[M_2]}{[M_1]} + \frac{k_{1C}}{k_{12}} \quad (27)$$

The ratios of rate constants, k_{2C}/k_{21} and k_{1C}/k_{12} , were determined from the slope and intercept of the straight line in the plot of $D([M_1], [M_2])$ versus $[M_2]/[M_1]$. Thus, the reactivity ratios, r_{12} , r_{21} , r_{1C} and r_{2C} can be obtained.

Application

With one of the monomer concentrations as low as possible, the copolymerizations of St/PMI at low conversion were repeated in chloroform at 50°C. The Mayo-Lewis equation was used to calculate the results (see Table 1). The curves of r_1 versus $[M_2]$ and r_2 versus $[M_1]$ (see Figs. 6 and 7) were simulated with a quadratic equation, and the reactivity ratios were obtained.

$$r_{12} = 0.034, r_{21} = 0.012$$

From the curve of $D([M_1], [M_2])$ versus $[M_2]/[M_1]$ (see Fig. 8), $k_{2C}/k_{21} = 3.42$ and $k_{1C}/k_{12} = 11.34$, the

following reactivity ratios of CTC were obtained.

$$r_{1C} = 0.0030, r_{21} = 0.0034$$

Table 1. Values of $[M_2]$ or $[M_1]$ and its corresponding r_1 or r_2 of St/PMI copolymerization in chloroform at 50°C

$[M_2]_0$	$[M_2]$	r_1	$[M_1]_0$	$[M_1]$	r_2
0.03	0.024	0.045	0.03	0.024	0.015
0.07	0.056	0.046	0.07	0.056	0.016
0.15	0.12	0.054	0.10	0.081	0.016
0.20	0.17	0.061	0.20	0.17	0.018
0.30	0.25	0.078	0.30	0.25	0.020

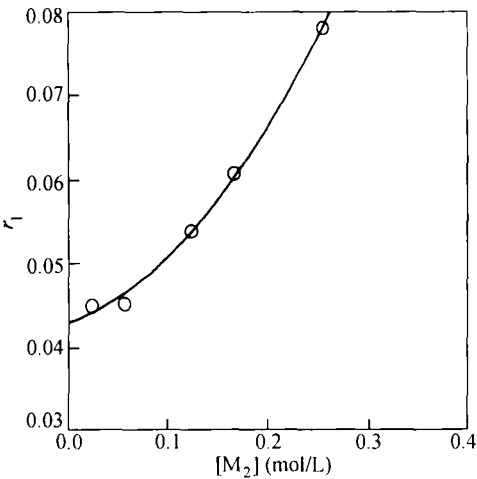


Fig. 6 Plot of $[M_2]$ versus r_1 for the St/PMI copolymerization in chloroform at 50°C

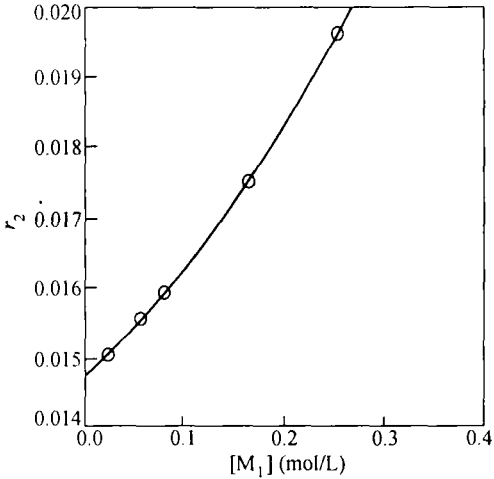


Fig. 7 Plot of $[M_1]$ versus r_2 for the St/PMI copolymerization in chloroform at 50°C

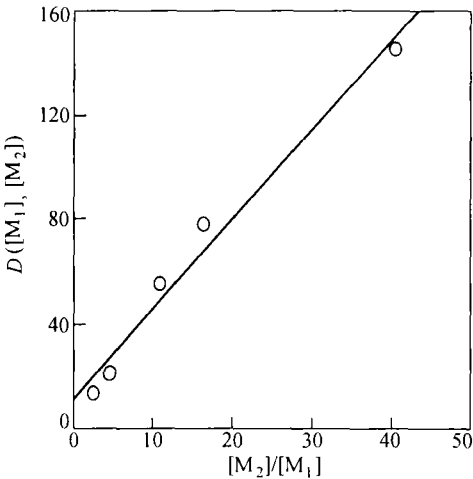


Fig. 8 Plot of $[M_2]/[M_1]$ versus $D([M_1], [M_2])$ for St/PMI copolymerization in chloroform at 50°C

The reactivity ratios and 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 is much faster than that reacting with the free monomers, and the rate constant of cross-propagation is much higher than that of homopropagation.

The results have been applied to calculate^[13] and simulate^[14] the copolymerization rate with the participation of CTC.

Table 2. Ratios of cross- to homo-propagation rate constants in chloroform at 50°C

r_{12}	0.034	k_{12}/k_{11}	29.67
r_{21}	0.012	k_{21}/k_{22}	86.42
r_{1C}	0.0030	k_{1C}/k_{11}	336.42
r_{2C}	0.0034	k_{2C}/k_{22}	295.95

CONCLUSION

The existence of a complex in the St/PMI system was proved by the evidence that the height and chemical shift of PMI's vinyl proton peak changed with St concentration. The equilibrium constant of St-PMI complex was determined by ¹H-NMR spectroscopy and was found to be 0.27 in chloroform at 50°C. The St-PMI complex is also proved to have a 1:1 composition of St and PMI. New elementary propagation reactions are proposed, they are different from those of Shirota in the existence of homopolymerization of two monomers, and different from those of Seiner and Litt in the possibility that the radical only cross-reacted with monomer units of CTC. The effects of equilibrium constant and total monomer concentration on the concentration and concentration ratio of free monomer are simulated. From the proposed elementary propagation reactions, a new determination method of reactivity ratios for copolymerization with the participation of CTC is presented. The method has been applied to the St/PMI copolymerization to obtain the four reactivity ratios and the relative reactivity of free monomer and CTC. They are $r_{12} = 0.034$, $r_{21} = 0.012$, $r_{1C} = 0.0030$, $r_{2C} = 0.0034$, and $k_{1C}/k_{12} = 11.34$, $k_{2C}/k_{21} = 3.42$.

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