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FREE RADICAL COPOLYMERIZATION OF N-PHENYLMALEIMIDE WITH CYCLOHEXENE

Hua-Ming Li[a]; Shang-An Lin[a]; Hong-Biao Chen[b]; 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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Hua-Ming Li* and Shang-An Lin

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

Hong-Biao Chen and Peng-Sheng Liu

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

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Key Words: Radical Copolymerization, Alternating Copolymer, Cyclohexene, N-phenylmaleimide

ABSTRACT

Radical copolymerization of cyclohexene (M_1) with N-phenylmaleimide (M_2) was carried out with 2,2'-azobis(isobutyronitrile) as an initiator in various solvents at 50°C. The copolymerization of cyclohexene with N-phenylmaleimide in chloroform and dioxane proceeded in a homogeneous system to give an alternating copolymer over a wide range of the comonomer composition in the feed. The initial rate of the copolymerization (R_p) was dependent on the monomer composition and was a maximum at about 65 mol% of N-phenylmaleimide in the feed. A solvent effect on the R_p and the reactivity ratio was investigated in this copolymerization system, i.e., copolymerization in benzene produced a higher R_p than that in chloroform and in dioxane, while in chloroform produced a higher alternating tendency compared with those in benzene and in dioxane (r_1=0, r_2=0.012 in chloro-

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*Author to whom correspondence should be addressed.

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form; $r_1=0$, $r_2=0.081$ in benzene and $r_1=0$, $r_2=0.073$ in dioxane). The copolymer was characterized by ^{1}H-NMR spectrum.

INTRODUCTION

In recent years, there has been considerable interest in the free radical copolymerization of N-substituted maleimide with vinyl monomer [1-6], especially, copolymerization with electron-donating monomer, e.g., styrene and vinyl ethers, is well-known to produce alternating copolymers over a wide range of comonomer composition in the feed. This powerful alternation tendency in the copolymerization has been explained by the addition of the growing chain radical to a charge-transfer complex, which was formed between N-substituted malimide, an electron acceptor and 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 (PMI) and donor olefins [11-13].

Polyimides such as polyPMI produced by radical polymerization are expected to show characteristics different from those of conventional polyimides produced by condensation, e.g., excellent transparency and excellent thermal stability. At present, the copolymerizations of N-(alkyl-substituted phenyl)maleimides with isobutene were investigated kinetically in details [14-16]. However, investigations on the radical copolymerization of PMI with cycloolefins such as cyclohexene (CH) appear quite limited in the literature. We recently became interested in this system, because CH is a difficult monomer to homopolymerize using any kind of initiators. In this paper, we deal with the radical copolymerization of PMI with CH, the effects of reaction conditions on the copolymerization were discussed.

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EXPERIMENTAL

Materials

CH was from Aldrich and distilled before use. PMI was prepared according to the method of Chen *et al.* [17]. 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 over a dropping funnel 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 with 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.

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Polymerization Procedures

A solution of PMI and CH was placed in a glass tube which contained a magnetic stirrer, the initiator AIBN was weighed and introduced into the tube, then the tube was degassed and swept with nitrogen three 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 yield of polymers was determined gravimetrically and the composition of the copolymers was determined by elemental analysis.

Measurements

The molecular weight of the resulting polymers was determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using Varian 5000 equipped with Ultrastyrogel 10000 and 500A columns with chloroform as an eluent at 35°C. ^{1}H-NMR spectra were taken by means of a Brucker DRX-400, deuterochloroform and tetramethylsilane were used as solvent and an internal standard, respectively.

RESULTS AND DISCUSSION

Charge-Transfer Complex

Colymerization of PMI and CH was carried out with AIBN in chloroform under various comonomer composition and a nearly alternating copolymer was obtained (Table 1). In the literature, the powerful alternating tendency in the copolymerization of maleimide with vinyl monomers has often been discussed in connection with the participation of charge-transfer complex. Olson and Butler, [18, 19] reported the participation of charge-transfer complex in the copolymerization of N-substituted maleimide and vinyl ether from the stereochermical analysis of resulting copolymers. Shan and his coworker, [20] proposed a new kinetic model and treatment method, which were successfully used to quantitatively estimate the participation of the charge–transfer complex and the free monomer in the alternating copolymerization of PMI and styrene. However, evidence against the participation of charge-transfer complex in the propagation has also been reported based on the results of the model reactions of simple alkyl radicals with PMI and donor olefins [11-13]. T. Doi [14] also showed the absence of charge-transfer complex between monomers in the polymerization of N-alkylmaleimides with isobutene.

In this work, ^{1}H-NMR method with use of the Hana-Ashbaugh equation [21] was applied to determine whether or not the charge-transfer complex between PMI and CH existed in this system. The concentration of acceptor monomer (PMI) in different mixtures with CH at [CH]>>[PMI] was constant at 0.2 mol/L. The concentration of CH varied from 1.0 to 8.0 mol/L. On the basis of ^{1}H-NMR spectra of free PMI (δ^f) and its different mixtures with (δ^c), the chemical shifts of PMI protons ($\Delta = \delta^f - \delta^c$) are determined. Then, from of the plot of $(\Delta)^{-1}$ vs. $[CH]^{-1}$, complex formation constant K is calculated. The value of K for PMI–CH complex in chloroform at 25°C is found to be zero (figure is not shown) which indicates that the charge–transfer complex between monomers do not exist in this polymerization system, meaning that the interaction between PMI and CH is very weak due to weak electron donating of CH.

Copolymerization Rate and Composition

Copolymerization of CH (M_1) and PMI (M_2) was carried out with AIBN in chloroform under various comonomer composition (f_1) at a constant total monomer concentration at 50°C. Figure 1 shows the relationship between the copolymer yield and the copolymerization time. The copolymerization proceeded homogeneously in all cases. The results of Figure 1 showed that the copolymer-

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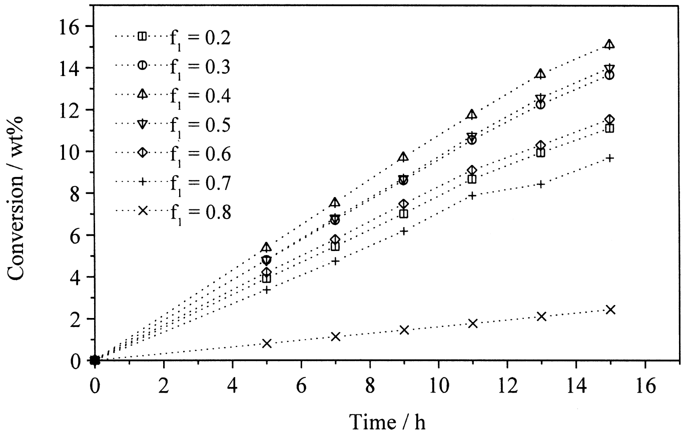

Figure 1. Relationships between reaction time and polymer yield for radical copolymerization of CH with PMI in chloroform at 50°C under various comonomer composition (f_I), [CH]+[PMI]=1.00 mol/L, [AIBN]=1.0 × 10^{-2} mol/L.

ization of PMI and CH proceeded at a very low rate, e.g., very low yields, and low molecular weight copolymer (Table 1). This indicates that the steric hindrance is more important in the copolymerization system because PMI and CH are all 1,2-disubstituted cyclic monomers.

TABLE 1. Results of Copolymerization of CH with PMI in Chloroform, Benzene, and Dioxane at 50°C[a].

Solvents	CH in Feed mol%	$R_p \times 10^6$ mol/L·s	$M_n \times 10^{-3}$	M_w/M_n	CH in Copolymer mol%
Chloroform	0	6.12	11.3	2.6	0
	5	1.36	4.6	2.4	6.5
	10	1.08	4.3	2.4	43.7
	20	1.71	4.3	2.6	48.6
	30	2.09	4.1	2.7	49.5
	40	2.35	4.5	2.3	50.0
	50	2.13	4.1	2.5	49.8
	60	1.82	4.3	2.5	49.7
	70	1.48	3.9	2.7	50.0
	80	0.35	3.9	2.7	50.2
Dioxane	50	1.19	3.1	2.6	48.7
Benzene	50	2.95	4.1	2.9	44.6

[a] [CH]+[PMI]=1.0mol/L, [AIBN]=1.0 × 10^{-2} mol/L.

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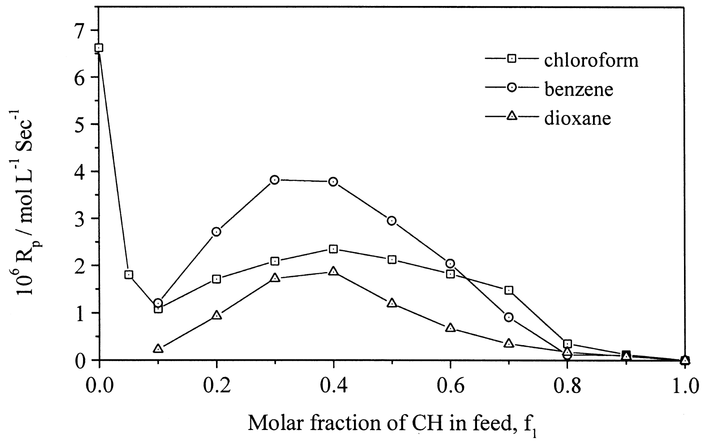

Figure 2. Effect of comonomer composition (f_1) on R_p for radical copolymerization of CH with PMI in several solvents at 50°C, [CH]+[PMI]=1.00mol/L, [AIBN] $= 1.0 \times 10^{-2}$ mol/L.

The initial rate of copolymerization of PMI and CH (R_p) was determined from the initial slope of the polymer yield-time curves in consideration of the composition of the copolymers obtained. It was presented in Figure 2 as a function of the initial molar fraction of CH in the feed (f_1). A variation in the R_p value depending on the comonomer composition was observed for the copolymerization systems in chloroform, benzene and dioxane, i.e., in chloroform 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 0.3~0.4 of f_1 value, and then decreased again. The R_p values in different solvents decreased in the following order: benzene > chloroform > dioxane. However, the values of f_1 of at the maximum R_p value were almost the same. The effects of solvents on the copolymerization are discussed later.

Figure 3 presented the comonomer–copolymer composition curves for the copolymerization of PMI and CH in these solvents, alternating copolymer was obtained over a wide range of comonomer composition regardless of the type of solvents. However, the alternating tendency was obviously dependent on the solvents. The monomer reactivity ratios were determined by the Kelen-Tüdos method [22], the overall procedure began with conducting CH and PMI copolymerizations at a variety of M_1/M_2 feed ratios, copolymerizations at low conversions (ca. 10%) were performed and the copolymer composition was analyzed by

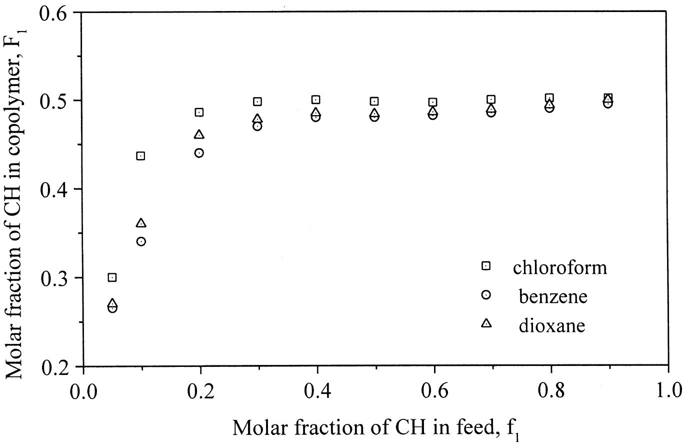

Figure 3. Relationships between comonomer composition (f_1) and copolymer composition (F_1) for radical copolymerization of CH with PMI in chloroform, benzene and dioxane at 50°C.

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elemental (N) analysis. The reactivity ratios (r_1, r_2) in different solvents are summarized in Table 2. The monomer reactivity ratios were determined to be $r_1=0$ and $r_2=0.012$ in chloroform, $r_1=0$ and $r_2=0.081$ in benzene, $r_1=0$ and $r_2=0.073$ in dioxane. These results indicated that the alternating tendency were influenced by the solvents and a higher alternating copolymer was obtained in chloroform than in dioxane or in benzene, and that the sequence of successive PMI units must exist in the polymers.

Solvent Effects

The experimental results suggested that the chain propagation manner influenced by the solvent in the copolymerization of CH and PMI. Figure 4 presented the relationships between the polymer yield and the reaction time in dif-

TABLE 2. **Monomer Reactivity Ratios for Radical Copolymerization of CH (M_1) and PMI (M_2) in Several Solvents at 50°C.**

Solvents	r_1	r_2
Chloroform	0	0.012
Dioxane	0	0.073
Benzene	0	0.081

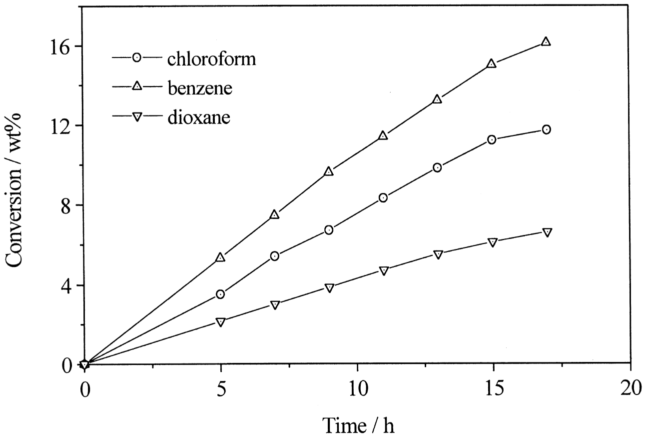

Figure 4. Relationships between reaction time and polymer yield for radical copolymerization of CH with PMI in several solvents at 50°C, f_1=0.50, [AIBN] = 1.0×10^{-2} mol/L, [CH]+[PMI]=1.00 mol/L.

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ferent solvents. The copolymerization rate in benzene was higher than that in chloroform and in dioxane, and these results are obviously seen in Figures 2 and 4. But, in contrast with our results, T. Doi *et al.* [23] reported higher R_p values in chloroform than those in benzene in the copolymerization of N-(alkyl-substituted phenyl)maleimides with isobutene or with 2,4,4-trimethylpentene. The solvent effect in the copolymerization of CH and PMI influenced not only the copolymerization rate, but also the copolymer composition, together with the monomer reactivity ratio. The copolymerization in chloroform proceeded with a higher alternating nature compared with those in benzene or in dioxane (Table 2). The r_2 values were 0.081 and 0.073 in benzene and in dioxane, respectively, whereas it was reduced to 0.012 in chloroform. These results are similar to the results of copolymerization of N-(alkyl-substituted phenyl)maleimide with isobutene and 2,4,4-trimethylpentene reported by T. Doi [23].

The fact that the alternating tendency for copolymerization of CH with PMI in chloroform was greater than those in benzene or dioxane may be interpreted by the assumption that the copolymerization proceeds through a highly polarized radical transition state [25] rather than attribute this phenomenon to the addition of the growing chain radical to a charge-transfer complex, which did not exist in this copolymerization system even when chloroform was used as the solvent as discussed before. The transition state for the addition of a CH terminated growing chain radical to a PMI molecule to be represented by I (Scheme 1),

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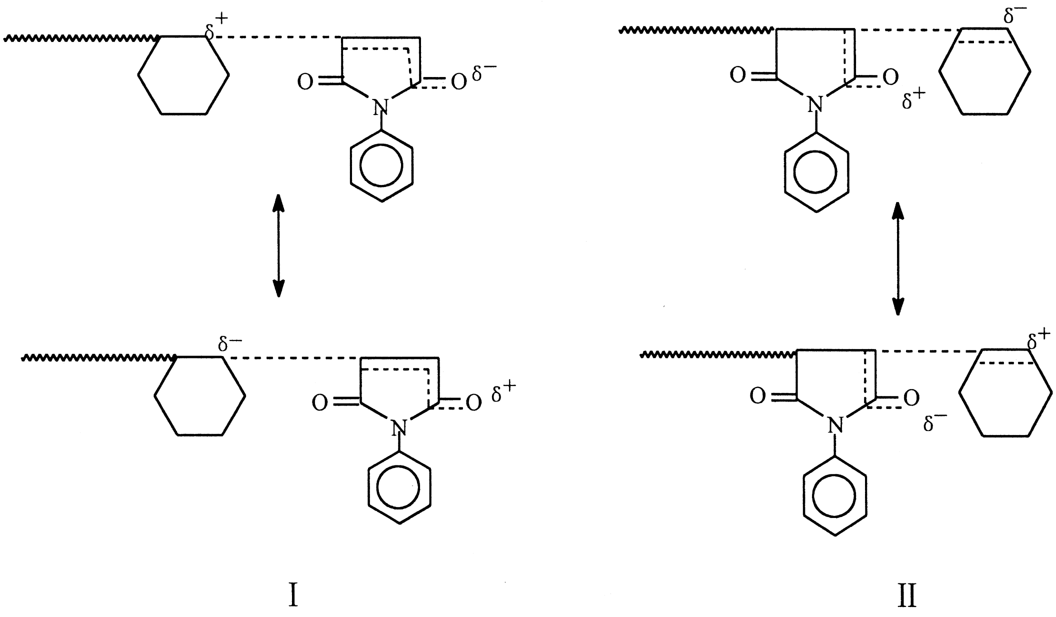

Scheme 1. Polar transition states for CH-PMI copolymerization.

while the transition state for the addition of a PMI terminated growing macroradical to a CH can be represented by II, both of those are highly polar. Polar solvents, such as chloroform, could preferentially solvate the highly polarized radical transition states I and II, relative to nonpolar transition states thereby promoting alternating copolymerization than can be observed in nonpolar solvents. Furthermore, such stabilization of transition states would enhance k_{12} and k_{21} relative to k_{11} and k_{22} (note that $k_{11}=0$, due to the lack of homopolymerizability of CH). The net effect is that r_2 become very small and an alternating polymer formed. Benzene and dioxane could not provide such stabilizing solvation due to their low polarity, e.g., lower dielectric constants than chloroform. Their dielectric constants at 25°C are 4.8 (chloroform), 2.3 (benzene) and 2.2 (dioxane) [24].

A. Matsumoto and his coworkers [23] studied the radical copolymerization of N-(2,6-dimethylphenyl)maleimide (DMPMI) and 2,2,4-trimethylpentene (TP) in several solvents at 60°C by using electron spin resonance spectroscopy. They found that termination rate constant k_t was very weakly dependent on the comonomer composition. The propagation rate constant k_p and the total polymer radical concentration [P•] were revealed to depend on the solvent, the copolymerization provided the following k_p values: 9.8, 21, 47 L/mol·s, and [P•] values: 5.8×10^{-6}, 1.8×10^{-6},

0.68×10^{-6} mol/L in chloroform, benzene and dioxane, respectively, at 50% of [TP] in the feed. Thus, they clarified that the greater R_p in chloroform than that in benzene and in dioxane was ascribed to the high [P•], that is, the slow termination which compensates for the small k_p values in chloroform. However, against these results we found a greater R_p in benzene than that in chloroform and in dioxane for the radical copolymerization of CH and PMI. This phenomenon could be explained by the high k_p, according to the results of the radical copolymerization of DMPMI and TP obtained by A. Matsumoto, and also the slow termination for the resulting polymer is insoluble in benzene. The effects of the occlusion of the reacting center may be not serious due to the low overall copolymerization rate. The slightly low R_p in chloroform may be attributed to the low k_p and slightly faster termination rate in chloroform than that in benzene for the copolymer is soluble in chloroform. The smallest R_p in dioxane might be ascribed to the lowest [P•] value, and in addition, a degradative chain transfer might occur during the copolymerization of CH and PMI in dioxane (lowest M_n, Table 1). Further investigation should be carried out for solvent effects in this radical copolymerization.

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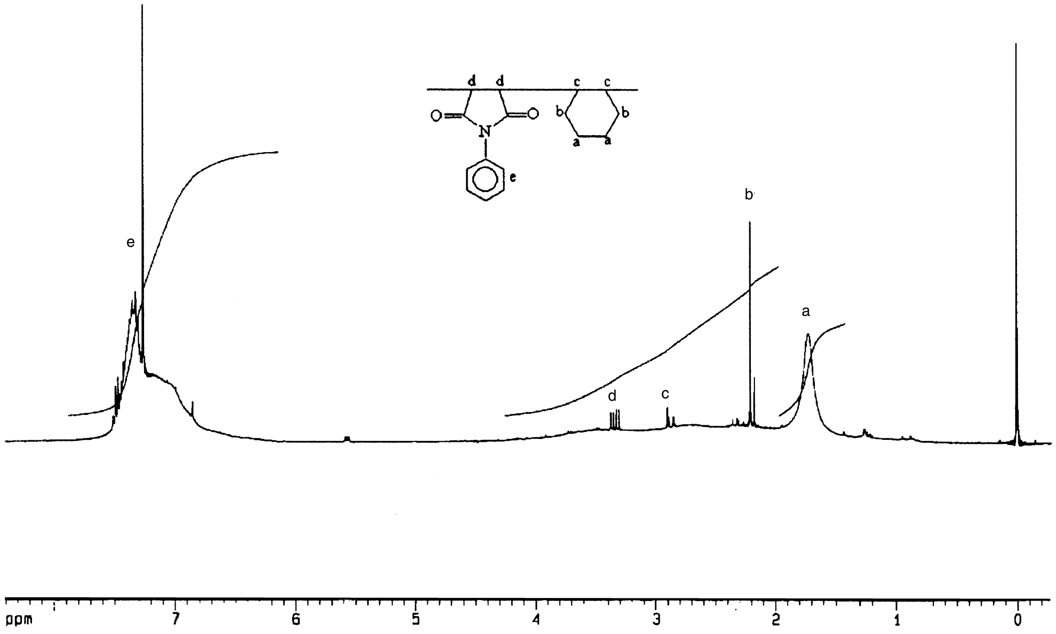

Figure 5. ^{1}H-NMR spectrum of poly(CH-alt-PMI) in deuterochloroform at ambient temperature.

Characterization of Copolymer

The resulting copolymers were soluble in many organic solvents including chloroform, acetone, N,N-dimethylformamide, dimethylsulfone and insoluble in benzene, toluene and n-hexane, as well the homopolymer of PMI. The ^{1}H-NMR spectrum of the alternating copolymer of PMI and CH is shown in Figure 5. In the spectrum, the peaks due to saturated, and aromatic protons observed at 1.72 ppm (a, 4H), 2.17-2.20 ppm (b, 4H), 2.85 ppm (c, 2H), 3.20 ppm (d, 2H) and 7.06-7.39 ppm (e, 5H), respectively, are assigned as shown in Figure 5. The NMR spectrum also confirmed the consumption of all the vinyl groups of the comonomers because only a negligible amount of vinyl proton absorption could be seen. For example, 5.60 ppm for vinyl protons of CH and 6.85 ppm for PMI, which may result from the unsaturated copolymer molecules produced by disproportionation termination. Furthermore, it is important to note that the almost equal areas under the peak 2.85 ppm (c, 2H) and the peak 3.20 ppm (d, 2H) show good agreement with the reactivity ratio values and the conclusion of the alternating copolymer of CH and PMI.

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CONCLUSION

The free radical copolymerization of CH with PMI showed a stronger tendency toward alternation in chloroform than that in benzene or in dioxane. The monomer reactivity ratios were determined to be $r_1 = 0$, $r_2 = 0.012$ in chloroform, $r_1 = 0$, $r_2 = 0.081$ in benzene and $r_1 = 0$, $r_2 = 0.073$ in dioxane. These results are explained by copolymerizations that proceed through highly polarized radical transition states rather than CH-PMI charge-transfer complex, which do not exist in this system. Polar solvents stabilize the highly polarized radical transition states thereby promoting alternating polymerization.

The initial rates of copolymerization of PMI and CH (R_p) are dependent on the comonomer composition and the solvents that used. The copolymerization rate in benzene is higher than that in chloroform and in dioxane.

The copolymer of PMI and CH is characterized by ^{1}H-NMR spectrum.

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