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An ESR Study on the Radical Copolymerization of *N*-Cyclohexylmaleimide and Di-*n*-butyl Itaconate in Benzene

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ABSTRACT: The copolymerization of *N*-cyclohexylmaleimide (CHMIm) (M_1) and di-*n*-butyl itaconate (DBI) (M_2) with dimethyl azobis(isobutyrate) was investigated kinetically and by ESR spectroscopy at 50 °C in benzene. Monomer reactivity ratios of $r_1 = 0.21 \pm 0.04$ and $r_2 = 0.34 \pm 0.04$ were obtained according to the Kelen–Tüdős method. The copolymerization rate (R_p) and molecular weight of the resulting copolymer increased with increasing CHMIm concentration when the total monomer concentration was fixed at 1 mol L^{-1}. The copolymerization system was found to involve ESR-observable propagating polymer radicals, the ESR spectrum of which is inexplicable in terms of any overlapping of the spectra of poly(CHMIm) and poly(DBI) radicals observed in the corresponding homopolymerization systems. This indicates that some penultimate monomer unit causes a change in the ESR spectrum, that is, the structure of the propagating radical center. The apparent rate constants of propagation (k_p) and termination (k_t) were estimated by using the total polymer radical concentration by ESR, R_p, and the initiation rate separately measured. The k_p (4.7–55 L mol^{-1} s^{-1}), which increased with the CHMim concentration, showed considerably lower values in the CHMIm-rich concentration range than those calculated based on the terminal model, affording another piece of evidence for a penultimate effect. The k_t ($5\text{–}47 \times 10^3$ L mol^{-1} s^{-1}), which decreased with the CHMIm concentration, showed a sudden depression near [CHMIm]/[DBI] = 1, suggesting a significant change in the conformation of the propagating polymer chain.

Introduction

Itaconate esters, α,α-disubstituted monomers, and maleimide derivatives, α,β-disubstituted monomers, are well-known to show a high homopolymerizability in the usual radical polymerization in spite of their two bulky substitutuents.[1-5]

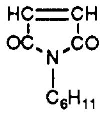
Recently we have found that the propagating polymer radicals are stable enough to be ESR-observable even at temperatures as high as 50–80 °C in the radical polymerization of *N*-cyclohexylmaleimide (CHMIm)[6] and some itaconate monomers[7,8] and reported kinetic and ESR studies on their radical polymerization.

On the other hand, recent reexamination of radical copolymerization kinetics by Fukuda et al.[9,10] shows that the rate of copolymerization is as yet not comprehensively understood in terms of the elementary processes of propagation and termination. Measurements of rate constants of propagation (k_p) and termination (k_t) by using the rotating sector method reveal that any abnormal effects in copolymerization kinetics are related to the propagation and not to the termination reaction. The copolymerization results by O'Driscoll et al. using a pulsed laser technique also led to the same conclusion.[11,12]

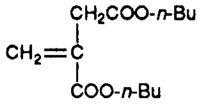
The copolymerization system of CHMIm and di-*n*-butyl itaconate (DBI) is also expected to involve ESR-observable propagation polymer radicals under the actual copolymerization conditions, since the termination reactions are diffusion-controlled. So, it is possible for this copolymerization system to afford a powerful tool for elucidating the radical copolymerization mechanisms. The present article describes kinetic and ESR results on the copolymerization of CHMIm and DBI with dimethyl azobis(isobutyrate) (MAIB).

Experimental Section

MAIB was purified by recrystallization from petroleum ether. Commercially available DBI was shaken several times with an aqueous NaOH solution, dried over sodium sulfate, and distilled. CHMIm (supplied by Nippon Oil & Fats Co.) was recrystallized from a water–methanol mixture and then once more from methanol. Benzene was used after the usual purification.

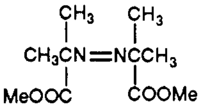


CHMIm



$CH_2{=}C(CH_2COO\text{-}n\text{-}Bu)(COO\text{-}n\text{-}Bu)$

DBI



$CH_3C(CH_3)(COOMe){-}N{=}N{-}C(CH_3)(COOMe)CH_3$

MAIB

Copolymerization of CHMIm and DBI was performed in a degassed and sealed tube with shaking. The resulting copolymer was isolated by pouring the polymerization mixture into a large excess of methanol.

The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the copolymer were determined by gel permeation chromatography (GPC) by using polystyrene standards. GPC was recorded by a TOSO-HLC 802A at 38 °C, with tetrahydrofuran as the carrier. An ESR spectrum of the copolymerization mixture in a degassed and sealed ESR tube was recorded with a JEOL-JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a TE mode cavity.

Results and Discussion

Copolymerization of CHMIm and DBI. The copolymerization of CHMIm (M_1) and DBI (M_2) with MAIB was conducted at 50 °C in benzene. The results obtained are presented in Table I. The composition of the copolymers was estimated from the nitrogen content by elemental analysis. Figure 1 shows the Kelen–Tüdős plot[13] for the copolymerization results. From the plot, the monomer reactivity ratios were determined as $r_1 = 0.21 \pm 0.04$ and $r_2 = 0.34 \pm 0.04$.

The time–conversion curves were made at various relative monomer concentrations, fixing the total monomer concentration of 1 mol L^{-1} (Figure 2). The copolymerization rate (R_p) was evaluated by using the time–conversion curves and the copolymer composition. Table II sum-

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Table I
Copolymerization of CHMIm (M_1) and DBI (M_2) with MAIB at 50 °C in Benzene

$[M_1]$ in the feed, mol %	yield, %	nitrogen content, %	$[M_1]$ in the copolymer, mol %
12.5	6.8	1.46	23.7
25.0	8.9	2.35	36.7
37.5	8.4	2.66	41.1
50.0	6.2	2.98	45.4
62.5	6.5	3.39	50.8
75.0	3.1	4.24	61.6
87.5	3.8	5.10	71.7

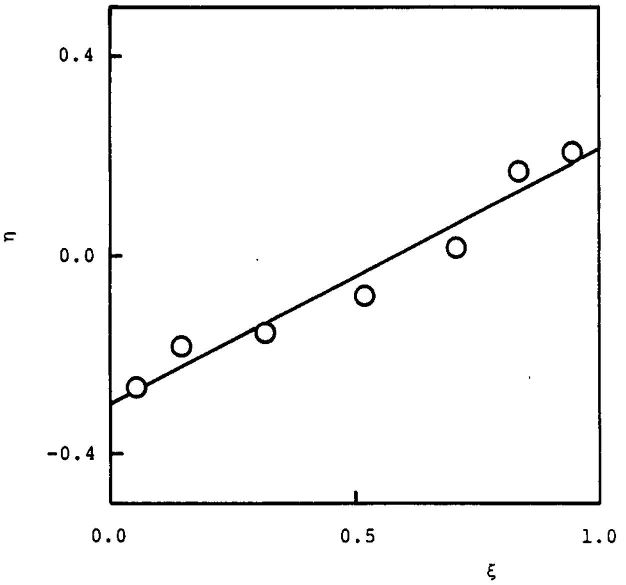


Figure 1. Kelen–Tüdös plot for the copolymerization of CHMIm (M_1) and DBI (M_2) at 50 °C in benzene.

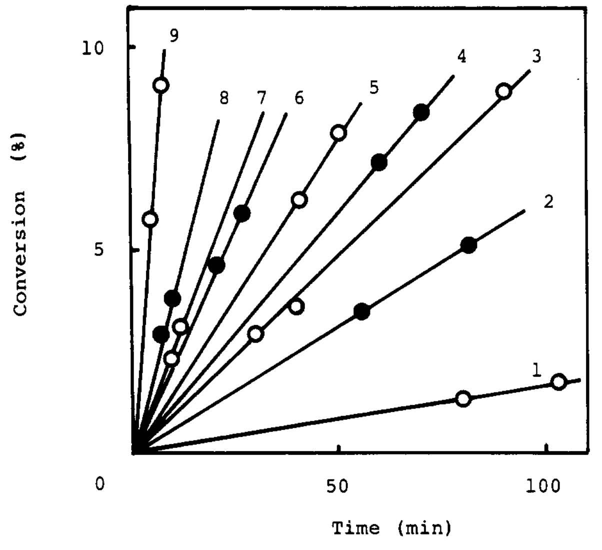


Figure 2. Time–conversion curves for the copolymerization of CHMIm and DBI with MAIB at 50 °C in benzene: [MAIB] = 5.00×10^{-2} mol L^{-1}; [CHMIm] + [DBI] = 1.00 mol L^{-1}. [CHMIm] × 10 (mol L^{-1}): (1) 0.0, (2) 1.26, (3) 2.53, (4) 3.79, (5) 4.96, (6) 6.32, (7) 7.58, (8) 8.85, (9) 10.0.

marizes the R_p's and the molecular weights of the resulting copolymers. Thus, R_p and $\bar{M}_n$ increase with increasing CHMIm concentration.

ESR Study on the Copolymerization System. As expected, the copolymerization system of CHMIm and DBI was also found to involve ESR-observable propagating polymer radicals under the practical polymerization conditions.

Table II
Copolymerization Rate (R_p) and Molecular Weight of Copolymer in the Copolymerization of CHMIm and DBI with MAIB at 50 °C in Benzene[a]

10[CHMIm], mol L^{-1}	$10^6 R_p$, mol L^{-1} s^{-1}	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	5.6	1.85	2.45	1.3
1.26	10.9	2.69	4.91	1.8
2.53	17.3	3.13	5.35	1.7
3.79	21.0	3.48	6.16	1.8
4.96	26.6	3.75	6.95	1.9
6.32	37.1	4.13	7.60	1.8
7.58	42.0	4.25	7.42	1.7
8.85	66.6	4.97	9.63	1.9
10	226			

[a] [MAIB] = 3.00×10^{-2} mol L^{-1}; [CHMIm] + [DBI] = 1.00 mol L^{-1}.

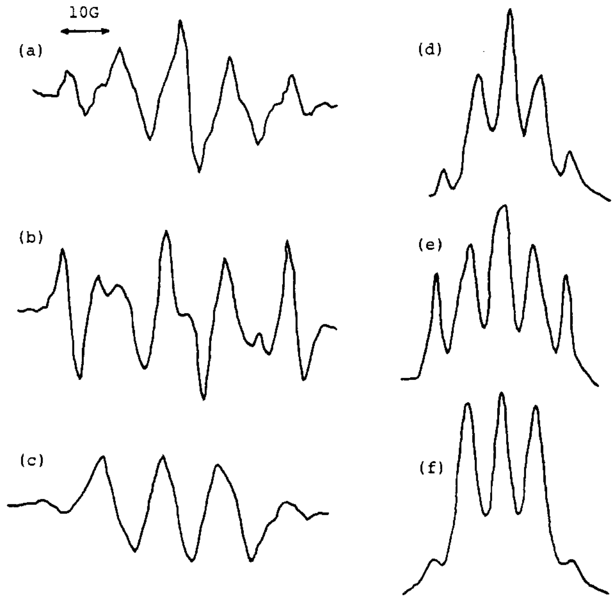
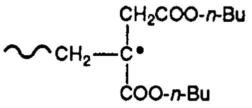


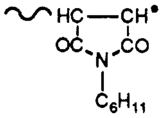
Figure 3. First derivative (a–c) and absorption (d–f) ESR spectra observed at 50 °C in the DBI/MAIB (a, d), CHMIm/DBI ([CHMIm]/[DBI] = 1 (b, e), and CHMIm/MAIB (c, f) systems.

Figure 3b shows a typical ESR spectrum of the copolymerization system observed at [CHMIm] = [DBI] = 0.50 mol/L. For comparison, the spectra of propagating radicals I (a) and II (c) observed in each homopolymerization system are also presented in Figure 3.



$$\sim CH_2-\overset{CH_2COO\text{-}n\text{-}Bu}{\underset{COO\text{-}n\text{-}Bu}{C}}\cdot$$

I



II

As can be seen from the figure, spectrum b has much stronger peaks at both sides compared to spectra a and c and hence is inexplicable in terms of any overlapping of spectra a and c. Such situations are clearer in comparison of the corresponding absorption spectra d–f, which were obtained by computer integration of spectra a–c. This indicates that some penultimate unit causes a change in the ESR spectrum, that is, the structure of the propagating radical center.

With use of the ESR spectra of copolymerization systems, the total concentration ([P•]) of propagating polymer radicals was determined at 50 °C, where the 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO), a stable radical, in the same medium was used as standard. The values thus determined are expected to have an error less than 25%. As shown in Table III, the total concen-

Table III
Propagating Polymer Radical Concentration ([P•]) and Apparent Rate Constants of Propagation (k_p) and Termination (k_t) in the Copolymerization of CHMIm and DBI with MAIB at 50 °C in Benzene[a]

10[CHMIm], mol L^{-1}	10^6[P•], mol L^{-1}	k_p, L mol^{-1} s^{-1}	10$^{-4}k_t$, L mol^{-1} s^{-1}
0	1.2	4.7	4.7
1.26	1.3	8.4	4.2
2.53	1.4	12.4	3.7
3.79	1.4	15.0	3.8
4.96	2.2	12.1	1.6
6.32	2.9	12.7	0.95
7.58	3.2	13.1	0.81
8.85	3.2	20.8	0.82
10	4.1	55.1	0.51

[a] [MAIB] = 3.00 × 10^{-2} mol L^{-1}, [CHMIm] + [DBI] = 1.00 mol L^{-1}.

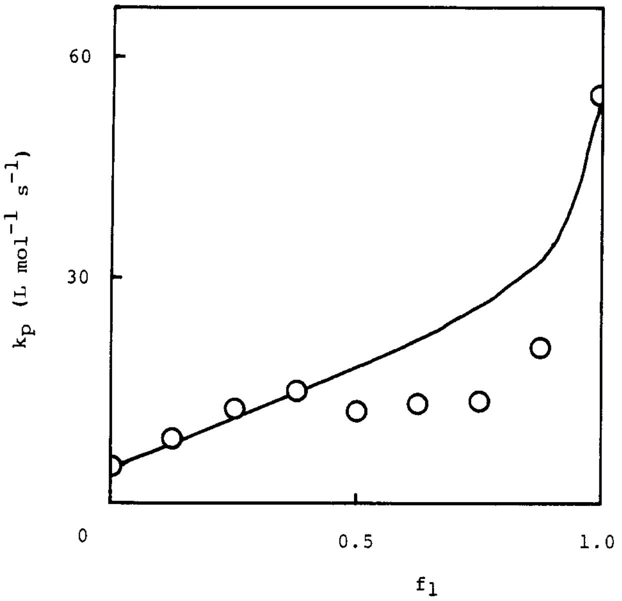


Figure 4. Plot of k_p vs f_1 ([CHMIm]/([CHMIm] + [DBI])) for the copolymerization of CHMIm and DBI. The circles are observed values, and the solid line represents the Mayo–Lewis model prediction.

tration of propagating radicals has a tendency to increase with increasing CHMIm concentration.

Determination of the Apparent Rate Constant of Propagation in the Copolymerization. Independently of termination, we could estimate the apparent rate constant (k_p) of propagation in the copolymerization according to eq 1, using R_p (Table II) and [P•] (Table III),

$$R_p = k_p[P^{\bullet}][M] \qquad (1)$$

where [M] = [CHMIm] + [DBI]. The k_p values determined at 50 °C are also shown in Table III. Thus the apparent rate constant of propagation for the copolymerization increases with the CHMIm concentration.

Figure 4 shows the relationship between k_p and the monomer feed composition (f_1 = [CHMIm]/([CHMIm] + [DBI])).

On the other hand, the apparent propagation rate constant of copolymerization is calculated by using eq 2 based on the Mayo–Lewis model,[9] where k_{11} is the rate

$$k_p = (r_1f_1 + 2f_1f_2 + r_2f_2)/(r_1f_1/k_{11} + r_2f_2/k_{22}) \qquad (2)$$

constant of the reaction of radical II with CHMIm, namely k_p of CHMIm, and k_{22} is that of the reaction of radical I with DBI, namely, k_p of DBI. The calculated k_p values are also plotted in Figure 4. As seen from the figure, the observed k_p values are much lower than the calculated ones in the higher CHMIm concentration range. Such deviations are attributed to the penultimate effect,[9] which suppresses the reactivity of the CHMIm radical (II). Such a large decrease in the reactivity of the CHMIm radical by the penultimate DBI unit is ascribable to the steric effect due to two bulky *n*-butoxycarbonyl groups of DBI. To clarify this point, the study on copolymerization of CHMIm and bis(2-ethylhexyl) itaconate is in progress.

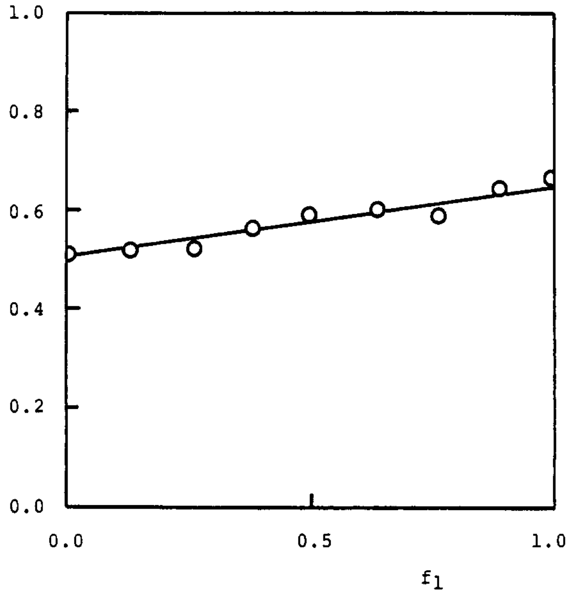


Figure 5. Relationship between initiator efficiency (f) and f_1 ([CHMIm]/([CHMIm] + [DBI])) in the copolymerization of CHMIm and DBI with MAIB at 50 °C in benzene.

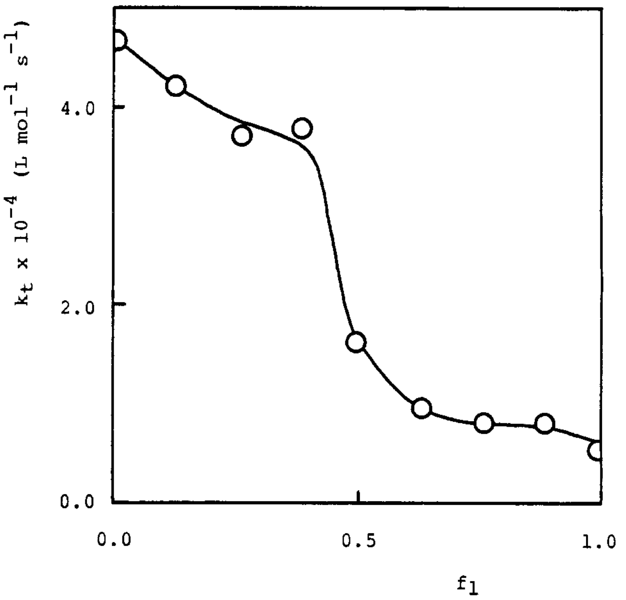


Figure 6. Plot k_t vs f_1 ([CHMIm]/([CHMIm] + [DBI])) for the copolymerization of CHMIm and DBI at 50 °C in benzene.

Determination of the Apparent Rate Constant of Termination in the Copolymerization. In order to estimate the apparent rate constant (k_t) of termination in the copolymerization, we have determined the initiator efficiency (f) of MAIB in the copolymerization system at 50 °C in the following manner.

MAIB (1.00 × 10^{-2} mol L^{-1}) was allowed to decompose at 50 °C in a benzene solution containing CHMIm, DBI, and TEMPO (2.20 × 10^{-4} mol L^{-1}). MAIB decomposes into 2-(methoxycarbonyl)propyl radicals and nitrogen.

Some of the primary radicals are deactivated by the cage reactions. The others diffuse through the solvent cage to react with TEMPO. So, the f value could be estimated from the disappearance rate of TEMPO by ESR, where the rate constant of $k_d = 2.22 \times 10^{-6}\ \text{s}^{-1}$ was used for the decomposition of MAIB at 50 °C.[14] The results obtained are shown in Figure 5. The f value exhibits a tendency to decrease with the DBI concentration, probably because of the high viscosity of DBI.

According to eq 3, the k_t value at each monomer feed composition was evaluated by using the propagating polymer radical concentration ([P•]) and the initiator efficiency (f) calculated from the straight line in Figure 5. Table III also compiles the k_t values of 5.1×10^3 –$4.7 \times 10^4\ \text{mol}^{-1}\ \text{s}^{-1}$. Figure 6 shows the plot of k_t vs the monomer feed composition (f_1). Thus k_t shows a precipitous depression near $f_1 = 0.5$. This might reflect a significant change in the conformation of the propagating polymer chain, since the termination reaction is diffusion-controlled.

$$2fk_d[\text{MAIB}] = k_t[\text{P}^\bullet]^2 \qquad (3)$$

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