

Reactivity Ratios of Free Monomers and Their Charge-Transfer Complex in the Copolymerization of *N*-Butyl Maleimide and Styrene

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ABSTRACT: As for the charge-transfer complex (CTC) formed by *N*-butyl maleimide (NMBI) and styrene in chloroform, the complex formation constant was determined by ¹H-NMR of Hanna–Ashbaugh. The copolymerization of NMBI (NMBI, M_1) and styrene (St, M_2) in chloroform using AIBN as an initiator was investigated. On the basis of the kinetic model proposed by Shan, the reactivity ratios of free monomers and CTC in the copolymerization were calculated to be $r_{12} = 0.0440$, $r_{21} = 0.0349$, $r_{1C} = 0.00688$, $r_{2C} = 0.00476$, and the ratios of rate constants were obtained to be $k_{1C}/k_{12} = 6.40$, $k_{2C}/k_{21} = 7.33$. In addition, the copolymer was characterized by IR, ¹H-NMR, DSC, and TGA.
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Key words: *N*-butyl maleimide; styrene; charge-transfer complex; solution copolymerization; reactivity ratios

INTRODUCTION

Reactivity ratios are among the most important parameters for composition equation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimate the copolymer composition. Recently, more and more researches are focused on copolymerizations with the participation of charge-transfer complex (CTC).^{1–6} To date, for such radical copolymerization systems, three kinetic models have been presented: (1) the Seiner and Litt model,⁷ the Shirota model,⁸ and the Shan model.⁹

It is well known that *N*-substituted maleimide and styrene (St) represent monomer pairs with a strong tendency toward radical alternating copolymerization.^{10–16} Moreover, after copolymerization, the thermal stability of polystyrene, which is widely used as a conventional plastic, will be greatly improved. So far, the copolymerization of *N*-butyl maleimide (NMBI) and styrene has been reported in literature^{17–19}; however, only the apparent monomer reactivity ratios were acquired ($r_{St} = 0.025 \pm 0.025$, $r_{NMBI} = 0.06 \pm 0.02$).

In this study, the existence of CTC was proved and the complex formation constant was acquired by means of ¹H-NMR. The copolymerization of NMBI and St in chloroform was carried out in sealed ampoules, initiated with 2,2'-azobis(isobutyronitrile) (AIBN). Based on the kinetic model

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Table I Chemical Shift Values from NMR Analysis of NBMI–St Complex Measured in CDCl₃ at 50°C

[St] (mol/L)	δ_{obsd}^A (ppm)	Δ_{obsd} (ppm)	$1/\Delta_{\text{obsd}}$ (ppm ⁻¹)	$1/[\text{St}]$ (L/mol)
2.0	6.48	0.18	5.56	0.50
3.0	6.42	0.24	4.17	0.33
4.5	6.34	0.32	3.13	0.22
5.5	6.29	0.37	2.70	0.17
8.0	6.25	0.41	2.44	0.13

proposed by Shan, four reactivity ratios and relative reactivities of free monomers and CTC were obtained.

EXPERIMENTAL

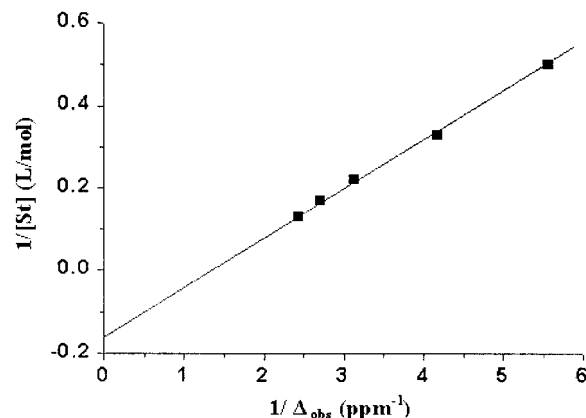
Materials and Instruments

N-Butyl maleimide was synthesized and purified according to the method described in the literature.²⁰ Styrene was distilled under reduced pressure after removal of the inhibitor and stored at low temperature. AIBN was twice recrystallized from ethanol. Chloroform was of analytical grade and distilled before use.

The infrared (IR) spectrum was recorded with a Perkin–Elmer 1710 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT). The ¹H-NMR spectrum was obtained on a Varian DRX-400 spectrometer (Varian Associates, Palo Alto, CA). Differential scanning calorimetry (DSC) was carried out on a Perkin–Elmer Model DSC-7, at a scanning rate of 10°C/min in nitrogen. Thermal stability of the copolymer (TGA) was determined on a Perkin–Elmer TG-40 thermogravimetric system.

Complex Formation Constant of CTC

By using CDCl₃ as the solvent, a series of mixtures consisting of different molar compositions of NBMI and St were prepared when the NBMI concentration was 0.05 mol/L. The chemical shift was obtained on the DRX-400 spectrometer at 50°C. The complex formation constant of CTC was determined by ¹H-NMR of Hanna–Ashbaugh.²¹

**Figure 1** Plot of $1/[\text{St}]$ versus $1/\Delta_{\text{obs}}$ for determination of complex constant (K).

Copolymerization

NBMI, St ($[M]_T = 1.0$ mol/L), and AIBN ($[\text{AIBN}] = 0.01$ mol/L) were accurately weighed and placed into 100-mL ampoules, after which chloroform was added. The copolymerization was carried out in sealed ampoules in an inert atmosphere at 50°C. At time intervals, the polymerizing solution was precipitated with methanol so as to keep the molar conversion less than 10%. The copolymer was dissolved in chloroform again, precipitated with a large amount of methanol, then dried under vacuum at 60°C. The weight conversion of copolymerization was obtained.

Copolymer Analysis

By using the following formula, the compositions of copolymers were calculated on the basis of nitrogen content in the copolymers, determined by a PE-2400 elemental analyzer.

$$14F_1/[M_1F_1 + M_2(1 - F_1)] \times 100\% = N\% \quad (1)$$

Table II Values of $[M_1]$ and $[M_2]$ and Their Corresponding Reactivity Ratios of NBMI/St Copolymerization in Chloroform at 50°C

$[M_2]_0$	$[M_2]$	r_1	$[M_1]_0$	$[M_1]$	r_2
0.03	0.0260	0.0516	0.03	0.0260	0.0411
0.08	0.0699	0.0540	0.08	0.0699	0.0422
0.12	0.106	0.0559	0.12	0.106	0.0440
0.15	0.133	0.0584	0.15	0.133	0.0451
0.20	0.178	0.0628	0.20	0.178	0.0480
0.30	0.271	0.0760	0.30	0.271	0.0542

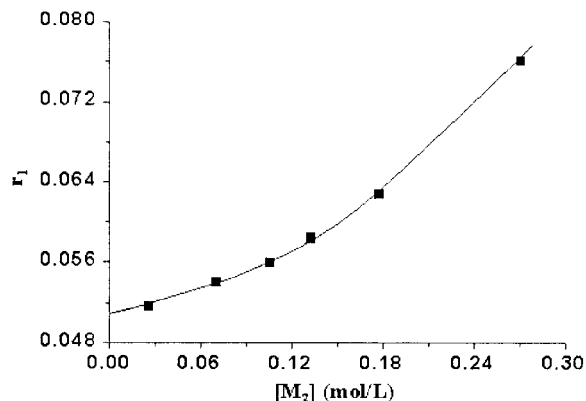


Figure 2 Plot of $[M_2]$ versus r_1 for the NBMI/St copolymerization in chloroform at 50°C.

Here F_1 represents the molar fraction of NBMI in copolymer; M_1 and M_2 are molecular weights of NBMI and St, respectively. On this basis, the molar conversion of NBMI/St copolymerization was acquired.

RESULTS AND DISCUSSION

Complex Formation Constant of CTC

From the $^1\text{H-NMR}$ spectra of NBMI/St mixtures, a shift of the resonance signals of the protons in NBMI was observed in the presence of excessive St. On increasing the St concentration, the peak height of St's vinyl protons increased and the chemical shifts of those protons were constant; however, the peak height and the chemical shift of NBMI's vinyl protons decreased, which indi-

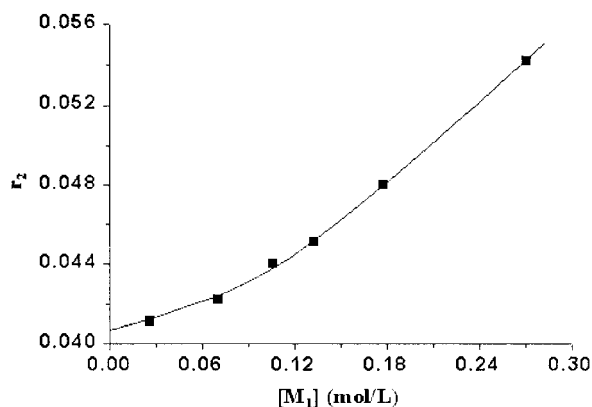


Figure 3 Plot of $[M_1]$ versus r_2 for the NBMI/St copolymerization in chloroform at 50°C.

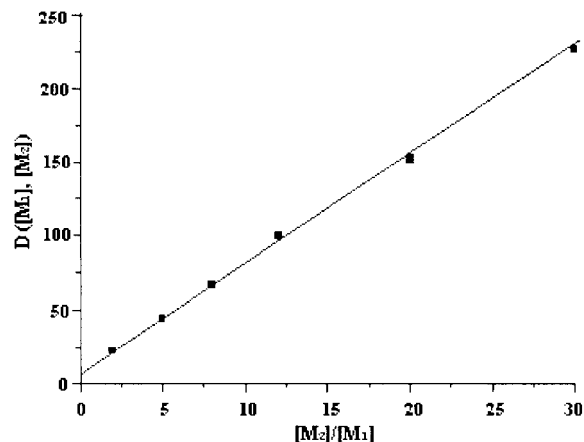


Figure 4 Plot of $D([M_1], [M_2])$ versus $[M_2]/[M_1]$ in the NBMI/St copolymerization in chloroform at 50°C.

cated the existence of CTC in solution.²² The data were treated according to the Hanna–Ashbaugh relation²¹:

$$1/[D]_0 = (\Delta_{\text{CTC}}/\Delta_{\text{obs}})K - K \quad (2)$$

Table I shows the values of chemical shift from NMR analysis of NBMI–St complex. Based on the concentration of monomers and the NMR data shown in Table I, the reciprocal of the concentration of St, $1/[D]_0$ (donor monomer), was plotted over the reciprocal of the change in chemical shift, $1/\Delta_{\text{obs}}$. The complex formation constant (K) was obtained to be 0.158 L/mol from the intercept of the line shown in Figure 1. These results strongly suggest that the CTC was involved in the copolymerization of NBMI and St.

Calculation of Reactivity Ratios of NBMI/St Copolymerization Formulas Cited in This Study

The major formulas cited here are as follows⁹:

$$y = \frac{d[M_1]}{d[M_2]} = \left(1 + r_1 \frac{[M_1]_0}{[M_2]_0}\right) / \left(1 + r_2 \frac{[M_2]_0}{[M_1]_0}\right) \quad (3)$$

$$[M_1] + K[M_1][M_2] = [M_1]_0 \quad (4)$$

$$[M_2] + K[M_1][M_2] = [M_2]_0 \quad (5)$$

$$[M_1]_0 + [M_2]_0 = [M]_T \quad (6)$$

Table III Ratios of Cross-Propagation to Homopropagation Rate Constants in Chloroform at 50°C^a

r_{12}	r_{21}	r_{1C}	r_{2C}	k_{12}/k_{11}	k_{21}/k_{22}	k_{1C}/k_{11}	k_{2C}/k_{22}
0.0440	0.0349	0.00688	0.00476	22.7	28.7	145.3	210.0

^a $[M]_T = 1.0$ mol/L; $[AIBN] = 0.01$ mol/L.

$$\lim_{[M_2] \rightarrow 0} r_1 = (1 + K[M]_T)r_{12} \quad (7)$$

$$\lim_{[M_1] \rightarrow 0} r_2 = (1 + K[M]_T)r_{21} \quad (8)$$

$$D([M_1], [M_2]) = \frac{y(1 + r_{12}[M_2]/[M_1]) - 1 - r_{12}[M_1]/[M_2]}{K[M_1](1 - y)} = \frac{k_{2C}[M_2]}{k_{21}[M_1]} + \frac{k_{1C}}{k_{12}} \quad (9)$$

Here y represents the molar ratio of NBMI and St in copolymer; $[M_1]_0$ and $[M_2]_0$ represent the initial M_1 and M_2 concentration at the assumption of $[CTC] = 0$; and r_1 and r_2 are the reactivity ratios calculated by the Mayo–Lewis equation.

Calculation of Reactivity Ratios of Free Monomers and CTC

In chloroform at 50°C, the complexation equilibrium constant of NBMI and St was 0.158 L/mol. The Mayo–Lewis equation (formula 3) was used to calculate the results when the molar conversion was as low as possible, and the data are listed in Table II.

From the curves of r_1 versus $[M_2]$ and r_2 versus $[M_1]$ (Figs. 2 and 3, respectively), the calculation

was simulated with a quadratic equation, and the corresponding reactivity ratios were obtained as follows: $r_{12} = 0.0440$; $r_{21} = 0.0349$.

The ratios of rate constants, k_{2C}/k_{21} and k_{1C}/k_{12} , were determined from the slope and intercept of the line in a plot of $D([M_1], [M_2])$ versus $[M_2]/[M_1]$. Calculated from Figure 4, $k_{2C}/k_{21} = 7.33$ and $k_{1C}/k_{12} = 6.40$. Combined with values of r_{12} and r_{21} , the values of r_{1C} and r_{2C} were acquired. As a result, the ratios of the cross-propagation to homopropagation rate constants are listed in Table III.

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

Characterization of Poly(NBMI-co-St)

The resulting copolymer was characterized by IR, ¹H-NMR, DSC, and TGA. The typical IR and ¹H-NMR spectra of poly(NBMI-co-St) are presented in Figures 5 and 6, respectively, and the corresponding data are shown as follows.

IR (KBr disk, cm⁻¹): 3114 (=C–H in Ph); 1772, 1698 (C=O in imide ring); 1495 (C=C in Ph); 1441, 1373 (CH₃); 1402 (CH₂); 1193 (CH); 705, 758 (=C–H in Ph).

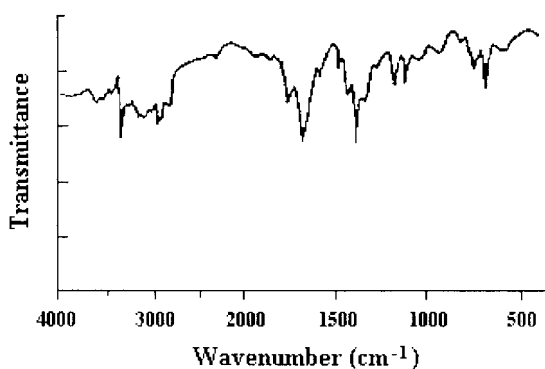


Figure 5 FTIR spectrum of poly(NBMI-co-St).

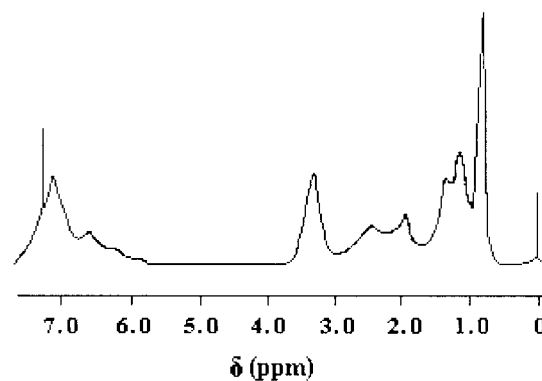


Figure 6 ¹H-NMR spectrum of poly(NBMI-co-St).

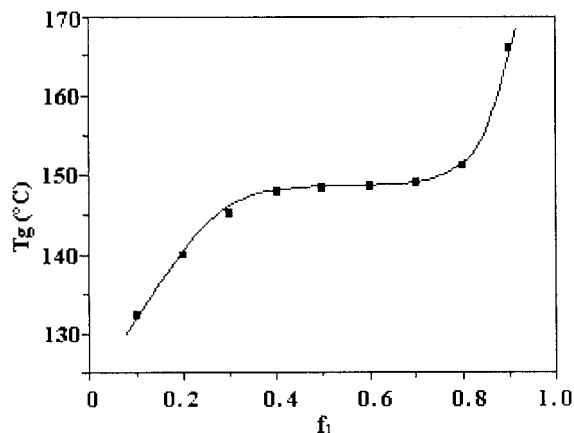


Figure 7 Curve of T_g versus monomer feed for poly(NBMI-*co*-St).

$^1\text{H-NMR}$ (300 MHz, CDCl_3 , ppm): $\delta = 7.12$, 6.59, 6.20 (CH in Ph); 3.28 (CH in imide ring and $-\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3$); 2.45, 1.90 (CH and CH_2 in St monomer unit); 1.32 ($-\text{CH}_2\text{CH}_2\text{CH}_3$); 1.12 ($-\text{CH}_2\text{CH}_3$); 0.85 ($-\text{CH}_3$).

To examine the thermal stability of poly(NBMI-*co*-St), DSC and TGA were carried out in a nitrogen stream. Figure 7 shows the relationship between the glass-transition temperature (T_g) and monomer feed (f_1). From the curve we can see that the value of T_g increases with increasing f_1 ; however, when f_1 changes from 0.4 to 0.7, the glass-transition temperature of poly(NBMI-*co*-St) was almost constant, which suggests the existence of alternating structure in the copolymer.

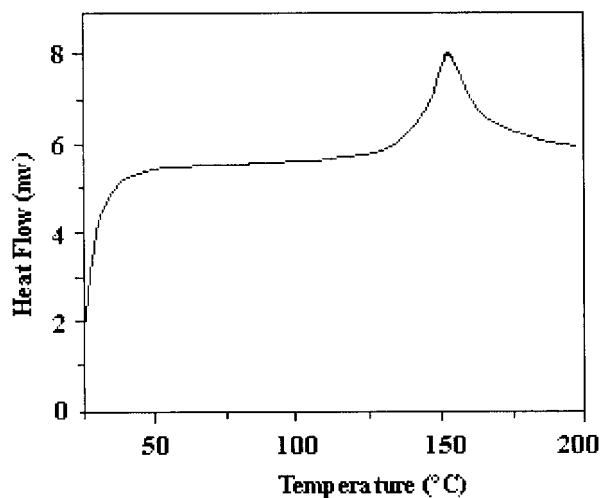


Figure 8 DSC curve of poly(NBMI-*alt*-St).

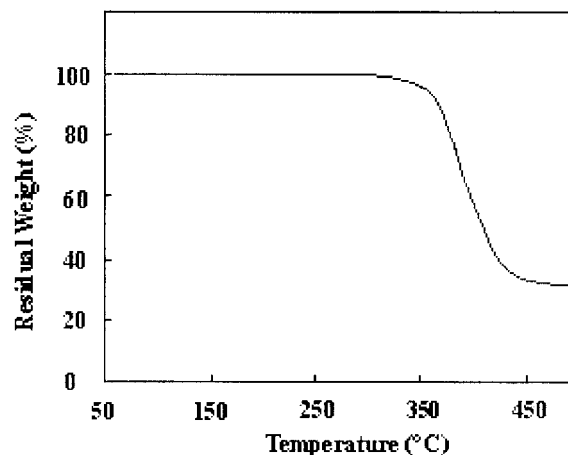


Figure 9 TGA curve of poly(NBMI-*alt*-St).

For the alternating copolymer of NBMI and St [poly(NBMI-*alt*-St)], the DSC and TGA curves are shown in Figures 8 and 9, respectively. It is found that its glass-transition temperature is 148.5°C , and the initial decomposition temperature is 298°C . From the results of thermal analysis, it is obvious that when St was copolymerized with NBMI, the thermal stability of polystyrene was significantly improved.

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