Radical Polymerization of *N*-(2-Alkoxycarbonylphenyl)Maleimides

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RADICAL POLYMERIZATION OF
N-(2-ALKOXYCARBONYLPHENYL)MALEIMIDES

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ABSTRACT

Radical polymerization of N-(2-methoxycarbonylphenyl)maleimide (2MCPhMI), N-(2-ethoxycarbonylphenyl)maleimide (2ECPhMI), and N-(2-n-butoxycarbonylphenyl)maleimide (2BCPhMI) was carried out in benzene at 60°C. The polymerization reactivity was examined as well as the solubility and the thermal properties of the resulting polymers. The effects of the alkyl groups in the 2-substituent on the reactivity and properties were discussed. Furthermore, the polymerization of 2BCPhMI was investigated kinetically in detail. It was revealed that the polymerization rate (R_p) is represented by $R_p = k[2BCPhMI]^{0.84} \cdot [MAIB]^{0.88}$, where MAIB is dimethyl 2,2'-azobis(isobutyrate). The propagation and termination rate constants were determined for these polymerization systems by ESR method. The large reaction order with respect to the initiator concentration was interpreted by the termination rate constant depending on the initiator concentration.

INTRODUCTION

N-Phenylmaleimide (PhMI) and N-(alkyl-substituted phenyl)maleimides polymerize readily in the presence of a radical initiator to give thermally stable polymers [1–5]. In a study of the polymerization of N-(alkyl-substituted phenyl)maleimides, we revealed that the resulting polymers show excellent thermal stabilities,

i.e., high glass transition temperature and decomposition temperatures as well as poly(PhMI), and that the solubility of the polymers depends on the position, number, and structure of the alkyl substituents [1]. For example, polymers with 2-alkyl-substituents in the N-phenyl groups were soluble in many organic solvents including nonpolar solvents. A similar effect of substitution on solubility was also observed for the polymers of N-(ethoxycarbonylphenyl)maleimides [2]. Namely, it was found that the polymer with the 2-ethoxycarbonylphenyl group was soluble in tetrahydro-furan, chloroform, cyclohexanone, dimethylformamide, and o-dichlorobenzene, whereas the 4-substituted polymer was insoluble in these solvents. The polymerization and copolymerization of PhMI bearing some alkoxycarbonyl groups at the 4-position of the N-phenyl ring have been reported by several authors [6–11], but the problem with the solubility of the polymers interfered with detailed studies of the structure and properties of the resulting polymers and the polymerization reactivities.

For the present work we studied the radical polymerization of N-(2-methoxycarbonylphenyl)maleimide (2MCPhMI), N-(2-ethoxycarbonylphenyl)maleimide (2ECPhMI), and N-(2-n-butoxycarbonylphenyl)maleimide (2BCPhMI). The solubility and thermal properties of the resulting polymers were examined, and the effects of the alkyl groups in the 2-substituents are discussed. Furthermore, the polymerization of 2BCPhMI was investigated kinetically in detail using ESR spectroscopy, which has recently been developed as a new method for determining the rate parameters during radical polymerization [12–16].

EXPERIMENTAL

Materials

2RCPhMIs were prepared from maleic anhydride and a corresponding aniline by literature methods (Scheme 1) [17]. The structure of the monomers was checked by NMR spectroscopy. The purity of the monomers was more than 99% by HPLC.
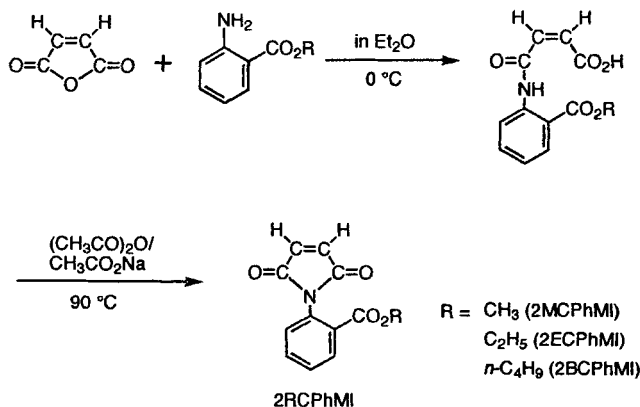
SCHEME 1.

The yield, melting points, and ^{1}H-NMR spectral data of 2RCPhMIs are shown in Table 1.

Dimethyl 2,2'-azobis(isobutyrate) (MAIB) and 2,2'-azobis(2,4,4-trimethylpentane) (ATMP) were recrystallized from ethanol.

Polymerization Procedure

The polymerization of 2RCPhMIs was carried out in the presence of MAIB or ATMP in benzene at 60°C. 2RCPhMI, MAIB, and benzene were placed in a glass ampule. The solution was degassed by the freeze-thaw technique, and then the ampule was sealed in vacuo. After polymerization for a given time, the polymerization mixture was poured into a large amount of methanol to precipitate the resulting polymers. The yield of polymers was determined gravimetrically. The photopolymerization was carried out in an ESR tube in the presence of ATMP as an initiator under UV irradiation with a 500-W xenon lamp at 60°C.

Measurements

The number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) in tetrahydrofuran with standard polystyrene for calibration using the Tosoh 8000 series GPC system. IR and ^{1}H-NMR spectra were recorded on a JASCO-A202 and a Hitachi R-24B (60 MHz) spectrometer, respectively. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed in a nitrogen stream with a scanning rate of 10°C/min by use of a Seiko DSC-200 and TG-200, respectively. ESR spectra were recorded on a Bruker ESP-300 spectrometer. The radical concentration was calibrated with 1,3,5-triphenylverdazyl [16].

TABLE 1.   Results of Preparation of 2RCPhMIs

Monomer	Yield, %	mp, °C	^{1}H-NMR chemical shift (ppm, 60 MHz, in CDCl$_3$)
2MCPhMI	66	114.0–115.0	6.99–7.97 (m, aromatic, 4H)
			6.65 (s, CH=, 2H)
			3.66 (s, CH$_3$, 3H)
2ECPhMI	59	97.5–99.0	7.04–8.00 (m, aromatic, 4H)
			6.67 (s, CH=, 2H)
			4.14 (q, J = 7 Hz, CH$_2$, 2H)
			1.20 (t, J = 7 Hz, CH$_3$, 3H)
2BCPhMI	71	44.0–46.0	6.93–7.89 (m, aromatic, 4H)
			6.54 (s, CH=, 2H)
			4.04 (t, J = 7 Hz, OCH$_2$, 2H)
			1.19–1.82 (m, CH$_2$CH$_2$, 4H)
			0.90 (t, J = 7 Hz, CH$_3$, 3H)

RESULTS AND DISCUSSION

Polymerization Reactivity of 2RCPhMIs

The radical polymerization of 2RCPhMIs was carried out with MAIB in benzene at 60°C. The polymerization of 2MCPhMI proceeded inhomogeneously; namely, the resulting polymers precipitated during the polymerization because poly-(2MCPhMI) was insoluble in benzene. The polymerization system of 2ECPhMI apparently remained homogeneous. Poly(2ECPhMI) was swollen with benzene, but insoluble, as described in the previous paper [2], whereas poly(2BCPhMI) was soluble in benzene and the polymerization of 2BCPhMI proceeded homogeneously. Despite the differences in the polymerization behaviors, these polymerizations proceeded at a similar rate as shown in the time–conversion relationship in Fig. 1.

Solubility of Poly(2RCPhMI)s

Table 2 summarizes the solubility of poly(2RCPhMI)s in several organic solvents. Poly(2RCPhMI)s were soluble in chloroform, 1,1,2-trichloroethane, and dimethylformamide. Poly(2BCPhMI) was also soluble in many other solvents, e.g., tetrahydrofuran, trichloroethylene, benzene, 2-butanone, anisole, cyclohexanone, and dioxane, whereas poly(2MCPhMI) was insoluble in these solvents. Poly-(2ECPhMI) showed an intermediate solubility.

Thermal Properties of Poly(2RCPhMI)s

The TGA thermograms of poly(2RCPhMI)s in a nitrogen stream are depicted in Fig. 2. The initial and maximum decomposition temperatures (T_{init} and T_{max}) determined from these thermograms are listed in Table 3, with the glass transition
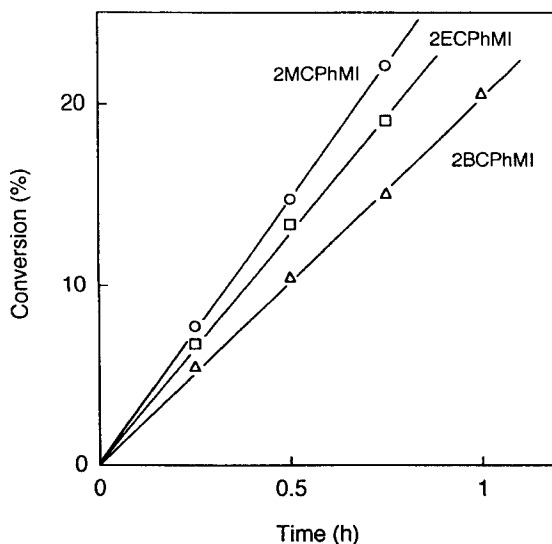
FIG. 1. Time–conversion relationships for radical polymerization of 2RCPhMIs in benzene at 60°C. [2RCPhMI] = 0.5 mol/L, [MAIB] = 5 × 10^{-3} mol/L. (○) 2MCPhMI, (□) 2ECPhMI, (△) 2BCPhMI.

TABLE 2.   Solubility of Poly(2RCPhMI)s[a]

Solvent[b]	Poly-(2MCPhMI)	Poly-(2ECPhMI)	Poly-(2BCPhMI)
Carbon tetrachloride (8.6)	i	i	sw
Tetrahydrofuran (9.1)	i	s	s
Trichloroethylene (9.2)	i	i	s
Benzene (9.2)	i	sw	s
2-Butanone (9.3)	i	i	s
Chloroform (9.3)	s	s	s
Anisole (9.5)	i	s	s
1,1,2-Trichloroethane (9.6)	s	s	s
Cyclohexanone (9.9)	i	s	s
o-Dichlorobenzene (10.0)	sw	s	s
1,4-Dioxane (10.0)	i	i	s
Acetonitrile (11.9)	i	i	i
Dimethylsulfoxide (12.0)	sw	sw	s
Dimethylformamide (12.1)	s	s	s

[a]s, soluble; sw, swelling; i, insoluble.
[b]The values in parentheses indicate a solubility parameter, $(cal/cm^3)^{1/2}$.
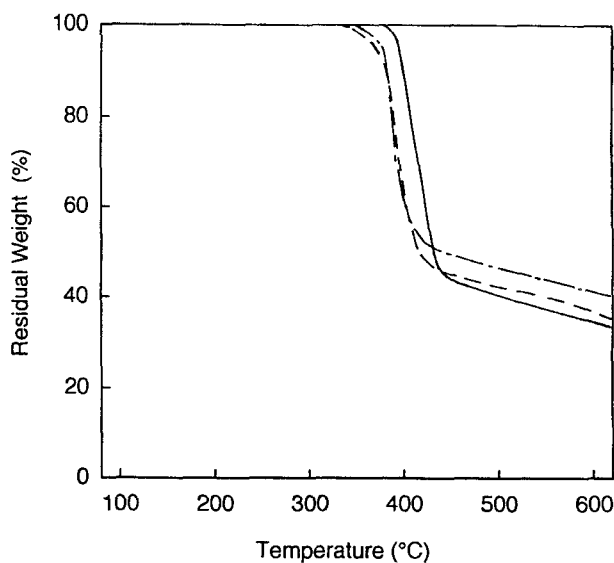
FIG. 2.   TGA curves of poly(2RCPhMI)s in a nitrogen stream with a heating rate of 10°C/min. (——) Poly(2MCPhMI), (- - -) poly(2ECPhMI), (---) poly(2BCPhMI).

TABLE 3.   Thermal Properties of Poly(2RCPhMI)s

Polymer	T_{init}, °C	T_{max}, °C	T_g, °C	Reference
Poly(2MCPhMI)	364	415	259	This work
Poly(2ECPhMI)	333	381	230	2
Poly(2BCPhMI)	328	391	181	This work
Poly(PhMI)	364	422	>decomp	1
Poly(2MPhMI)[a]	392	427	335	1, 25
Poly(2TFMPhMI)[b]	368	434	328	26

[a]Poly[N-(2-methylphenyl)maleimide].
[b]Poly[N-(2-trifluoromethylphenyl)maleimide].

temperature (T_g) determined by DSC. The T_{init} and T_{max} of poly(2RCPhMI)s were 328–364°C and 381–415°C, respectively. Poly(2MCPhMI) especially showed excellent thermal stability, similar to poly(PhMI) and the other 2-substituted poly-(PhMI)s [1, 25, 26]. The lower T_{init} for poly(2ECPhMI) and poly(2BCPhMI) may be due to the decomposition of the ester alkyl groups in the side chain, presumably olefin elimination by thermolysis [18–22], which could start at a lower temperature than the decomposition temperature of the polymaleimides accompanying the main-chain scission.

The T_g depended on the carbon number in the ester alkyl group on the N-phenyl ring. It decreased in the order poly(2MCPhMI) (259°C) > poly(2ECPhMI) (230°C) > poly(2BCPhMI) (181°C) in a fashion similar to the T_g of poly(N-n-alkylmaleimide)s [23, 24]. These T_g values are lower than those of poly(PhMI) and other 2-substituted poly(PhMI) derivatives, e.g., 335°C for poly[N-(2-methylphenyl)maleimide] [25] and 328°C for poly[N-(2-trifluoromethylphenyl)maleimide] [26].

Polymerization Kinetics

In this work we revealed that the polymerization of 2BCPhMI proceeded homogeneously in benzene at 60°C. Therefore, we analyzed this polymerization kinetically in detail. In Figs. 3 and 4 the time–conversion relationships for the polymerization of 2BCPhMI in benzene at 60°C at various monomer and initiator concentrations, respectively, are shown. From the initial slope of the time–conversion curves obtained, the polymerization rate (R_p) was determined. The results are shown in Table 4. In this table, the M_n and M_w/M_n values of the resulting polymers are also summarized. The reaction orders with respect to the monomer and initiator concentrations were determined to be 0.84 and 0.88 from the slope of the curves in Figs. 5 and 6, respectively. Thus, R_p is represented as

$$R_p = k[2BCPhMI]^{0.84}[MAIB]^{0.88} \qquad (1)$$

The reaction order with respect to the monomer concentration is approximately unity, while that to the initiator concentration was larger than 0.5, which is expected for bimolecular termination. Similar larger reaction orders have been reported for the radical polymerization of the other maleimides, e.g., N-n-hexylmaleimide [27],

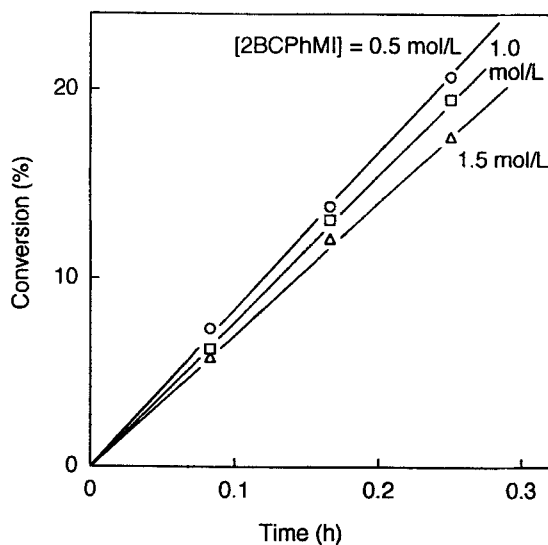**FIG. 3.** Time–conversion relationships for radical polymerization of 2BCPhMI with AIB in benzene at 60°C. [2BCPhMI] = 0.5–1.5 mol/L, [MAIB] = 2 × 10^{-2} mol/L.
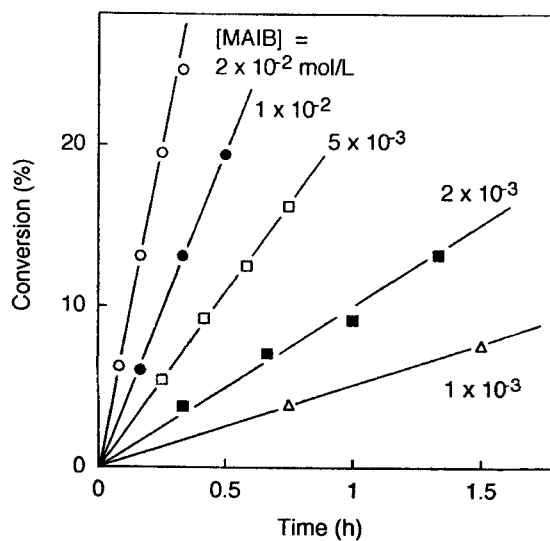
FIG. 4. Time–conversion relationships for radical polymerization of 2BCPhMI with AIB in benzene at 60°C. [2BCPhMI] = 1.0 mol/L, [MAIB] = 1 × 10^{-3} to 2 × 10^{-2} ɔl/L.

TABLE 4.   Results of Radical Polymerization of 2BCPhMI with
MAIB in Benzene at 60°C

[2BCPhMI], mol/L	[MAIB] $\times$ 10^3, mol/L	R_p $\times$ 10^4, mol/L$\cdot$s	M_n $\times$ 10^{-5}	M_w/M_n
0.5	5	0.29	1.09	2.0
0.5	20	1.18	0.67	2.4
1.0	1	0.14	1.40	2.1
1.0	2	0.29	1.32	1.8
1.0	5	0.60	1.35	2.2
1.0	10	1.06	1.05	2.2
1.0	20	2.15	1.08	2.1
1.5	20	2.96	1.09	2.1

N-cyclohexylmaleimide [27, 28], N-phenylmaleimide [29], and maleimide [30]. In earlier papers this was accounted for by poor solubility of the polymer, i.e., occlusion of the polymer radicals. However, the polymerization system of 2BCPhMI in benzene is completely homogeneous. Recently, many workers have not accepted the interpretation of occlusion for the high orders [28, 29]. The reason is discussed in the next section.

When the initiator concentration was varied from 1×10^{-3} to 2×10^{-2} mol/L, the M_n value decreased only from 1.4×10^5 to 1.1×10^5. Thus, the change in the
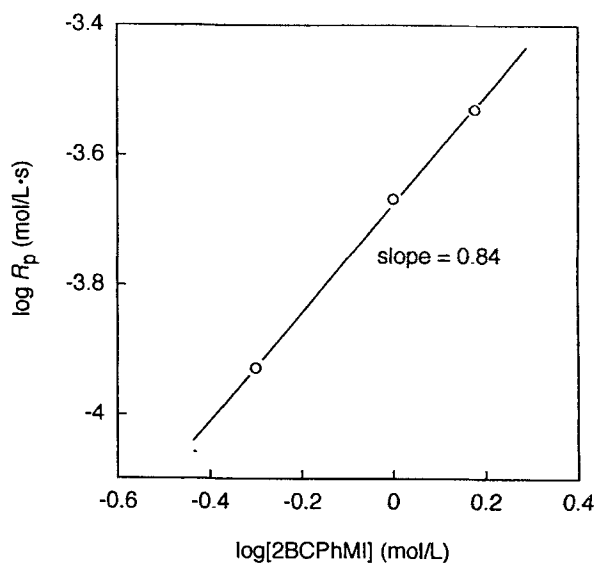

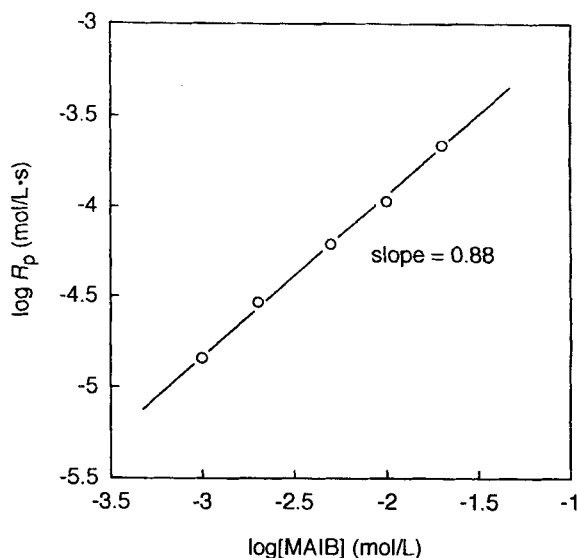FIG. 5.   Relationship between log[2BCPhMI] and log R_p for radical polymerization of 2BCPhMI in benzene at 60°C.

FIG. 6.   Relationship between log[MAIB] and log R_p for radical polymerization of 2BCPhMI in benzene at 60°C.

M_n was smaller than expected, suggesting a chain transfer during the polymerization.

Determination of k_p and k_t

The k_p and k_t values for the polymerization of 2BCPhMI were determined by the ESR method [13–16] to clarify the reason for the greater dependence of R_p on the initiator concentration. During the polymerization of 2BCPhMI with MAIB in benzene at 60°C, the ESR spectrum of the propagating radicals was observed, as depicted in Fig. 7. It was very similar to those observed for the propagating radicals of *N*-(alkyl-substituted phenyl)maleimides [15]. The spectrum intensity was con-

FIG. 7.   ESR spectrum observed during radical polymerization of 2BCPhMI with MAIB in benzene at 60°C. [2BCPhMI] = 1.0 mol/L, [MAIB] = 2 × 10^{-2} mol/L.

stant during 20 minutes of polymerization (up to approximately 25% conversion), indicating strongly that occlusion of the propagating radicals never occurred in this polymerization and the radical concentration ($[P\cdot]$) was constant.

The k_p value was determined for the polymerizations at various MAIB concentrations with Eq. (2):

$$k_p = R_p / ([P\cdot][2BCPhMI])$$ (2)

The average k_p value was 90 L/mol·s in the range of MAIB concentration used in this work. A very small dependence of k_p on the MAIB concentration was observed. This value is smaller than 190 L/mol·s for N-(2-methylphenyl)maleimide and larger than 14 L/mol·s for N-(2,6-dimethylphenyl)maleimide previously reported [14, 15]. These results reflect the magnitude of steric hindrance due to the ortho substituents of the N-phenyl ring in propagation.

Subsequently, k_t was estimated by analyses of the nonsteady state and the steady state of $[P\cdot]$ during polymerization. Figure 8 shows the change of $[P\cdot]$ for photopolymerization of 2BCPhMI with ATMP as a photoinitiator in benzene at 60°C after UV irradiation and interception. After the irradiation, $[P\cdot]$ increased and reached a constant value within a few minutes. $[P\cdot]$ decayed after inception of irradiation according to the following equation:

$$-d[P\cdot]/dt = k_t[P\cdot]^2$$ (3)

Equation (3) gives Eq. (4) by integration:

$$[P\cdot]_s/[P\cdot]_t = k_t[P\cdot]_s t + 1$$ (4)

where t is the time passed after the incepting of irradiation and $[P\cdot]_t$ is the radical concentration at time t. $[P\cdot]_s$ is $[P\cdot]$ at steady state under continuous irradiation.
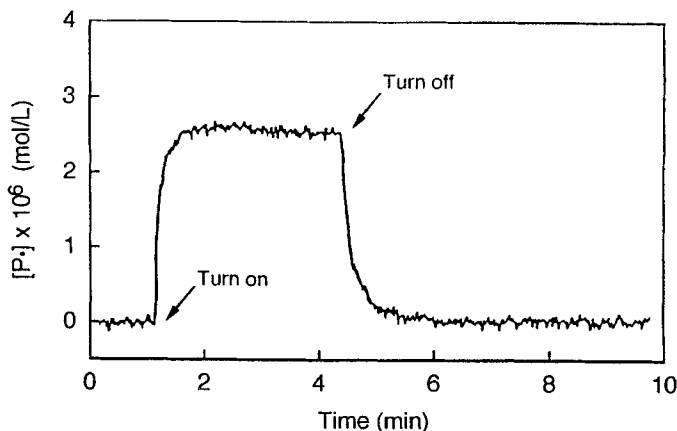

FIG. 8.   Time dependence of $[P\cdot]$ for photopolymerization of 2BCPhMI with ATMP in benzene at 60°C after UV irradiation and interception. [2BCPhMI] = 1.0 mol/L, [ATMP] = 2 × 10^{-2} mol/L.

TABLE 5.   Determination of k_p and k_t for Radical Polymerization of 2BCPhMI in Benzene at 60°C

[2BCPhMI], mol/L	[MAIB] $\times 10^3$, mol/L	$R_p \times 10^4$, mol/L·s	[P·] $\times 10^6$, mol/L	k_p, L/mol·s	f	$k_t \times 10^{-5}$, L/mol·s
1.0	5	0.60	0.63	96	0.49	1.0^a
1.0	10	1.06	1.15	92	—	—
1.0	20	2.15	2.65	81	0.41	0.20^a
1.0	20^b	—	2.58	—	—	0.67^c

$^a k_t = 2k_d f[\text{MAIB}]/[\text{P·}]^2$.
^{b}Photopolymerization with ATMP.
$^c -d[\text{P·}]/dt = k_t[\text{P·}]^2$.

The k_t values were also estimated by Eq. (5), which is derived from a steady state of [P·] for the polymerization with MAIB, i.e., the termination rate ($R_t = k_t[\text{P·}]^2$) equal to the initiation rate ($R_i = 2k_d f[\text{MAIB}]$) during polymerization.

$$k_t = 2k_d f[\text{MAIB}]/[\text{P·}]^2 \qquad (5)$$

where f and k_d are the efficiency and the decomposition rate constant of the initiator, respectively. The primary radical trapping experiment with a stable radical gives the $2k_d f[\text{MAIB}]$ value.

The k_t values determined are shown in Table 5. They were intermediate of the values for N-(2-methylphenyl)maleimide (5.9 × 10⁵ L/mol·s) and N-(2,6-dimethylphenyl)maleimide (3.4 × 10⁴ L/mol·s) [14] as were the k_p values. When the MAIB concentration was changed from 5 × 10⁻³ to 2 × 10⁻² mol/L, the k_t value varied from 1.0 × 10⁵ to 2.0 × 10⁴ L/mol·s. A similar dependence of k_t as well as of k_p on the initiator concentration has also been reported for the polymerization of N-cyclohexylmaleimide [28]. Because the chain length of the propagating radical is shorter at a higher MAIB concentration ($M_n = 1.35 \times 10^5$ and 1.08×10^5 at 5 × 10⁻³ and 2 × 10⁻² mol/L of MAIB as shown in Table 4), the polymerization at a higher MAIB concentration might yield larger k_t values [31]. However, the results obtained in this work were opposite. The k_t dependence on the MAIB concentration is responsible for the high order with respect to the MAIB concentration in Eq. (1).

From the R_p and R_t values determined experimentally, the kinetic chain length (ν) was calculated.

$$\nu = R_p/R_t \qquad (6)$$

The ν values were 1500 and 710 for the polymerization with MAIB at 5.0 × 10⁻³ and 2.0 × 10⁻² mol/L, respectively. The ν values changed depending on the MAIB concentration, whereas the difference in the experimental M_n values was small, indicating that chain transfer occurred during polymerization. If chain transfer to the monomer is not negligible and a reinitiation proceeds slower than propagation, the polymerization rate would be proportional to the order of the monomer concentration when it is less than unity. This might account for the small order with respect to monomer concentration in Eq. (1) in this work.

CONCLUSION

The radical polymerization of 2RCPhMIs, i.e., 2MCPhMI, 2ECPhMI, and 2BCPhMI, with 2-methoxycarbonyl, 2-ethoxycarbonyl, and 2-n-butoxycarbonyl groups as the substituents on the N-phenyl ring, respectively, was carried out with MAIB in benzene at 60°C. The solubility of the resulting polymers depended on the alkyl substituents: poly(2BCPhMI) was soluble in many organic solvents whereas poly(2MCPhMI) was insoluble in tetrahydrofuran, trichloroethylene, benzene, 2-butanone, anisole, cyclohexanone, and dioxane. The T_{init} and T_{max} of poly(2RCPhMI)s have been revealed to be as high as 328–364°C and 381–415°C, respectively. The T_g was found to depend on the carbon number of the alkyl groups: 259, 230, and 181°C for poly(2MCPhMI), poly(2ECPhMI), and poly(2BCPhMI), respectively. From a kinetic study of the polymerization of 2BCPhMI, the reaction orders with respect to the monomer and initiator concentrations were determined to be 0.84 and 0.88, respectively. Furthermore, the k_p and k_t values were also determined by the ESR method. The k_p value was 90 L/mol·s, and the k_t value varied from 1.0×10^5 to 2.0×10^4 L/mol·s in the range of MAIB concentrations from 5×10^{-3} to 2×10^{-2} mol/L. The k_p is dependent on the MAIB concentration, and the chain transfer to the monomer might account for the kinetic orders of this polymerization.

REFERENCES

[1]   A. Matsumoto, T. Kubota, and T. Otsu, *Macromolecules, 23*, 4508 (1990).
[2]   A. Matsumoto, Y. Oki, and T. Otsu, *J. Macromol. Sci. – Pure Appl. Chem., A29*, 831 (1992).
[3]   J. M. Barrales-Rienda, J. I. G. De la Campa, and J. G. Ramos, *J. Macromol. Sci. – Chem., A11*, 267 (1977).
[4]   H. Aida, M. Urushizaki, H. Maegawa, and S. Okazaki, *Kobunshi Ronbunshu, 45*, 333 (1988).
[5]   I. Takase, K. Kawazu, H. Aida, and H. Hohkame, *Ibid., 47*, 569 (1990).
[6]   M. Yamada, I. Takase, and T. Mishima, *Kobunshi Kagaku, 26*, 393 (1969).
[7]   M. Yamada, I. Takase, and T. Mishima, *Ibid., 24*, 326 (1967).
[8]   M. Z. Elsabee, M. G. Mikhael, M. W. Sabaa, and A. A. Yassin, *Angew. Makromol. Chem., 157*, 43 (1988).
[9]   J. Iroh, J. P. Bell, and D. A. Scola, *J. Appl. Polym. Sci., 41*, 735 (1990).
[10] T. Oishi, M. Iwahara, and M. Fujimoto, *Polym. J., 23*, 1409 (1991).
[11] T. Oishi and M. Fujimoto, *J. Polym. Sci., Part A, Polym. Chem., 30*, 1821 (1992).
[12] M. Kamachi, *Adv. Polym. Sci., 82*, 207 (1987).
[13] A. Matsumoto, Y. Oki, and T. Otsu, *Polym. J., 25*, 237 (1993).
[14] A. Matsumoto, Y. Oki, and T. Otsu, *Eur. Polym. J., 29*, 1225 (1993).
[15] A. Matsumoto, Y. Oki, and T. Otsu, *Macromolecules, 25*, 3323 (1992).
[16] A. Matsumoto and K. Mizuta, *Ibid., 27*, 5863 (1994).
[17] M. P. Cava, A. A. Deana, K. Muth, and M. J. Mitchell, *Organic Synthesis, Collective Vol. V*, Wiley, New York, 1973, p. 944.
[18] T. Otsu, T. Yasuhara, K. Shiraishi, and S. Mori, *Polym. Bull., 12*, 449 (1984).

[19] T. Otsu, M. Yoshioka, A. Matsumoto, and K. Shiraishi, *Ibid., 26*, 159 (1991).

[20] A. Matsumoto, K. Mizuta, and T. Otsu, *J. Polym. Sci., Part A, Polym. Chem., 31*, 2531 (1993).

[21] D. H. Grant and N. Grassie, *Polymer, 1*, 415 (1960).

[22] W. P. Ratchford, *Organic Synthesis, Collective Vol. III*, Wiley, New York, 1955, p. 30.

[23] A. Matsumoto, Y. Oki, and T. Otsu, *Polym. J., 23*, 201 (1991).

[24] J. M. Barrales-Rlenda, F. Fernandez-Martin, C. R. Galicia, and M. S. Chaves, *Makromol. Chem., 184*, 2643 (1983).

[25] T. Doi, A. Akimoto, Y. Oki, A. Matsumoto, and T. Otsu, *J. Polym. Sci., Part A, Polym. Chem.*, In Press.

[26] A. Matsumoto and T. Kimura, Unpublished Results.

[27] T. Oishi and N. Kimura, *Kobunshi Ronbunshu, 33*, 685 (1976).

[28] T. Sato, K. Arimoto, H. Tanaka, T. Ota, K. Kato, and K. Doiuchi, *Macromolecules, 22*, 2219 (1989).

[29] S. Iwatsuki, M. Kubo, M. Wakita, Y. Matsui, and H. Kanoh, *Ibid., 24*, 5009 (1991).

[30] Y. Nakayama and G. Smets, *J. Polym. Sci., A1, 5*, 1619 (1967).

[31] A. Matsumoto and K. Mizuta, *Macromolecules, 27*, 1657 (1994).