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Hua-Ming Li[a]; Hong-Biao Chen[b]; Bing-Hong Luo[a]; Peng-Sheng Liu[b]
[a] Institute of Polymer Science, Zhongshan University, Guangzhou, P. R. China [b] Institute of Polymer Science, Xiangtan University, Xiangtan, P. R. China

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FREE RADICAL COPOLYMERIZATION AND KINETIC TREATMENT OF CYCLOHEXENE WITH N-PHENYLMALEIMIDE

Hua-Ming Li,[1,2,*] Hong-Biao Chen,[2] Bing-Hong Luo,[1] and Peng-Sheng Liu[2]

[1]Institute of Polymer Science
Zhongshan University
Guangzhou 510275, P. R. China

[2]Institute of Polymer Science
Xiangtan University
Xiangtan 411105, P. R. China

Key Words: Radical Copolymerization, Kinetic Treatment, Cyclohexene, N-Phenylmaleimide

ABSTRACT

The copolymerization of cyclohexene (M_1) and N-phenylmaleimide (M_2) in chloroform with 2,2'-azo-bis(isobutyronitrile) as an initiator was investigated. The copolymerization of N-phenylmaleimide with cyclohexene in chloroform proceeded in a homogeneous system to give an alternating copolymer over a wide range of the comonomer composition in the feed. The kinetic parameters, such as reactivity ratio, overall activity energy and the effect of comonomer composition on the initial copolymerization rate (R_p) were determined. The bimolecular termination of the copolymerization was proved. A kinetic treatment based on the model of mechanism was proposed and used to test the copolymerization of cyclohexene and N-phenylmaleimide and to quantitatively estimate the k_{21}/k_{12} value.

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*Author to whom correspondence should be addressed.

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INTRODUCTION

Free radical copolymerizations of N-substituted maleimides with vinyl monomers have been reported in many papers [1-6], and usually an alternating copolymer was obtained. This powerful alternating tendency in the copolymerization has often been explained by the addition of the growing chain radical to a charge-transfer complex, which was formed between N-substituted maleimide, an electron acceptor, and vinyl monomer such as styrene or vinyl ether, an electron donor [7-10]. However, evidence against the participation of charge-transfer complex in the propagation has also been reported based on the results of the model reaction of simple alkyl radicals with N-phenylmaleimide and donor olefins [11-13].

At present, there has been considerable interest in the free radical copolymerization and kinetic treatment of N-substituted maleimides with vinyl monomers. In 1971, Seiner and Litt [14] first presented a mathematical formulation for alternating copolymerization system in terms of the participation of a monomer-monomer complex in propagation, which could be only used under certain conditions. In 1976, Yoshimura and colleagues [15] presented a model and gave the kinetic treatment for 1:1 alternating radical copolymerization system. They viewed the alternation in the resulting copolymers by the transition states in cross-reaction between the free monomers and the complex. However, all the models were only suitable for some certain systems i.e., for systems which charge-transfer complex existed, and did not represent the real situation in most cases.

In this paper, the copolymerization of cyclohexene (CH) with N-phenylmaleimide (PMI) in chloroform with 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator was investigated to determine the kinetic parameters. A kinetic model and treatment method were proposed and used to test the copolymerization of cyclohexene with N-phenylmaleimide and to quantitively estimate the k_{21}/k_{12} value.

EXPERIMENTAL

Materials

CH was distilled under nitrogen atmosphere before use. PMI was prepared according to the method of Chen *et al.* [16]. The typical procedure was as follows:

Maleic anhydride, 120 g (1.22 mol), dissolved in 170 mL acetone were placed in a four-necked flask (1L) provided with a dropping funnel, a reflux condenser, a nitrogen inlet and an agitator. A solution of 100 g (1.08 mol) of aniline in 170 mL acetone was slowly added to the maleic anhydride solution under nitrogen atmosphere with stirring at ice bath temperature, the resulting suspension was then stirred for 1 hour at room temperature. Then, 155 mL of acetic anhydride, 65 mL triethylamine and 0.2 mL of aqueous solution of nickelous sulfate (11.5%) were added and the reaction mixture was refluxed at 75°C under stirring for 4 hours. Finally, the reaction mixture was cooled and poured into a large amount of distilled water to precipitate the crude PMI and filtered. The crude PMI was recrystallized several times from ethanol/water mixture (volume ratio = 1:2). The yield of PMI based on aniline was 76%. The purity of the PMI was checked by ^{1}H –NMR, IR spectroscopy, and elemental analysis.

Elemental Anal. Calcd. For $C_{10}H_7O_2N$ (173.17): C, 69.359; H, 4.074; N, 8.088.
Found: C, 69.301; H, 4.068; N, 8.100.

IR spectrum (KBr, cm^{-1}): 3098 (=C–H, aromatics), 1775 and 1780 (–C=O, imide), 1595 (–C=C–), 1509 –C=C–, aromatics), 1400 (=C–H), 1140 (=C–C–), 835 (=C–H), 755 and 697 (=C–H, aromatics).

^{1}H -NMR spectrum (δ, ppm), ($CDCl_3$): 6.85 (2H, –CH=CH–), 7.39 (5H, aromatics).

2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Solvents were purified by distillation before use.

Polymerization Procedures

A solution of PMI and CH was placed in a glass tube, the initiator AIBN was weighed and introduced into the tube which contained a magnetic stirrer, then the tube was degassed and swept with nitrogen 3 times and finally, the tube was sealed. After polymerization for a given time at 50°C with stirring, the polymerization mixture was poured into a large amount of methanol to precipitate the polymer. The polymers were purified by repeated reprecipitation. The yield (wt%) of polymer was determined gravimetrically (Figure 2).

Copolymer Analysis

The composition of copolymer was calculated on the basis of the nitrogen content in the copolymer measured by an elemental analyzer (Elementar Vario EL).

RESULTS AND DISCUSSION

Kinetics of CH-PMI Copolymerization in Chloroform

The free radical copolymerization of CH (M_1) and PMI (M_2) was performed in chloroform by using AIBN as initiator. The effect of the initial molar fraction of CH in the comonomer feed (f_1) on the molar composition of CH unit in the copolymer (F_1) is shown in Figure 1 and Table 1. By using the Kelen-Tüdos method [17], the monomer reactivity ratios $r_1=0$ and $r_2=0.012$ were obtained. It is sure that the CH-PMI copolymerization is nearly alternating and the tendency to form an alternating copolymer is evident from the copolymer composition in Figure 1 and Table 1. The powerful alternating tendency in this copolymerization can be explained by the very low r_1 and r_2 values and $r_1 \times r_2=0$, but not by the addition of the growing chain radical to a charge-transfer complex formed between CH and PMI. The absence of the CH-PMI charge-transfer complex in the system under this condition was proved by using ^{1}H-NMR method (results are not shown), due to the weak electron donating of CH and the weak intermolecular interactions between CH and PMI.

The molar conversion of copolymerization was calculated by using the data of weight conversion (Figure 2) and copolymer composition. The initial copolymerization rate, R_p, was determined from the initial slope of the time-polymer molar conversion curves (Figure 4).

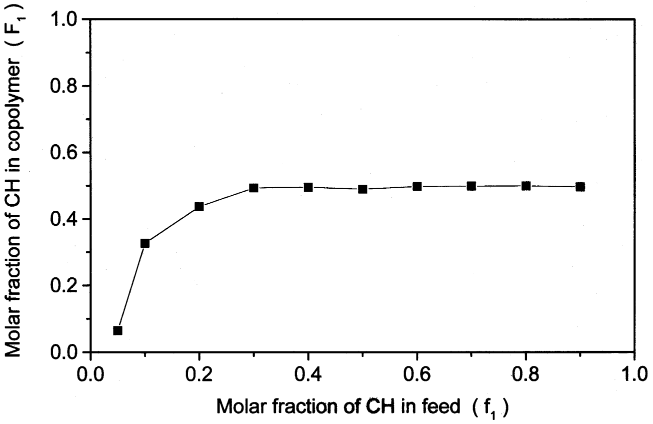

Figure 1. Copolymer composition curve for CH (M_1) and PMI (M_2) copolymerization in chloroform at 50°C with AIBN as initiator.

TABLE 1. Relationship between Comonomer Composition (f_1) and Copolymer Composition (F_1) for CH (M_1)–PMI (M_2) Copolymerization in Chloroform at 50°C with AIBN as Initiator [a]

f_1	Conversion (Wt%)	N Content (%)	F_1
0.05	7.63	7.399	0.165
0.1	3.91	6.578	0.327
0.2	5.26	5.916	0.437
0.3	7.10	5.538	0.493
0.4	8.62	5.520	0.496
0.5	8.38	5.562	0.490
0.6	7.67	5.504	0.498
0.7	5.76	5.499	0.498
0.8	1.88	5.490	0.500
0.9	1.02	5.509	0.497

[a] $[M_1] + [M_2] = 1.0$ mol/L, $[AIBN] = 1.0 \times 10^{-2}$ mol/L and the reaction time is about 11 hours.

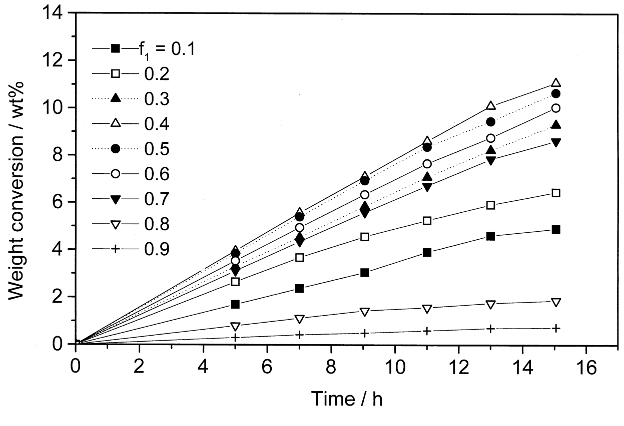

Figure 2. Relationships between reaction time and polymer weight conversion (wt%) for radical copolymerization of CH (M_1) and PMI (M_2) in chloroform at 50°C under various comonomer composition (f_1), [CH]+[PMI] = 1.0 mol/L, [AIBN] = 1.0×10^{-2} mol/L.

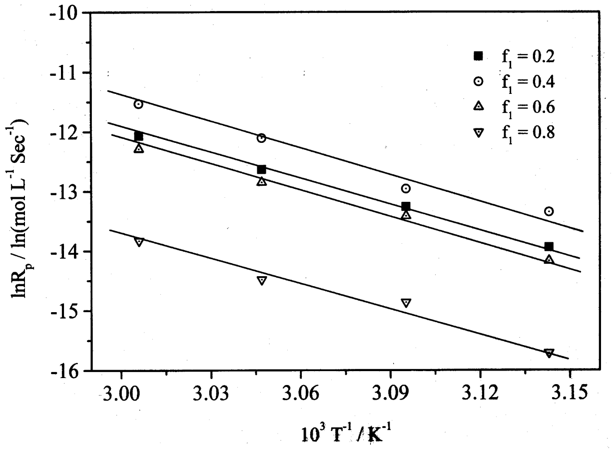

Figure 3. Arrhenius plots of copolymerization of CH (M_1) and PMI (M_2) in chloroform, [CH]+[PMI] = 1.0 mol/L, [AIBN] = 1.0×10^{-2} mol/L.

The overall energy of activation, E_a, was calculated using the data in Table 2 by using of Arrhenius plots (Figure 3). The values are shown in Table 3. Despite the difference in comonomer composition (f_1), the overall energies of activation obtained by this method are nearly the same. It is well known that in copolymerization the expression of the overall rate of polymerization is very complicated and it is impossible to assign an activation energy to each elemental reaction. It appears that the rate constants of initiation, propagation, and termination of this radical copolymerization may not be affected by the change of comonomer composition (f_1 changes from 0.2 to 0.8) in the feed. This result is in

TABLE 2. Initial Rate of Copolymerization of CH (M_1)-PMI (M_2) in Chloroform[a]

	$R_p \times 10^6$ (mol/L·s)			
Temperature (°C)	$f_1 = 0.2$	$f_1 = 0.4$	$f_1 = 0.6$	$f_1 = 0.8$
45	0.883	1.594	0.702	0.150
50	1.708	2.353	1.822	0.350
55	3.270	5.523	2.626	0.513
60	5.729	9.831	4.597	0.986

[a] $[M_1] + [M_2] = 1.0$ mol/L, [AIBN] = $1.0\text{x}10^{-2}$ mol/L.

TABLE 3. Overall Activation Energies of Copolymerization of CH (M_1)-PMI (M_2) in Chloroform at Various f_1

f_1	0.2	0.4	0.6	0.8
Ea (KJ/mol)	112.94	109.11	112.37	113.97

agreement with the fact that the charge-transfer complex of CH and PMI does not exist in this copolymerization system.

The molar conversion-time curves and the initial copolymerization rate (R_p)- comonomer composition (f_1) curves of the copolymerization were calculated and presented in Figures 4 and 5. It is clearly evident that the initial copolymerization rate, R_p, depended on the comonomer composition (f_1), and the R_p value decreased drastically with the addition of a small amount of CH until it reached a minimum value when f_1 was ca. 0.1. As the f_1 value increased further, the R_p value increased quickly, showed a maximum at about 0.4 of f_1 value, and then decreased again. This is in agreement with the results that reported by A. Matsumoto and his coworkers [18] in the radical copolymerization of N-(2,6-dimethylphenyl)-maleimide and 2,4,4-trimethyl-pentene in chloroform at 60°C. Shan *et al.* [19] had also found that the initial copolymerization rate was influenced by the comonomer composition in the copolymerization of PMI and styrene, and they attributed this phenomenon to the participation of charge-trans-

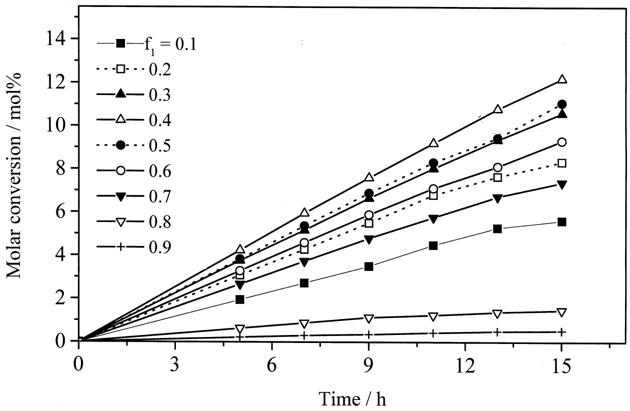

Figure 4. Effect of the initial molar fraction f_1 on the molar conversion versus time in the copolymerization of CH (M_1) and PMI (M_2) in chloroform at 50°C, [CH]+[PMI] = 1.0 mol/L, [AIBN] = 1.0×10^{-2} mol/L.

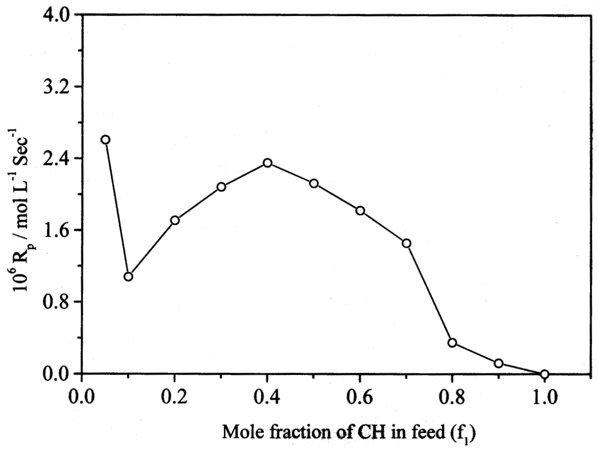

Figure 5. Dependence of the initial rate (R_p) and f_1 in the copolymerization of CH (M_1) and PMI (M_2) in chloroform at 50°C, [CH]+[PMI] = 1.0 mol/L, [AIBN] = 1.0 × 10^{-2} mol/L.

fer complex of PMI and styrene in the copolymerization. However, for the copolymerization of CH and PMI, it is clearly shown that the absence of charge-transfer complex between CH and PMI. The fact that the R_p was affected by the comonomer composition (f_1), and caused the maximum R_p to shift to higher PMI concentrations could be explained by the high steric hindrance in the PMI addition to the CH radical chain end.

Figure 6 showed the dependence of R_p on $[AIBN]^{0.5}$. A straight line passing through the origin demonstrates the bimolecular termination of the copolymerization process.

Kinetic Treatment of CH-PMI Copolymerization

A kinetic treatment of the radical copolymerization of CH (M_1) and PMI (M_2) based on the model of mechanism was proposed, as follows:

Initiation:

$$I \xrightarrow{k_d} 2R\cdot \qquad (1)$$

$$R\cdot + M_1 \xrightarrow{k_{i1}} M_1\cdot \qquad (2)$$

$$R\cdot + M_2 \xrightarrow{k_{i2}} M_2\cdot \qquad (3)$$

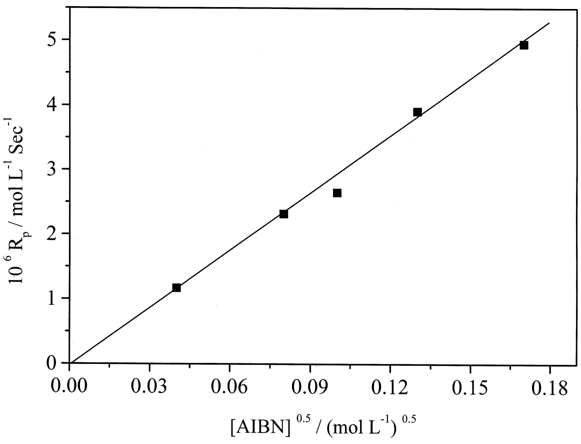

Figure 6. Initial rate (R_p) of CH (M_1) and PMI (M_2) copolymerization versus $[AIBN]^{0.5}$ at 50°C in chloroform, $f_1 = 0.4$, [CH]+[PMI] = 1.0 mol/L.

Propagation:

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_1 M_2\cdot \quad (4)$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_2 M_1\cdot \quad (5)$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2 M_2\cdot \quad (6)$$

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1 M_1\cdot \quad (7)$$

Termination:

$$\sim M_i\cdot + M_j\cdot \xrightarrow{k_{tc}} P \qquad (i, j = 1 \text{ or } 2) \quad (8)$$

where ~ $M_1\cdot$ is the propagating radical of CH as a terminal unit and ~ $M_2\cdot$ is that of PMI, k is the reaction rate constants of each elemental reaction.

In the proposed propagation, the kinetic scheme is still based on the classical model of mechanism of free radical copolymerization. The experimental results indicated that the charge-transfer complex between CH and PMI did not exist in this copolymerization system and so there had not charge-transfer complexes participated in the propagation reactions. In addition, the experimental results had also indicated that the copolymer composition deviated from 0.5 (F_1) when the concentration of PMI was much higher (Table1). So the homoreaction of PMI must exist in the propagation. However, the homoreaction of ~ $M_1\cdot$ with M_1 (7) may not occur due to a lack of homo-polymerizability of CH. In termination, the radical termination steps (bimolecular termination) were controlled by diffusion and they could be described in terms of a single rate constant (k_{tc}).

The overall copolymerization rate, R_p, is the sum of the rate of each elemental reaction in the propagation, and is expressed as:

$$R_p = k_{12}[M_1\cdot][M_2] + k_{21}[M_2\cdot][M_1] + k_{22}[M_2\cdot][M_2] \tag{9}$$

where $[M_1]$, $[M_2]$ represent the concentration of the monomer M_1 and M_2, respectively, $[M_1\cdot]$ and $[M_2\cdot]$ represent the concentration of the growing chain radicals with an end of M_1 and M_2, respectively, k_{12}, k_{21} and k_{22} represent the cross-propagation and homo-propagation rate constants, respectively.

The steady-state approximation is:

$$k_{12}[M_1\cdot][M_2] = k_{21}[M_2\cdot][M_1] \tag{10}$$

Introducing Equation 10 into Equation 9, we have

$$R_p = 2k_{21}[M_2\cdot][M_1] + k_{22}[M_2\cdot][M_2] \tag{11}$$

For bimolecular termination:

$$R_i = R_t = 2k_{tc}([M_1\cdot] + [M_2\cdot])^2 \tag{12}$$

Introducing Equation 10 into Equation 12, we have:

$$[M_2\cdot] = k_{12}[M_2](R_i / 2k_{tc})^{1/2}/(k_{12}[M_2] + k_{21}[M_1]) \tag{13}$$

thus,

$$\begin{aligned} R_p &= (R_i/2k_{tc})^{1/2}(2k_{12}k_{21}[M_1][M_2] + k_{12}k_{22}[M_2]^2)/(k_{12}[M_2] + k_{21}[M_1]) \\ &= (R_i/2k_{tc})^{1/2}[M_2](2k_{12}k_{21}[M_1] + k_{12}k_{22}[M_2])/(k_{12}[M_2] + k_{21}[M_1]) \\ &= (R_i/2k_{tc})^{1/2}[M_2](2k_{12}k_{21}[M_1]/[M_2] + k_{12}k_{22})/(k_{12} + k_{21}[M_1]/[M_2]) \end{aligned} \tag{14}$$

$$\text{let } x = [M_1]/[M_2] \tag{15}$$

thus,

$$\begin{aligned} R_p &= (R_i/2k_{tc})^{1/2}[M_2]\,(2k_{12}k_{21}x + k_{12}k_{22})/(k_{12} + k_{21}x) \\ &= B(x)[M_2] \end{aligned} \tag{16}$$

where

$$B(x) = (R_i/2k_{tc})^{1/2}(2k_{12}k_{21}x + k_{12}k_{22})/(k_{12} + k_{21}x) \tag{17}$$

and $R_i = 2k_d f[I]$ is rate of initiation, k_{tc} is the rate constant of termination as indicated in Equation 8.

In Equation 17,

$$\begin{aligned} B(x) &= (R_i/2k_{tc})^{1/2}(2k_{12}k_{21}x + k_{12}k_{22})/(k_{12} + k_{21}x) \\ &= (R_i / 2k_{tc})^{1/2} k_{21}(2x + r_2)/\{(k_{21}/k_{12})x + 1\} \end{aligned} \tag{18}$$

where $r_2 = k_{22}/k_{21}$. Rearrangement in the form of Equation 18 results in

$$(2x + r_2)/B(x) = 1/a + (1/a)(k_{21}/k_{12})x \tag{19}$$

where $a = (R_i/2k_{tc})^{1/2} k_{21}$.

Thus, the application of this kinetic treatment to CH and PMI radical copolymerization has been tested.

As shown in Figure 7, the plots of R_p versus $[M_2]$ according to Equation 16 showed a good line for each x. The slope of the lines is B(x) (Table 4). The introduction of these obtained values into eq19 allows calculation of the values of $(2x + r_2)/B(x)$. The ratio of cross-propagation rate constants, k_{21}/k_{12}, was determined from the slope and intercept of the line in the plot of $(2x + r_2)/B(x)$ versus x . Calculated from Figure 8,

$$k_{21}/k_{12} = 2.5376$$

The result indicated that the cross-propagation rate constant of k_{21} was higher than that of k_{12}, and the rate of cross-propagation of chain radicals with an end of M_2 reacting with M_1 was faster than that of the chain radicals with an end of M_1 reacting with M_2. This result was in agreement with the explanation of the

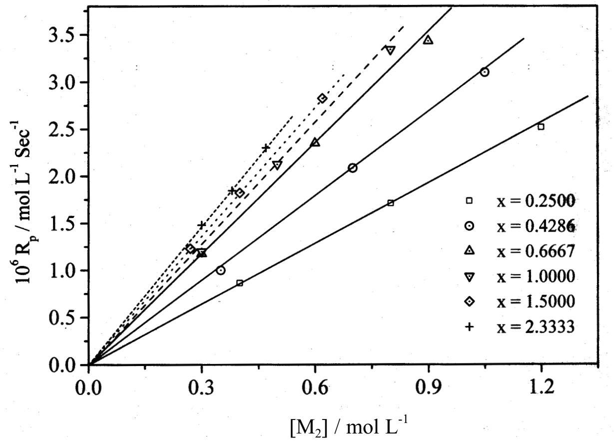

Figure 7. Dependence of the initial rate R_p on [M_2] at various monomer feed ratios(x) in chloroform at 50°C, [AIBN] = 1.0 × 10^{-2} mol/L.

TABLE 4. Values of R_p and B(x) in CH (M_1)-PMI (M_2) Copolymerization at 50°C in Chloroform

f_1	x	[M_2] mol/L	$R_p \times 10^6$ mol/L·s	B(x) x 10^6
		0.40	0.854	
0.2	0.2500	0.80	1.712	2.1430
		1.20	2.572	
0.3	0.4286	0.35	1.003	2.9786
		0.70	2.085	
		1.05	3.102	
0.4	0.6667	0.30	1.177	3.9167
		0.60	2.351	
		0.90	3.432	
		0.30	1.198	
0.5	1.0000	0.50	2.125	4.2500
		0.80	3.441	
0.6	1.5000	0.27	1.230	4.5552
		0.40	1.822	
		0.62	2.825	
0.7	2.3333	0.30	1.480	4.9333
		0.38	1.843	
		0.47	2.301	

[AIBN] = 1.0x10^{-2} mol/L .

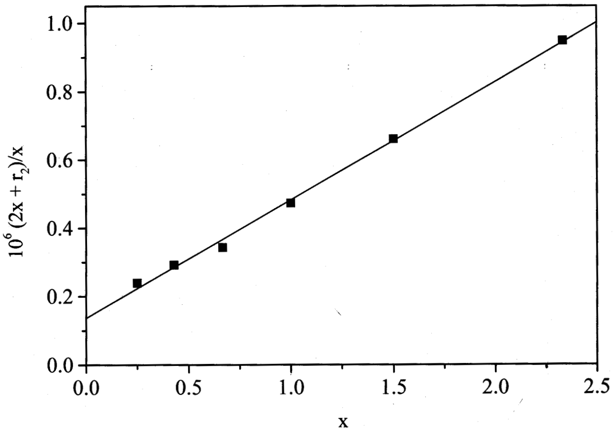

Figure 8. Plot of $(2x + r_2)/B(x)$ versus x in the copolymerization of CH (M_1) and PMI (M_2) in chloroform at 50°C, [AIBN] = 1.0×10^{-2} mol/L.

high steric hindrance in the PMI addition to the CH radical chain end, and causing the maximum R_p to shifts to higher PMI concentration.

CONCLUSION

The free radical copolymerization of CH with PMI showed a strong tendency toward alternation. The monomer reactivity ratios were found to be $r_1 = 0$ and $r_2 = 0.012$ in chloroform. The overall activation energies of the copolymerization for four feed ratios were obtained and found that despite the difference in comonomer composition (f_1), the overall activation energies were nearly the same. The bimolecular termination was proved. A model of CH and PMI copolymerization kinetics was proposed. The propagation reactions included homoreaction and cross-reaction, and its termination controlled by diffusion. A kinetic treatment based on this mechanistic model was used to quantitatively estimate the k_{21}/k_{12} value. The result provided an evidence that the rate of cross-propagation of chain radicals with an end of M_2 reacting with M_1 was faster than that of the chain radicals with an end of M_1 reacting with M_2, and causing the maximum R_p to shift to higher PMI concentration.

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