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# Kinetic and Electron Spin Resonance Studies on the Radical Polymerization of *N*-Cyclohexylmaleimide in Benzene

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ABSTRACT: The polymerization of *N*-cyclohexylmaleimide (CHMIm) with azobis(isobutyronitrile) (AIBN) was investigated kinetically and ESR spectroscopically in benzene at 40–60 °C. The polymerization rate ($R_p$) at 50 °C was expressed by $R_p = k[\mathrm{AIBN}]^{0.8}[\mathrm{CHMIm}]^{1.2-2.3}$. Thus, no definite relationship was observed between $R_p$ and [CHMIm]. The dependence of $R_p$ on [CHMIm] increased with increasing monomer concentration. A somewhat higher overall activation energy of 23.1 kcal mol$^{-1}$ was obtained for the polymerization. Propagating poly(CHMIm) radical was found to be stable enough to be observable by ESR under the actual polymerization conditions. By using the propagating polymer radical concentration by ESR, $R_p$, and the initiation rate separately measured, the rate constants of propagation ($k_p$) and termination ($k_t$) were determined. The $k_p$ value was 4.3–5.8 × 10 L mol$^{-1}$ s$^{-1}$ at 50 °C. The $k_t$ value of 3.1–10 × 10$^4$ L mol$^{-1}$ s$^{-1}$ at 50 °C was significantly dependent on the concentrations of initiator and monomer. Such dependence of $k_t$ is responsible for the unusual kinetics observed above. The activation energies of propagation and termination were estimated to be 9.8 and 4.8 kcal mol$^{-1}$, respectively, from the values of $k_p$ and $k_t$ obtained at 40, 50, and 60 °C. The high activation energy of propagation caused the high overall activation energy of the polymerization.

## Introduction

Crotonate esters and α-methylstyrene are well-known to show no homopolymerizability in the usual radical polymerization, while the anionic polymerization of the former and the cationic one of the latter proceed smoothly. This has been explained in terms of much more significant steric effect in the radical polymerization compared to the ionic ones.[1] However, recently some sterically crowded monomers such as fumarate[2-4] and itaconate esters[5,6] were found to be radically hompolymerized at moderate rates to high polymers, where unusual kinetic behaviors were observed. It is noteworthy that the homogeneous polymerization systems of these monomers contained ESR-observable propagating polymer radicals even at temperatures as high as 50–80 °C.

Maleimide derivatives, 1,2-disubstituted ethylene, were also reported to have high homopolymerizabilities in the radical polymerization. A kinetic study on the radical polymerization of N-substituted maleimides in tetrahydrofuran (THF) revealed that they similarly showed unusual polymerization behaviors.[7]

More recently, we have found that the propagating polymer radical of *N*-cyclohexylmaleimide (CHMIm) in benzene is stable enough to be observable by ESR under the actual polymerization conditions. This article describes the results of the kinetic and ESR studies on the polymerization of CHMIm with azobis(isobutyronitrile) (AIBN) in benzene.

## Experimental Section

CHMIm was recrystallized from a water–methanol mixture, and then once more from methanol. AIBN was purified by recrystallization from methanol. Benzene was used after conventional purification.

Polymerization of CHMIm with AIBN was carried out in a degassed and sealed glass tube. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of methanol.

The ESR spectrum of the polymerization 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

**Kinetic Study on the Polymerization of CHMIm with AIBN in Benzene.** The polymerization of CHMIm with AIBN was investigated kinetically in benzene, where the polymerization appeared to proceed homogeneously.

Figure 1 shows the time–conversion curves in the temperature range from 40 to 60 °C, where the concentrations of AIBN and CHMIm were 5.00 × 10$^{-3}$ and 5.59 × 10$^{-1}$ mol L$^{-1}$, respectively. The Arrhenius plot of the polymerization rate ($R_p$) determined from Figure 1 is shown in Figure 2. The slope of the plot allowed the overall activation energy of 23.1 kcal mol$^{-1}$ to be calculated for the polymerization. This value is consideralby higher than those (ca. 20 kcal mol$^{-1}$) reported for the polymerizations of methyl methacrylate (MMA) and styrene (St) with AIBN.[8]

Figure 3 shows the relationship between $R_p$ and the AIBN concentration at 50 °C, where the concentration of CHMIm was 5.59 × 10$^{-1}$ mol L$^{-1}$. $R_p$ increased in proportion to the 0.8th order of the initiator concentration. Similar higher dependence of $R_p$ on the initiator concentration was also reported for AIBN-initiated polymerizations in THF of some N-substituted maleimides including CHMIm.[7]

Figure 4 shows the dependence of $R_p$ on the monomer concentration at 50 °C, where the AIBN concentration was kept constant at 1.00 × 10$^{-2}$ mol L$^{-1}$. Thus, no definite relationship was observed between $R_p$ and the monomer concentration. The effect of the monomer concentration on $R_p$ increased with increasing monomer concentration. At higher CHMIm concentrations, $R_p$ was proportional to the 2.3th order of the monomer concentration. Nearly the same order was also reported for the polymerization of CHMIm in THF.[7]

Thus, the polymerization of CHMIm with AIBN in benzene was found to give apparently unusual kinetics as follows:

$$R_p = k[\mathrm{AIBN}]^{0.8}[\mathrm{CHMIm}]^{1.2-2.3} \quad (1)$$

**Determination of the Initiator Efficiency.** AIBN decomposes into cyanopropyl radicals and nitrogen (eq 2). Some of the primary radicals are deactivated by the cage

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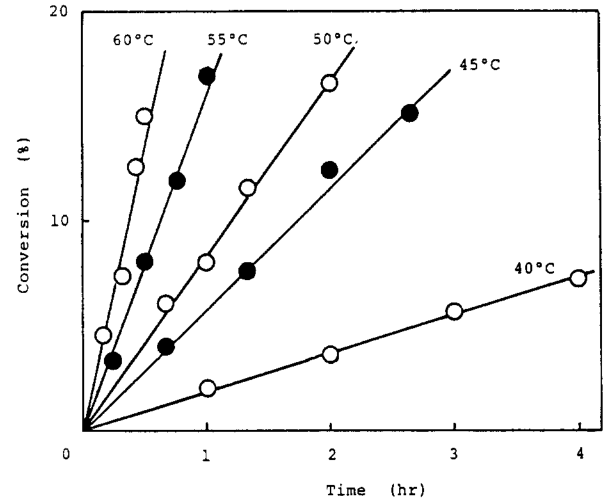


**Figure 1.** Time-conversion curves in the polymerization of CHMIm with AIBN in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol L$^{-1}$; [AIBN] = $5.00 \times 10^{-3}$ mol L$^{-1}$.

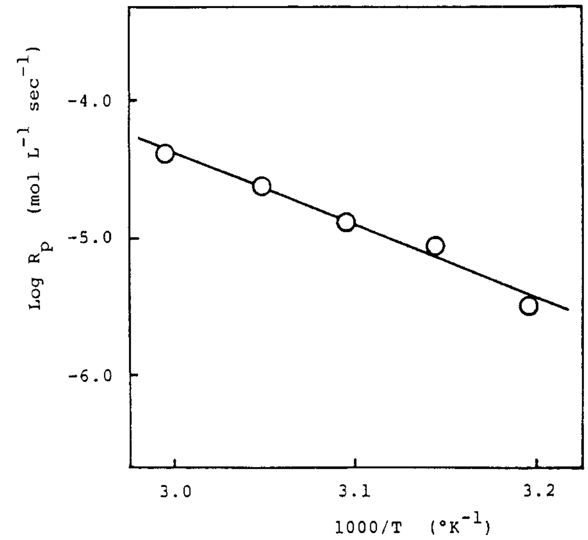


**Figure 2.** Temperature effect on the polymerization rate ($R_p$): [CHMIm] = $5.59 \times 10^{-1}$ mol L$^{-1}$; [AIBN] = $5.00 \times 10^{-3}$ mol L$^{-1}$.

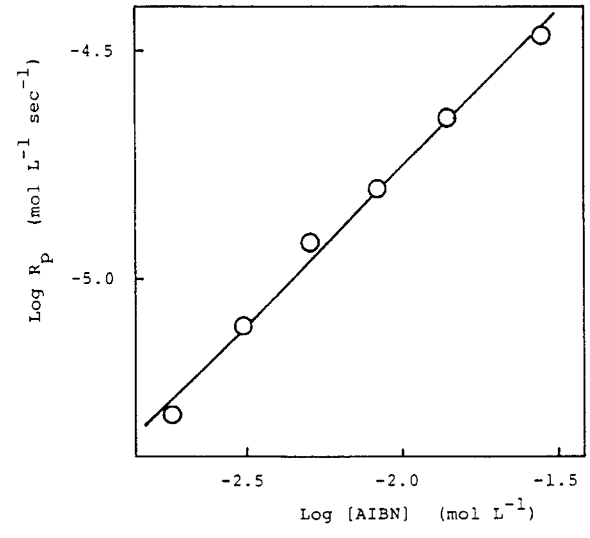


**Figure 3.** Effect of the AIBN concentration on the polymerization rate ($R_p$) at 50 °C in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol L$^{-1}$.

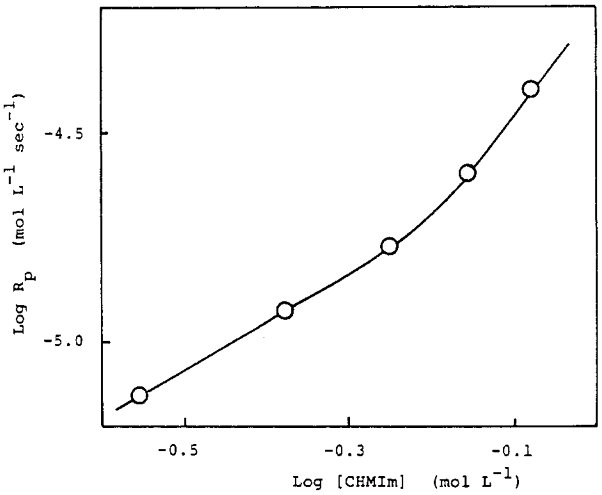


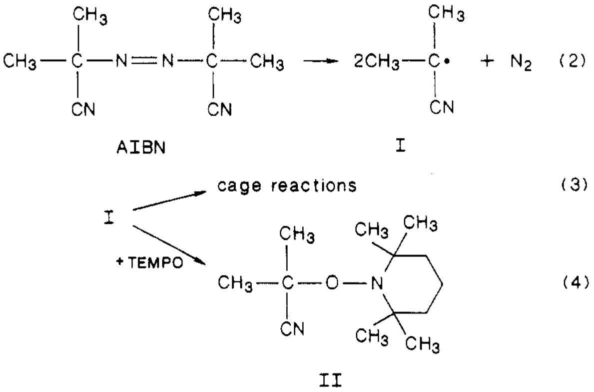
**Figure 4.** Effect of the CHMIm concentration on the polymerization rate ($R_p$) at 50 °C in benzene: [AIBN] = $1.00 \times 10^{-2}$ mol L$^{-1}$.

**Table I**
**Rate of Disappearance ($R_t$) of TEMPO on Decomposition of AIBN[a] and Initiator Efficiency ($f$)**

| temp, °C | 10[CHMIm], mol L$^{-1}$ | $10^8R_t$, mol L$^{-1}$ s$^{-1}$ | $10^8R_d$,[b] mol L$^{-1}$ s$^{-1}$ | $f$[c] |
|---|---|---|---|---|
| 50 | 2.79 | 2.5 | 2.2 | 0.56 |
| 50 | 5.59 | 2.4 | 2.2 | 0.55 |
| 50 | 8.80 | 2.5 | 2.2 | 0.57 |
| 40 | 5.59 | 0.49 | 0.48 | 0.52 |
| 60 | 5.59 | 11 | 9.4 | 0.58 |

[a] [AIBN] = $1.00 \times 10^{-2}$ mol L$^{-1}$, [TEMPO] = $2.14 \times 10^{-4}$ mol L$^{-1}$. [b] $R_d$ (decomposition rate of AIBN) was calculated by using $k_d$(s$^{-1}$) = $1.58 \times 10^{15}$ exp(−30.8(kcal)/$RT$). [c] $f = R_t/2R_d$.

reactions (eq 3). The others diffuse through the solvent cage to react with the monomer, leading to the polymerization. When 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO), a stable radical, is present in the polymerization system, the cage-escaping primary radicals are trapped by TEMPO to yield a coupling product (II) (eq 4). ESR determination of the rate of TEMPO disappearance allowed the initiator efficiency ($f$) to be calculated.



$$(CH_3)_2C(CN)\text{—}N{=}N\text{—}C(CN)(CH_3)_2 \longrightarrow 2CH_3\text{—}\dot{C}(CH_3)(CN) + N_2 \quad (2)$$

Figure 5 shows typical plots of the TEMPO concentration against time observed in the polymerization of CHMIm with AIBN in benzene at 40 and 50 °C, where the concentrations of CHMIm and AIBN were $5.59 \times 10^{-1}$ and $1.00 \times 10^{-2}$ mol L$^{-1}$, respectively. From the slopes of the plots, the rates ($R_t$) of TEMPO disappearance were estimated and are summarized in Table I, along with the decomposition rates ($R_d$) of AIBN calculated by using the following rate constant equation:[9]

$$k_d(\mathrm{s}^{-1}) = 1.58 \times 10^{15} \exp(-30.8(\mathrm{kcal})/RT) \quad (5)$$

Table I also comprises the $f$ values estimated from $R_t$ and

**Table II**
**Propagating Polymer Radical Concentration ([P•]) and Propagation Rate ($k_p$) and Termination Rate ($k_t$) Constants in the Polymerization of CHMIm with AIBN in Benzene**

| | temp, °C | $10^2$[AIBN], mol L$^{-1}$ | 10[CHMIm], mol L$^{-1}$ | $10^6$[P•], mol L$^{-1}$ | $10^{-1}k_p$, L mol$^{-1}$ s$^{-1}$ | $10^{-4}k_t$, L mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 50 | 0.833 | 5.59 | 0.5 | 5.4 | 8.3 |
| 2 | 50 | 1.00 | 5.59 | 0.6 | 5.1 | 6.9 |
| 3 | 50 | 1.39 | 5.59 | 0.8 | 4.9 | 5.4 |
| 4 | 50 | 2.78 | 5.59 | 1.4 | 4.3 | 3.6 |
| 5 | 50 | 1.00 | 2.79 | 0.5 | 5.8 | 10 |
| 6 | 50 | 1.00 | 6.98 | 0.7 | 5.5 | 6.9 |
| 7 | 50 | 1.00 | 8.40 | 0.9 | 5.4 | 3.1 |
| 8 | 40 | 1.00 | 5.59 | 0.3 | 2.8 | 5.5 |
| 9 | 60 | 1.00 | 5.59 | 1.1 | 6.5 | 9.0 |

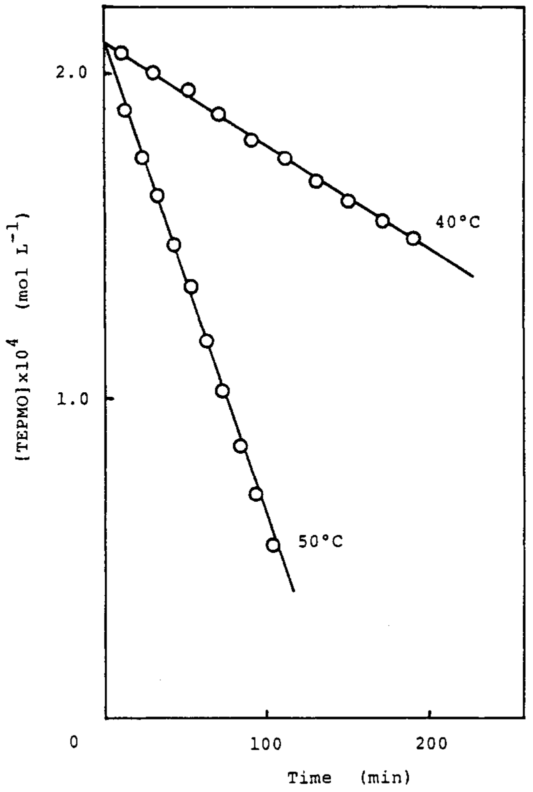
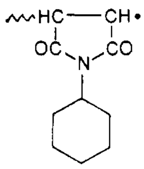


**Figure 5.** Relationship between time and the TEMPO concentration during the polymerization of CHMIm with AIBN at 40 and 50 °C in benzene: [CHMIm] = 5.59 × 10$^{-1}$ mol L$^{-1}$; [AIBN] = 1.00 × 10$^{-2}$ mol L$^{-1}$.

$R_d$. Thus the $f$ value is almost independent of the monomer concentration used here and shows a reasonable trend of increasing slightly with increasing temperature.

**ESR Study on the Polymerization of CHMIm with AIBN in Benzene.** Figure 6 shows ESR spectra observed in the polymerization of CHMIm with AIBN in benzene at 40, 50, and 60 °C, where the concentrations of CHMIm and AIBN were 5.59 × 10$^{-1}$ and 1.00 × 10$^{-2}$ mol L$^{-1}$. The broad three-line spectrum is assignable to the propagating polymer radical (III) of CHMIm. Greater spectrum intensity observed at higher temperatures stems from promoted decomposition of AIBN at higher temperatures. After several minutes, the intensity of each spectrum was almost unchanged at least for 2 h, indicating that a stationary state was reached for the propagating poly(CHMIm) radical. It is worth noting that the propagating polymer radical of CHMIm of the stationary state, thus, is stable enough to be observable by ESR in the homogeneous polymerization system even in the high temperature range from 40 to 60 °C.



III

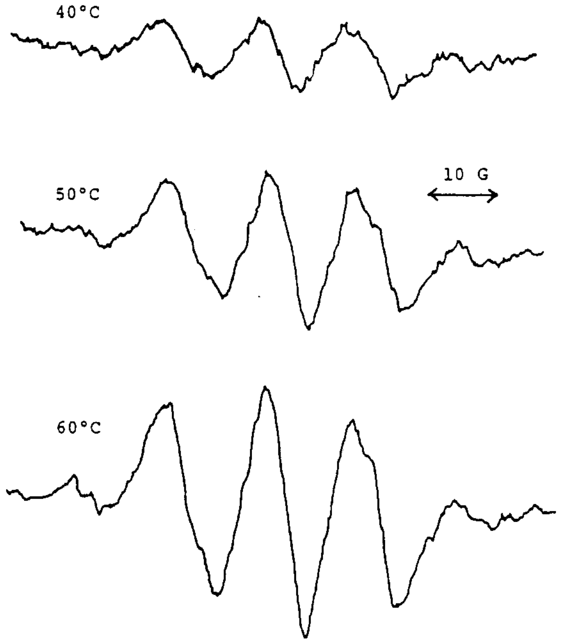


**Figure 6.** ESR spectral change with temperature observed in the polymerization of CHMIm with AIBN in benzene: [CHMIm] = 5.59 × 10$^{-1}$ mol L$^{-1}$; [AIBN] = 1.00 × 10$^{-2}$ mol L$^{-1}$.

The concentration of poly(CHMIm) radical under various polymerization conditions was determined by computer integration of the observed first-derivative ESR spectrum, where TEMPO in the same media was used as standard. The results obtained are presented in Table II. The polymer radical concentration under the present conditions was in the range 5–15 × 10$^{-7}$ mol L$^{-1}$ at 50 °C and increased with increasing concentrations of both initiator and monomer and also with temperature.

As mentioned above, the present polymerization system contained the propagating poly(CHMIm) radicals of a stationary state. In order to see whether the polymer radicals undergo bimolecular termination, we have carried out the photopolymerization of CHMIm with di-*tert*-butyl peroxide (DBPO) in benzene, where the stationary state poly(CHMIm) radicals were also observed. Then the decay of the polymer radicals was examined at 40 °C after turning off the light, and the resulting decay curve is shown in Figure 7.

Figure 8 shows the second-order plot of the poly(CHMIm) radical concentration obtained from the decay curve. Thus a straight line was obtained although some

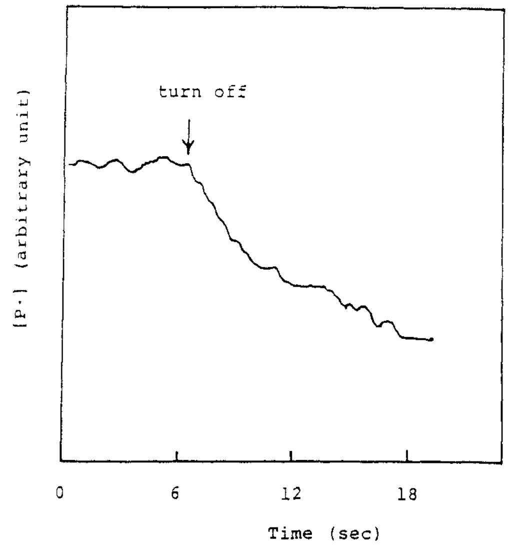


**Figure 7.** Decay curve of poly(CHMIm) radical ($P^{\bullet}$) at 40 °C after turning off the light in the photopolymerization of CHMIm with DBPO in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol $L^{-1}$; [DBPO] = $5.00 \times 10^{-2}$ mol $L^{-1}$.

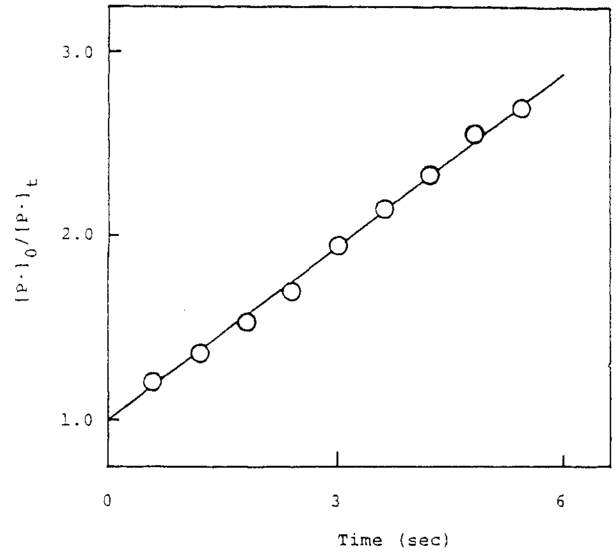


**Figure 8.** Second-order plot of the poly(CHMIm) radical concentration ($[P^{\bullet}]$) at 40 °C after turning off the light.

cross–linking of the resulting polymer was observed during irradiation, indicating bimolecular reaction between the polymer radicals.

In spite of the unusual overall rate equation (1) observed above, these findings reveal that a normal stationary state polymerization proceeds under the definite polymerization conditions.

Using the polymer radical concentration ($[P^{\bullet}]$), $R_p$, and the initiation rate determined above, the rate constants of propagation ($k_p$) and termination ($k_t$) were estimated according to the conventional equations (eq 6 and 7) for

$$R_p = k_p[P^{\bullet}][\text{CHMIm}] \qquad (6)$$

$$2fk_d[\text{AIBN}] = k_t[P^{\bullet}]^2 \qquad (7)$$

the stationary state polymerization. Table II also summarizes the values of $k_p$ and $k_t$. The $k_p$ value is 4.3–5.8 × 10 L $mol^{-1}$ $s^{-1}$ at 50 °C, which is 1 order smaller than that (410 L $mol^{-1}$ $s^{-1}$ at 50 °C)[10] of MMA and 1 order larger than that (5.3–12 L $mol^{-1}$ $s^{-1}$ at 50 °C)[5] of di-*n*-butyl itaconate (DBI). The $k_t$ value of $3.1\text{–}10 \times 10^4$ L $mol^{-1}$ $s^{-1}$ at 50 °C is fairly dependent on the concentrations of initiator and monomer. This value is 3 orders lower than that ($2.4 \times 10^7$ L $mol^{-1}$ $s^{-1}$ at 50 °C)[10] of MMA and similar to that ($5.7\text{–}8.5 \times 10^4$ L $mol^{-1}$ $s^{-1}$ at 50 °C)[5] of DBI.

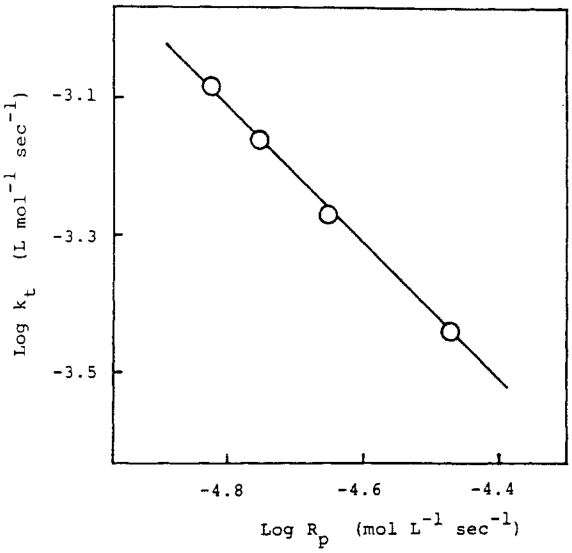


**Figure 9.** Relationship between the polymerization rate ($R_p$) and termination rate constant ($k_t$) in the polymerization of CHMIm with AIBN at 50 °C in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol $L^{-1}$.

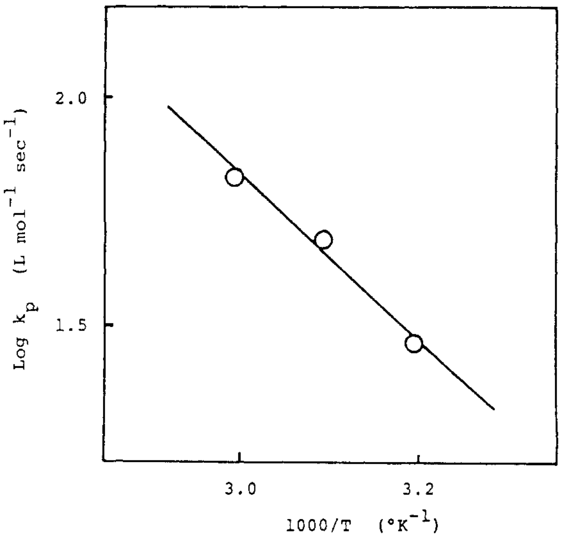


**Figure 10.** Temperature effect on propagation rate constant ($k_p$) in the polymerization of CHMIm with AIBN in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol $L^{-1}$; [AIBN] = $1.00 \times 10^{-2}$ mol $L^{-1}$.

$k_p$ shows a little decrease with increasing AIBN concentration (no. 1–4 in Table II), which is contrary to the higher dependence of $R_p$ on the initiator concentration observed above. On the other hand, $k_t$ decreases considerably with increasing AIBN concentration (no. 1–4). This seems to be mainly responsible for the higher order with respect to the initiator concentration.

As shown in Figure 9, a linear relationship was observed between log $R_p$ and log $k_t$ obtained when the AIBN concentration was varied. This result suggests that the newly formed polymer retards termination. The propagating poly(CHMIm) radicals might tend to associate with the polymers in benzene. This leads the situation in which the propagating polymer radicals are covered with the newly formed polymers to prevent termination. The slight decrease in $k_p$ with increasing AIBN concentration might reflect suppressed access of the monomer to the propa-

**Table III**
**Relative Viscosity ($\eta_{rel}$) of the CHMIm/Benzene System at 50 °C**[a]

| 10[CHMIm], mol $L^{-1}$ | $\eta_{rel}$[b] | 10[CHMIm], mol $L^{-1}$ | $\eta_{rel}$[b] |
|---|---|---|---|
| 0 | 1.00 | 5.59 | 1.11 |
| 2.79 | 1.05 | 6.98 | 1.15 |
| 4.20 | 1.08 | 8.40 | 1.18 |

[a] Determined by using an Ubbelohde viscometer. [b] The viscosity of benzene was taken as unity. The difference in density was neglected.

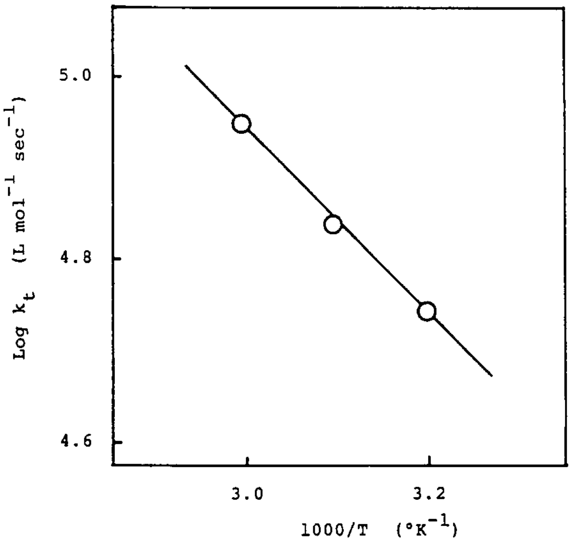


**Figure 11.** Temperature effect on termination rate constant ($k_t$) in the polymerization of CHMIm with AIBN in benzene: [CHMIm] = $5.59 \times 10^{-1}$ mol $L^{-1}$; [AIBN] = $1.00 \times 10^{-2}$ mol $L^{-1}$.

gating center in the associated polymers.[11]

The $k_p$ value is almost independent of the monomer concentration (no. 5, 2, 6, and 7, Table II), although $R_p$ increases with the monomer concentration. Depression of $k_p$ by polymer association might be compensated by increase in $k_p$ due to enhanced association of monomer with the polymer.

The $k_t$ value decreases remarkably with increasing monomer concentration, which is a predominant reason for the high dependence of $R_p$ on the monomer concentration. In addition to enhanced polymer association mentioned above, the increased viscosity of the polymerization system by increased monomer concentration also possibly depresses termination. To examine this, the viscosity of the polymerization system was measured at varied monomer concentrations and is presented in Table III. Thus only a slight change in the viscosity was observed in the range of monomer concentration used. The viscosity effect on $k_t$ due to the monomer, if any, is probably small.

Figures 10 and 11 show the Arrhenius plots for the $k_p$ and $k_t$ values observed at 40, 50, and 60 °C (no. 8, 2, and 9). From the slope of the straight line in Figure 8, the activation energy ($E_p$) for the propagation reaction of CHMIm was calculated to be 9.8 kcal $mol^{-1}$, which is fairly large compared to those of MMA (6.8 kcal $mol^{-1}$)[12] and St (4.3 kcal $mol^{-1}$).[12] This high value causes the high overall activation energy of the polymerization observed above.

The activation energy ($E_t$) for the termination reaction of poly(CHMIm) radical was estimated to be 4.8 kcal $mol^{-1}$. This $E_t$ is somewhat higher compared to those of MMA (2.3 kcal $mol^{-1}$)[12] and St (0.7 kcal $mol^{-1}$).[12]

Substituting the values of $E_p$, $E_t$, and $E_d$ (activation energy of the AIBN decomposition) in the familiar equation (eq 8) for the usual radical polymerization yields the

$$E_a = E_d/2 + E_p - E_t/2 \qquad (8)$$

overall activation energy ($E_a$) of the polymerization. The calculated $E_a$ of 22.8 kcal $mol^{-1}$ is in good agreement with that (23.1 kcal $mol^{-1}$) observed above.

**Registry No.** CHMIm, 1631-25-0; AIBN, 78-67-1.

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