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Free Radical Copolymerization of N-Cyclohexylmaleimide with Cyclohexene

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The radical copolymerization of cyclohexene (M_1) and N-cyclohexylmaleimide (M_2) was carried out with 2,2′-azobis(isobutyronitrile) as an initiator in various solvents at 55°C. The copolymerization of cyclohexene with N-cyclohexylmaleimide in chloroform, dioxane and benzene proceeded in a homogeneous system to give an alternating copolymer when the monomer of cyclohexene was over 40 mol% in the feed. It was found that the initial rate of the copolymerization (R_p), as well as the number-average molecular weight of copolymers, were dependent on the monomer composition and was at maximum at about 30 mol% of cyclohexene in the feed. The effects of solvents on the R_p and reactivity ratios were also investigated in this copolymerization system. The copolymerization in dioxane produced a higher R_p than that in chloroform and benzene, and the monomer reactivity ratios were found to be $r_1 = 0$, $r_2 = 0.032$ in chloroform; $r_1 = 0$, $r_2 = 0.065$ in benzene and $r_1 = 0$, $r_2 = 0.14$ in dioxane, respectively.

Keywords radical copolymerization, alternating copolymer, cyclohexene, N-cyclohexylmaleimide

Introduction

In recent years, there has been considerable interest in the free radical copolymerization of N-substituted maleimides with various vinyl monomers such as styrene, vinyl ethers, vinyl acetate, vinyl chloride, and alkyl acrylates or methacrylates (1–6). This great interest originates in copolymerization allowing the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the monomer units in the copolymer product. Moreover, the N-substituted maleimide has a 1,2-disubstituted cyclic structure, and its N-substituted groups are versatile. Thus, many unsaturated polymeric systems have been modified with it to obtain improved heat strength (5, 6).

As reported in the literature, copolymerization of maleimide with electron-donating monomer is well known to produce alternating copolymers over a wide range of comonomer composition in the feed. The powerful 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

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styrene or vinyl ether, an electron donor (7–9). 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 (1, 2, 6, 10).

In previous articles (10, 11), we reported the free radical copolymerization and kinetic treatment of cyclohexene with PMI. It was found that this copolymerization system showed a stronger tendency toward alternation in chloroform than that in benzene or in dioxane. This result was explained by the propagation proceeding through highly polarized radical transition states rather than by the addition of the growing chain radical to the cyclohexene-PMI charge-transfer complex, which do not exist in this system. In addition, 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.

The radical copolymerization behavior of maleimide with cyclohexene is of considerable interest, since maleimide and cyclohexene are all 1,2-disubstituted cyclic olefinic monomers. Furthermore, cyclohexene is a difficult monomer to homopolymerize using any kind of initiators. In this paper, we present further studies on the free radical copolymerization of N-cyclohexylmaleimide with cyclohexene. The main objective of the present work is to compare the influence of the substituted groups in maleimide ring on the copolymerization behaviors.

Experimental

Materials

Cyclohexene (CH, 99.8%) was from Aldrich and distilled before use. 2,2′-Azobis(isobutyronitrile) (AIBN, 99.8%) was from Aldrich and purified by recrystallization from methanol. Solvents were purified by distillation before use. The N-cyclohexylmaleimide (CHMI) used in these studies was synthesized in our laboratory (12), and the typical procedure was as follows:

Maleic anhydride, 108.0 g (1.10 mol), dissolved in 150 mL acetone was placed in a four-neck flask (500 mL) provided with a dropping funnel, reflux condenser, nitrogen inlet, and an agitator. A solution of 99.0 g (1.00 mol) of cyclohexylamine in 150 mL acetone was slowly added to the maleic anhydride solution under nitrogen atmosphere with stirring at ice bath temperature and allowed to stand for 5 h to attain slurry of N-cyclohexylmaleamic acid (CHMA). Then, the slurry was filtered, washed several times with acetone, and dried under vacuum at 50°C for 24 h.

The dehydration of CHMA (49.3 g, 0.25 mol) was conducted for 6 h in 300 mL of o-xylene/toluene (50/50 v/v) mixed solvent at reflux temperature (about 125°C). The formed water was continuously removed after the addition of the catalyst to the CHMA slurry. After reaction, the solvents were distilled off from the reaction system under reduced pressure, and then the product was distilled at 140–150°C under about 5 mmHg to obtain CHMI. The CHMI was further purified by recrystallization from toluene. The yield of CHMI based on cyclohexylamine was 54 wt%, m.p. 89.5–90.3°C. The purity of the CHMI was checked by ^{1}H-NMR and IR spectroscopy.

IR spectrum (KBr, cm^{-1}): 3020 (CH), 2937 (CH_2), 1650 and 1700 (CO, imide). ^{1}H-NMR spectrum (δ, ppm), ($CDCl_3$): 1.2–2.1 (10H, CH_2 in cyclohexyl group), 3.88–3.94 (1H, NCH), 6.62 (2H, CHCH).

Copolymerization

A solution of CHMI and CH was placed in a glass tube, which contained a magnetic stirrer, and the initiator AIBN was introduced into the tube, then the tube was degassed and swept with nitrogen 3 times and finally the tube was sealed. After polymerization for a given time at 55°C with stirring, the polymerization mixture was poured into a large amount of methanol to precipitate the polymer. The yield of polymer was determined gravimetrically and the composition of the copolymer was determined by elemental analysis and ^{1}H-NMR spectroscopy.

Copolymer Analysis

The molecular weight of the resulting polymers was determined by gel permeation chromatography (GPC) calibrated with polystyrene standards using Waters 515 with tetrahydrofuran (THF) as an eluent at 30°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

Copolymerization of CH with CHMI

The copolymerization of CH (M_1) with CHMI (M_2) was carried out with AIBN in benzene, chloroform and dioxane under various comonomer compositions (f_1) at a constant total monomer concentration at 55°C. The copolymerization proceeded homogeneously in all cases and no precipitation was observed in the reaction.

^{1}H-NMR spectra of the CHMI homopolymer and the copolymer of CH with CHMI are shown in Figure 1. In the spectrum of poly(CHMI), methine protons of the main

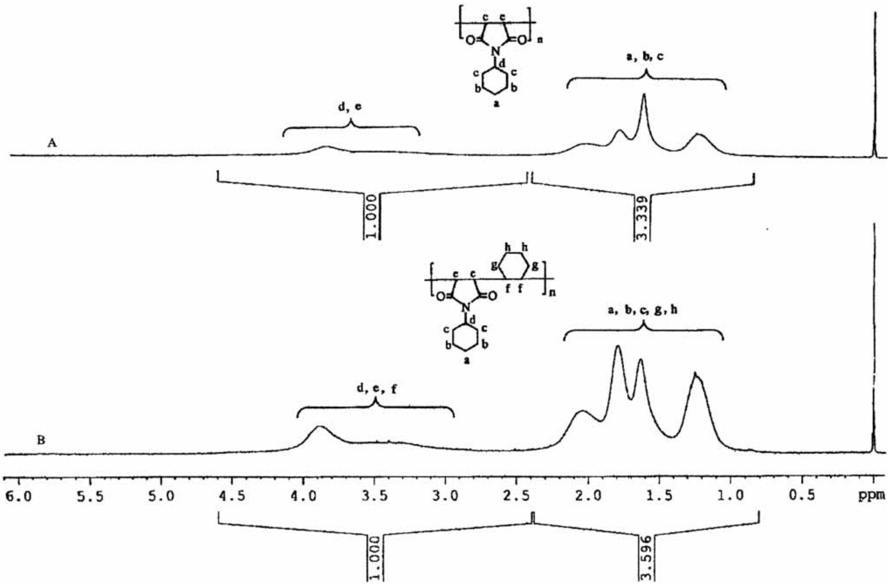

Figure 1. ^{1}H-NMR spectrum of (A) poly(CHMI) and (B) copolymer of CH and CHMI at $f_1 = 0.6$.

chain and of the cyclohexyl group attached to nitrogen atom were observed at about 3.5–4.0 ppm, while the methylene protons of cyclohexyl group were observed at 1.0–2.4 ppm. In the ^{1}H-NMR spectrum of CH and CHMI copolymer, four broad peaks were observed at 1.0–2.4 ppm for the methylene protons of N-substituted cyclohexyl group and the methylene protons for the CH segment. The resonance signals for the backbone methine protons of the CH unit and of the CHMI unit, as well as the methine proton of cyclohexyl group in the CHMI unit can be found at about 3.0–4.3 ppm. It is important to note that the ^{1}H-NMR spectrum of CH-CHMI copolymer is very similar to that of poly(CHMI) homopolymer.

To determine the copolymer composition, the ratio of the integration of the 0.8–2.4 ppm region and of the 2.4–4.6 ppm region was measured. CH molar fraction in the copolymer was obtained using the following equation:

$$\text{CH (mol\%)} = 1.5 \times \frac{A_2}{A_1} - 5$$

where CH (mol%) is the molar fraction of CH in the copolymer, A_1 is the integrated area of the peaks at 2.4–4.6 ppm region. A_2 is the integrated area of the peaks at 0.8–2.4 ppm region. It is calculated that the copolymer consists of about 50 mol% CH and 50 mol% CHMI. This result is very much in agreement with the result determined by elemental analysis and is expected because the comonomer composition is $f_1 = 0.6$.

Table 1 summarizes the results of radical copolymerization of CH with CHMI in benzene at 55°C. All the copolymerization was kept at very low yields in order to keep the steady conditions. The results in Table 1 indicated that an alternating copolymer of CH and CHMI was obtained over a relatively wide range of the comonomer composition in the feed.

The powerful alternating tendency in the copolymerization of maleimide with vinyl monomers has often been discussed in the literature in connection with the participation

Table 1

Results of copolymerization of CH (M_1) and CHMI (M_2) in chloroform, benzene, and dioxane at 55°C

Solvents	CH in feed mol%	Conversion wt%	$M_n \times 10^{-3}$	M_w/M_n	CH in copolymer mol%
Benzene	10	6.8	3.28	1.98	17.0
Benzene	20	7.30	3.22	2.39	35.0
Benzene	30	9.14	5.11	1.42	45.0
Benzene	40	8.69	4.79	1.41	48.5
Benzene	50	8.50	3.69	1.83	49.6
Benzene	60	7.44	3.32	1.62	49.5
Benzene	70	5.82	2.13	1.44	49.7
Benzene	80	2.68	1.81	1.55	50.0
Benzene	90	2.55	1.79	1.75	49.8
Chloroform	50	5.97	1.74	1.58	49.8
Dioxane	50	8.01	3.58	1.63	48.5

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

of charge-transfer complex (CTC) (7–9). However, evidence against the participation of charge-transfer complex in the propagation has also been reported (1, 2, 6, 10, 11).

In this work, ^{1}H-NMR method was applied to determine the formation of the charge-transfer complex between CHMI and CH. The equilibrium constant K was obtained according to an analogue to the Benesi-Hildebrand equation (13):

$$\frac{1}{C_{\mathrm{D}}} = \frac{1}{\Delta_{\mathrm{obsd}}} K\Delta_{\mathrm{comp}} - K$$

where K is the equilibrium constant, C_D represents the molar concentration of the donor (i.e., CH), $\Delta_{\mathrm{obsd}} = \delta_{\mathrm{free}} - \delta_{\mathrm{obsd}}$, $\Delta_{\mathrm{comp}} = \delta_{\mathrm{free}} - \delta_{\mathrm{comp}}$, where δ_{free} is the chemical shift of the free CHMI, δ_{obsd} is the observed chemical shift of CHMI, and δ_{comp} is the chemical shift of the complexed CHMI. An equilibrium constant can be determined from the intercept of the plot of $1/C_{\mathrm{D}}$ vs. $1/\Delta_{\mathrm{obsd}}$. Thus, the value of K for CHMI–CH complex in chloroform at 25°C is estimated to be zero (figure not shown), which indicates that the charge–transfer complex between comonomers do not exist in this polymerization system, meaning that the interaction between CHMI and CH is very weak due to weak electron donating of CH. Previously, similar results have been reported for the radical copolymerization of N-phenylmaleimide with CH (10).

Figure 2 shows the relationship between the copolymer yield and copolymerization time. The results of Figure 2 showed that the copolymerization of CH and CHMI preceded 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 CHMI and CH are all 1,2-disubstituted cyclic monomers.

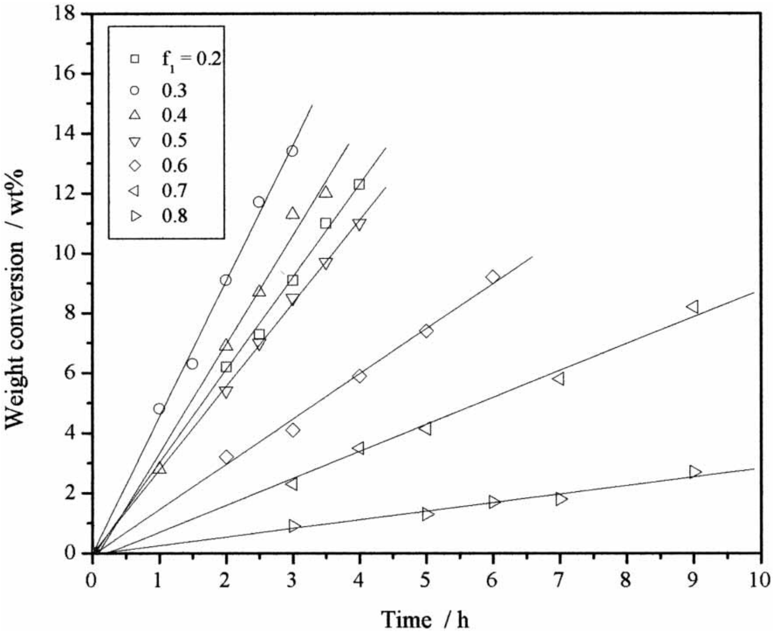

Figure 2. Relationships between reaction time and polymer yield for copolymerization of CH with CHMI in benzene at 55°C under various comonomer composition (f_1), [CH] + [CHMI] = 1.0 mol/L, [AIBN] = 1.0×10^{-2} mol/L.

The number-average molecular weight and molecular weight distribution of these CH-CHMI copolymers as determined by gel permeation chromatography (GPC) are also given in Table 1. It is evident that the number-average molecular weight of the copolymer (M_n) was dependent on the comonomer composition (f_1) and was a maximum at about the 70 mol% of CHMI in the feed. This result is very much in agreement with the result of copolymerization of N-phenylmaleimide with ethyl phenylacrylate in dioxane reported by J. Huang (14).

Copolymerization Rate and Composition

The initial rate of copolymerization of CH and CHMI (R_p) was determined from the initial slope of the copolymerization yield-time curves in consideration of the composition of the copolymers produced, which was presented in Figure 3. A variation in the R_p values depending on the comonomer composition was observed for the copolymerization system in several solvents, i.e., the R_p value decreased drastically with the addition of a small amount of CH until it reached a minimum value at 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 of f_1 value, and then decreased again. In our previous paper, similar results have been obtained for the radical copolymerization of N-phenylmaleimide with CH (10).

Figure 4 presented the comonomer-copolymer composition curves for the copolymerization of CH and CHMI in benzene, chloroform and dioxane, an 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.

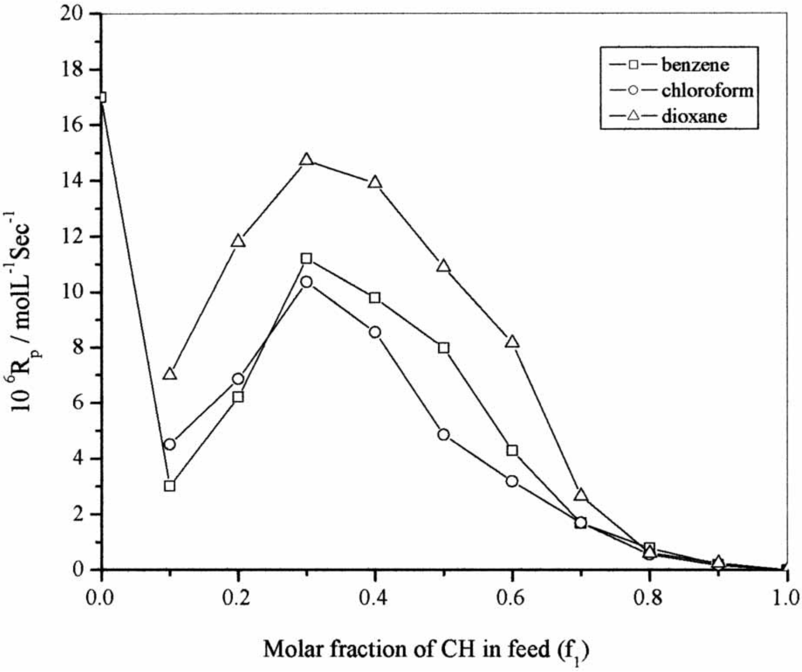

Figure 3. Effect of comonomer composition (f_1) on R_p for radical copolymerization of CH with CHMI in chloroform, benzene and dioxane at 55°C, $[CH] + [CHMI] = 1.00\,mol/L$, $[AIBN] = 1.0 \times 10^{-2}\,mol/L$.

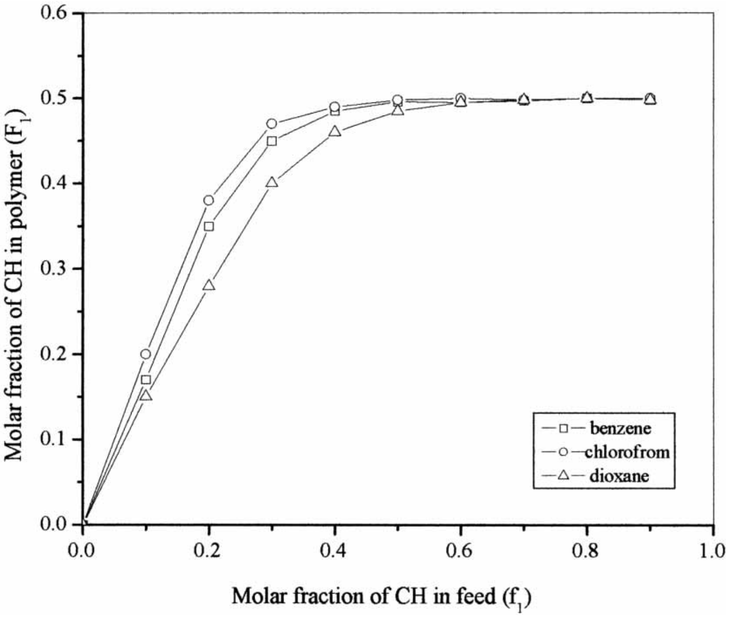

Figure 4. Relationships between comonomer composition (f_1) and copolymer composition (F_1) for radical copolymerization of CH with CHMI in chloroform, benzene and dioxane at 55°C.

The monomer reactivity ratios were determined by the Kelen-Tüdos equation, which like other differential methods, is obviously suitable for low-conversion data (<10 wt%). The K-T procedure, in brief, is applied as follow:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$$

where

$$\eta = \frac{G}{\alpha + F};\ \xi = \frac{F}{\alpha + F};\ G = \frac{X(Y-1)}{Y};\ F = \frac{X^2}{Y};\ X = \frac{M_1}{M_2};\ Y = \frac{m_1}{m_2}$$

M_1 and M_2 are the molar concentrations in the monomer feed; m_1 and m_2 are the molar concentrations in the final copolymer.

$$\alpha = \sqrt{F_m \times F_M}$$

is an appropriately chosen constant to obtain a uniform spread of the data ($\alpha > 0$). F_m and F_M are the lowest and highest values from experimental data. Thus, by plotting the η values calculated from experimental data against ξ, a straight line is obtained, when extrapolated to $\xi = 0$ and $\xi = 1$, it gives $-r_2/\alpha$, and r_1 (both as intercepts). The monomer 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 $r_2 = 0.032$ in chloroform, $r_1 = 0$ and $r_2 = 0.065$ in benzene, and $r_1 = 0$ and $r_2 = 0.14$ in dioxane. These results indicated that the alternating tendency was influenced by the solvent and a higher alternating copolymer was obtained in chloroform than in dioxane or in benzene, and that the sequence of successive CHMI units must exist in the polymers.

Table 2
Monomer reactivity ratios for radical copolymerization of CH (M_1) and CHMI (M_2) in several solvents at 55°C

Solvents	r_1	r_2
Benzene	0	0.065
Chloroform	0	0.032
Dioxane	0	0.14

Solvent Effects

The experimental results suggested that the chain propagation manner influenced by the solvent in the copolymerization of CH and CHMI. Figure 5 presented the relationships between the polymer yield and the reaction time in different solvents. Solvent dependence on R_p was observed in this copolymerization system, i.e., the R_p value in dioxane was higher than that in benzene and in chloroform (Figures 3 and 5). Elsabee et al. reported a similar solvent effect on R_p in the copolymerization of N-(2-chlorophenyl)maleimide with styrene (1). However, in contrast with these results, T. Doi et al. (6) reported a higher R_p value in chloroform than that in dioxane in the copolymerization of N-alkylmaleimides or N-(alkyl-substituted phenyl)maleimides (RMI) with isobutene, which is explained by the mutual interaction between the RMI propagating radical and the solvent, i.e., the addition of electron-accepting RMI radical to isobutene is suppressed

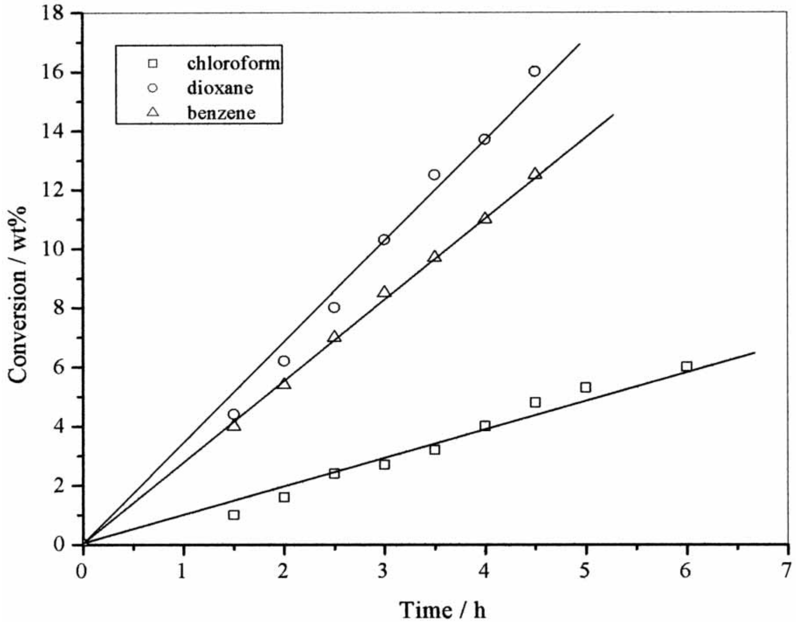

Figure 5. Relationships between reaction time and polymer yield for radical copolymerization of CH with CHMI in several solvents at 55°C, $f_1 = 0.50$, $[CH] + [CHMI] = 1.00\,mol/L$, $[AIBN] = 1.0 \times 10^{-2}\,mol/L$.

in the electron-donating dioxane, resulting in a decrease in the rate constant for cross-propagation (k_{21}) in dioxane compared to the electron-accepting chloroform.

The solvent effect observed in the variation of the R_p values for the copolymerization in this work can be interpreted by the terms of the donor-acceptor interaction (1, 15). The CHMI is an electron-deficient monomer, which acts as a typical electron-acceptor. Therefore, the acceptor-donor interaction between the CHMI and the solvent molecules as electron-donor would be important. Undoubtedly, dioxane has greater donicity than benzene and chloroform, e.g., the donicity numbers are determined to be 15, 10 and 0 for dioxane, benzene and chloroform, respectively (16). During the copolymerization of CH with CHMI, the solvent molecules act as donor and interact strongly with the CHMI growing radicals, rendering the radicals more reactive in dioxane than in benzene and chloroform (1). Further evidence may be observed in the radical terpolymerization of allylglycidyl ether (AGE), maleic anhydride (MA) and methyl methacrylate (MMA) (15), in which the complexated MA formed by strong acceptor-donor interaction between MA and AGE has activity higher than free MA in copolymerization with MMA. The slightly low R_p in benzene may be attributed to the slightly low donor-acceptor interacts between benzene molecules and CHMI growing radicals. On the other hand, chloroform hardly interacts with CHMI because of its weak donicity. Therefore, there is no enhancement in the reactivity of CHMI radicals in the copolymerization system.

The solvent effect in the copolymerization of CH and CHMI 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 and dioxane, respectively. These results are similar to the results of copolymerization of N-alkylmaleimides with isobutene reported by T. Doi (6). The fact that the alternating tendency for copolymerization of CH with CHMI in chloroform was greater than those in benzene or dioxane may be interpreted by the increase of k_{12} and k_{21} relative to the k_{11} and k_{22} in polar solvent (note that $k_{11} = 0$, due to the lack of homopolymerizability of CH).

Conclusions

The free radical copolymerization of CH with CHMI showed a stronger tendency toward alternation in chloroform than that in benzene or in dioxane. The monomer reactivity ratios were determined to be $r_1 = 0$, $r_2 = 0.032$ in chloroform, $r_1 = 0$, $r_2 = 0.065$ in benzene and $r_1 = 0$, $r_2 = 0.14$ in dioxane. These results are explained by the increase of k_{12} and k_{21} relative to the k_{11} and k_{22} in polar solvent. The initial rates of copolymerization of CHMI and CH (R_p) are dependent on the comonomer composition and the solvents that used. The copolymerization rate in dioxane is higher than that in chloroform and in benzene. In addition, the copolymer of CHMI and CH is characterized by ^{1}H-NMR spectrum.

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