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### Radical Polymerization of *N*-(Ethoxycarbonylphenyl) Maleimides and Characterization of the Polymers

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## **RADICAL POLYMERIZATION OF *N*-(ETHOXYCARBONYLPHENYL)MALEIMIDES AND CHARACTERIZATION OF THE POLYMERS**

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### **ABSTRACT**

Three *N*-phenylmaleimides bearing an ethoxycarbonyl group, i.e., *N*-(*o*-ethoxycarbonylphenyl)maleimide (OPMI), *N*-(*m*-ethoxycarbonylphenyl)maleimide (MPMI), and *N*-(*p*-ethoxycarbonylphenyl)maleimide (PPMI), were prepared and polymerized with 2,2'-azobisisobutyronitrile (AIBN) or dimethyl 2,2'-azobisisobutyrate (MAIB) as a radical initiator in benzene at 60°C. The polymer yield depended drastically on the position of the ethoxycarbonyl group on the *N*-phenyl ring in the following order: PPMI ≥ MPMI > OPMI, agreeing with the order of the steric hindrance in propagation. It was found that polymerization with MAIB gave a higher polymer yield than that with AIBN, although both the initiators used have similar decomposition rates. Some characterizations of the resulting polymers were carried out. These substituted polymaleimides showed excellent thermal stability, i.e., high glass transition temperatures and decomposition temperatures, as did poly(*N*-phenylmaleimide). The solubility of the polymers depended on the position of the ethoxycarbonyl group.

### **INTRODUCTION**

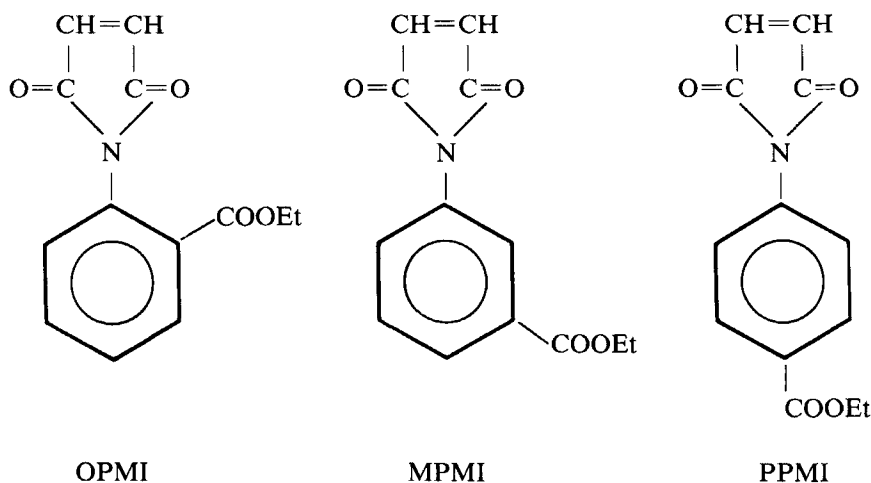
In previous papers [1–8] we reported that *N*-substituted maleimides such as *N*-alkylmaleimides and *N*-(alkyl-substituted phenylmaleimide)s polymerize readily in the presence of a radical initiator. We showed that they give thermally stable

polymers consisting of substituted polymethylene structures in a series of studies on the synthesis and characterization of substituted polymethylenes by polymerization of 1,2-disubstituted ethylenes [9].

In a study of the polymerization of *N*-(alkyl-substituted phenyl)maleimides [2], it was revealed that the position, number, and bulkiness of the alkyl substituents has a significant influence on the polymerization reactivities and solubilities of the resulting polymers, whereas these alkyl-substituted polymers show excellent thermal stability as does poly(*N*-phenylmaleimide) (poly(PhMI)) [10–15]. Polymers with an alkyl-substituted *N*-phenyl group are soluble in many organic solvents, including such nonpolar solvents as benzene, but the polymerization reactivities varied according to the alkyl substitution, i.e., the introduction of alkyl groups into the ortho position of the phenyl group decreased the yield and molecular weight of the resulting polymers because of steric hindrance. It was also found that ortho substitution reduced the relative reactivities of the monomers in copolymerizations with styrene and methyl methacrylate [2].

Some investigations on the polymerization and copolymerization of PhMI with an alkoxy-carbonyl group at the para position have been reported [16–20]. The properties of the resulting polymers and the polymerization reactivities were investigated, but further detailed studies have not been made because of problems with the solubilities of the polymers in spite of their thermal stability. There is no report of meta and ortho substitutions although they are expected to give a soluble polymer similar to the alkyl-substituted PhMIs mentioned above.

In this work we prepared and polymerized the following three maleimides bearing an ethoxycarbonyl group at the ortho, meta, and para positions of the *N*-phenyl group. The thermal properties and solubilities of the polymers obtained were examined.



## EXPERIMENTAL

### Materials

*N*-(*o*-Ethoxycarbonylphenyl)maleimide (OPMI), *N*-(*m*-ethoxycarbonylphenyl)maleimide (MPMI), and *N*-(*p*-ethoxycarbonylphenyl)maleimide (PPMI) were

prepared from maleic anhydride and a corresponding aniline by literature methods [2, 21]; The maleimides obtained were purified by recrystallization from ethyl acetate after they had been passed through an alumina column with benzene as an eluent. The purity of the maleimides was checked by IR and NMR spectroscopies and HPLC. The  $^1\text{H-NMR}$  spectra of these maleimides are shown in Fig. 1.

OPMI: mp  $99^\circ\text{C}$ . IR (KBr) 3090, 1775, 1720, 1705, 1690, 1640, 1600, 1490, 1475, 1450, 1400, 1360, 1290, 1265, 1210, 1155, 1140, 1090, 1070, 1020, 835, 760, 710,  $685\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 60 MHz)  $\delta$  7.04–8.00 (m, aromatic, 4H), 6.67 (s,  $\text{CH}=\text{}$ , 2H), 4.14 (q,  $\text{CH}_2$ ,  $J = 7\text{ Hz}$ , 2H), 1.20 (t,  $\text{CH}_3$ ,  $J = 7\text{ Hz}$ , 3H).

MPMI: mp  $119^\circ\text{C}$ . IR (KBr) 3080, 2990, 1720, 1705, 1650, 1590, 1500, 1485, 1445, 1405, 1390, 1300, 1280, 1205, 1160, 835, 750,  $700\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 60 MHz)  $\delta$  6.86–7.99 (m, aromatic, 4H), 6.73 (s,  $\text{CH}=\text{}$ , 2H), 4.54 (q,  $\text{CH}_2$ ,  $J = 7\text{ Hz}$ , 3H), 1.37 (t,  $\text{CH}_3$ ,  $J = 7\text{ Hz}$ , 3H).

PPMI: mp  $112^\circ\text{C}$ . IR (KBr) 3080, 1720, 1700, 1660, 1600, 1510, 1375, 1300, 1270, 1210, 1175, 1140, 1125, 1110, 1020, 855, 830, 765, 700,  $685\text{ cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 60 MHz)  $\delta$  8.06 (d, aromatic,  $J = 10\text{ Hz}$ , 2H), 7.41 (d, aromatic,  $J = 10\text{ Hz}$ , 2H), 6.78 (s,  $\text{CH}=\text{}$ , 2H), 4.35 (q,  $\text{CH}_2$ ,  $J = 7\text{ Hz}$ , 2H), 1.38 (t,  $\text{CH}_3$ ,  $J = 7\text{ Hz}$ , 3H).

Other reagents and solvents were used after ordinary purification.

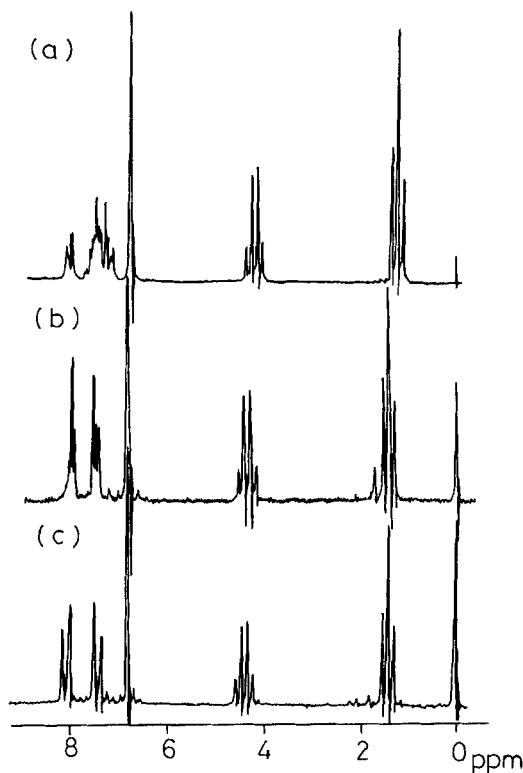


FIG. 1.  $^1\text{H-NMR}$  spectra of (a) OPMI, (b) MPMI, and (c) PPMI in  $\text{CDCl}_3$ .

### Polymerization Procedure

Polymerization was carried out in the presence of 2,2'-azobisisobutyronitrile (AIBN) or dimethyl 2,2'-azobisisobutyrate (MAIB) in benzene at 60°C in a sealed glass tube. The polymerization mixture was poured into a large amount of methanol to isolate the resulting polymer. The polymer was filtered, washed with methanol, and then dried under vacuum.

### Measurements

The number- and weight-average molecular weights ( $\bar{M}_n$  and  $\bar{M}_w$ ) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) with standard polystyrenes for calibration.

IR and <sup>1</sup>H-NMR spectra were recorded on a JASCO A-202 and a Hitachi R-24B (60 MHz) or JEOL GX-400 (400 MHz) spectrometer, respectively.

Differential scanning calorimetry (DSC) was performed with a scanning rate of 10°C/min by use of a Seiko DSC-200. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Polymerization Reactivity

Table 1 shows the results of polymerization of the maleimides with AIBN or MAIB in benzene at 60°C. Because of the low solubilities of MPMI and PPMI in benzene, polymerization was performed at a rather low monomer concentration (0.1 mol/L). All the maleimides gave polymers in high yield as well as other substituted PhMIs [2] and *N*-alkylmaleimides [1]. The polymerization of MPMI and PPMI proceeded in a heterogeneous system from the first stage of polymerization, whereas the polymerization solution of OPMI apparently remained homogeneous during polymerization. The polymer yields were in the following order in both cases

TABLE 1. Radical Polymerization of *N*-(Ethoxycarbonylphenyl)maleimides in Benzene at 60°C

Monomer, mol/L	Initiator, mmol/L	Time, h	Yield, %	$\bar{M}_n \times 10^{-4}$ <sup>a</sup>	$\bar{M}_w/\bar{M}_n$ <sup>a</sup>
OPMI (0.1)	AIBN (5)	5	56.8	1.13	1.73
OPMI (0.1)	MAIB (5)	5	88.8	1.13	1.95
OPMI (1.0)	MAIB (5)	10	91.8	2.92	1.74
MPMI (0.1)	AIBN (5)	5	82.6	— <sup>b</sup>	— <sup>b</sup>
MPMI (0.1)	MAIB (5)	5	90.1	— <sup>b</sup>	— <sup>b</sup>
PPMI (0.1)	AIBN (5)	5	88.7	— <sup>b</sup>	— <sup>b</sup>
PPMI (0.1)	MAIB (5)	5	91.1	— <sup>b</sup>	— <sup>b</sup>

<sup>a</sup>Determined by GPC in THF.

<sup>b</sup>Insoluble in THF.

initiated with AIBN and MAIB: PPMI  $\geq$  MPMI  $>$  OPMI. The decrease in the polymerization reactivity by ortho substitution has been also observed for various alkyl-substituted PhMIs, i.e., the polymer yield and molecular weight of the polymer depended on the position, number, and bulkiness of the alkyl substituents [2]. We recently determined the propagation rate constants of alkyl-substituted PhMIs by means of electron spin resonance spectroscopy [22]. It was revealed that the reduced reactivities of polymer radicals and monomers, especially the former, had a significant role in the decrease of the propagation rate constants for ortho substitution. In the present case, similar steric effects are expected to decrease the polymerization reactivities of the ethoxycarbonyl-substituted PhMIs.

It was also found that MAIB always gave a higher polymer yield than AIBN, although the decomposition rates of AIBN and MAIB resemble each other, i.e.,  $k_d = 9.8 \times 10^{-6} \text{ s}^{-1}$  (60°C) for AIBN [23] and  $k_d = 8.4 \times 10^{-6} \text{ s}^{-1}$  (60°C) for MAIB [24]. Although detailed kinetic data for these polymerizations are not available at the present time, low reactivity of the primary radical from AIBN in addition to monomers, especially in the case of sterically hindered 1,2-disubstituted ethylene monomers [25–27], are expected. Similar polymerization behaviors have recently been observed for many polymerization systems of 1,1- or 1,2-disubstituted ethylenes such as dialkyl fumarates and dialkyl itaconates and of less-reactive nonconjugated monomers [26].

### Structure of the Polymers

Figure 2 shows the  $^1\text{H-NMR}$  spectrum of poly(OPMI), and it indicates the disappearance of the peak at 6.7 ppm due to an olefinic proton through polymerization. Similar results were also observed in the IR spectra as shown in Fig. 3, i.e., a peak due to the  $\text{C}=\text{C}$  bond at  $1640 \text{ cm}^{-1}$  of OPMI disappeared upon polymerization. These results confirm the formation of a substituted polymethylene via ordinary vinyl polymerization.

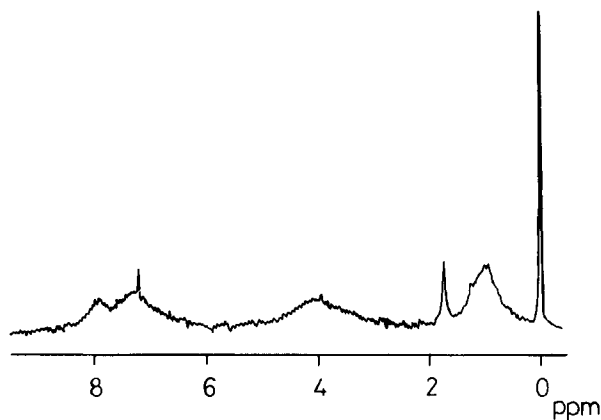


FIG. 2.  $^1\text{H-NMR}$  spectrum of poly(OPMI) in  $\text{CDCl}_3$ .

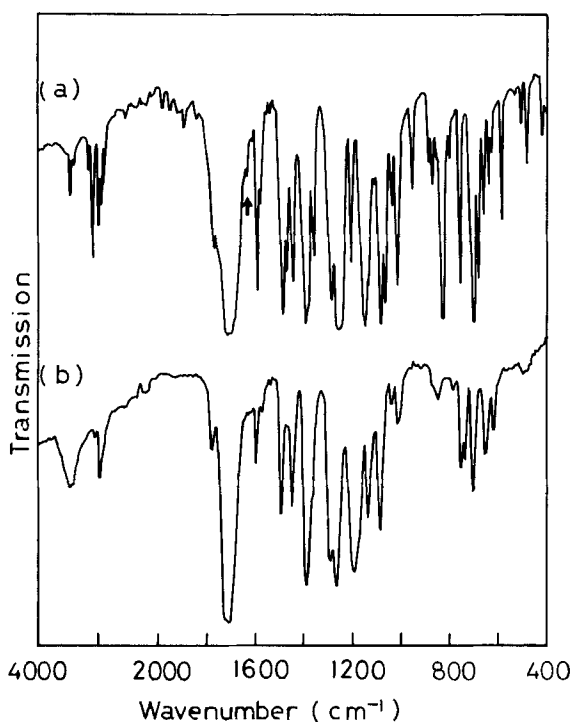


FIG. 3. IR spectra of (a) OPMI and (b) poly(OPMI).

### Thermal Property

The thermal properties of the polymers obtained in this work were examined. From DSC measurements it was shown that the substituted poly(PhMI)s have high glass transition temperatures ( $T_g$ );  $T_g$  was observed at 230°C for poly(OPMI), but no  $T_g$ s were detected below the decomposition temperatures for poly(MPMI) and poly(PPMI). From the TGA thermograms shown in Fig. 4, the initial and maximum decomposition temperatures ( $T_{init}$  and  $T_{max}$ ) were determined. The results are summarized in Table 2 with the results of poly(PhMI). The  $T_{init}$  and  $T_{max}$  of these polymers were 333–342 and 381–413°C, respectively. This indicates that the ethoxy-carbonyl-substituted poly(PhMI)s are thermally stable, as well as are other poly(*N*-substituted maleimide)s including poly(PhMI) ( $T_{init} = 364^\circ\text{C}$  and  $T_{max} = 422^\circ\text{C}$ ) [1, 2, 10–15].

### Solubility

Table 3 shows the solubility of the resulting polymers in several organic solvents. Poly(OPMI) is soluble in THF, chloroform, anisole, 1, 1, 2-trichloroethane, cyclohexane, and *o*-dichlorobenzene, and poly(MPMI) is soluble in chloroform and 1,1,2-trichloroethane and swells in THF, anisole, cyclohexane, and *o*-dichlorobenzene. On the other hand, poly(PPMI) is insoluble in all the organic solvents examined. Thus, it has been found that the solubility of poly(PhMI)s

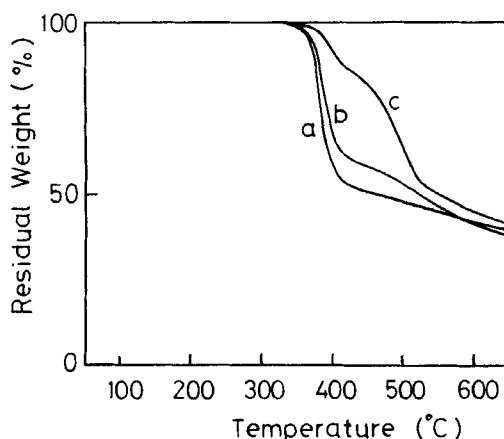


FIG. 4. Thermogravimetric analysis in a nitrogen stream with a heating rate of 10°C/min: (a) poly(OPMI), (b) poly(MPMI), and (c) poly(PPMI).

bearing an ethoxycarbonyl group drastically changes because of the position of the substituents. This is very similar to the results obtained for alkyl-substituted poly(PhMI)s [2].

### Reaction with Dodecanol

By casting chloroform solutions of poly(OPMI) and poly(MPMI), transparent films were obtained, but they were very brittle. Therefore, we attempted to modify these polymers by introducing a dodecyl group as a flexible alkyl chain into the side chain by polymer reaction. Poly(OPMI) and poly(MPMI) were reacted with dodecanol in 1,1,2-trichloroethane for 15 h in the presence of *p*-toluenesulfonic acid following the removal of ethanol by distillation. The reaction mixtures were poured into a large amount of methanol to recover the polymer. Figure 5 shows the <sup>1</sup>H-NMR spectrum of the polymer recovered after the reaction of poly(MPMI) with dodecanol. From the absorption intensities of the phenyl ring and the ethoxy group in the side chain in the spectrum, it was found that *trans*-esterification proceeded to

TABLE 2. Thermal Properties of Poly(PhMI) Derivatives Bearing an Ethoxycarbonyl Group<sup>a</sup>

Polymer	$T_g$ , °C	$T_{init}$ , °C	$T_{max}$ , °C
Poly(OPMI)	230	333	381
Poly(MPMI)	— <sup>b</sup>	342	387
Poly(PPMI)	— <sup>b</sup>	340	413
Poly(PhMI)	— <sup>b</sup>	364	422

<sup>a</sup>Heating rate of 10°C/min in a nitrogen stream.

<sup>b</sup>Not detected below the decomposition temperatures.



TABLE 3. Solubility of Poly(PhMI) Derivatives Bearing an Ethoxycarbonyl Group<sup>a</sup>

Solvent <sup>b</sup>	Poly(OPMI)	Poly(MPMI)	Poly(PPMI)	Poly(PhMI)
Carbon tetrachloride (8.6)	i	i	i	i
Tetrahydrofuran (9.1)	s	sw	i	i
Trichloroethylene (9.2)	i	i	i	sw
Benzene (9.2)	sw	i	i	i
Methyl ethyl ketone (9.3)	i	i	i	i
Chloroform (9.3)	s	s	i	i
Anisole (9.5)	s	sw	i	sw
1,1,2-Trichloroethane (9.6)	s	s	i	s
Cyclohexanone (9.9)	s	sw	i	s
<i>o</i> -Dichlorobenzene (10.0)	s	sw	i	sw
1,4-Dioxane (10.0)	i	i	i	sw
Acetonitrile (11.9)	i	i	i	i
Dimethylsulfoxide (12.0)	sw	sw	i	s
Dimethylformamide (12.1)	s	sw	i	s

<sup>a</sup>s, soluble; sw, swelling; i, insoluble.

<sup>b</sup>The values in parentheses indicate a solubility parameter, (cal/cm<sup>3</sup>)<sup>1/2</sup>.

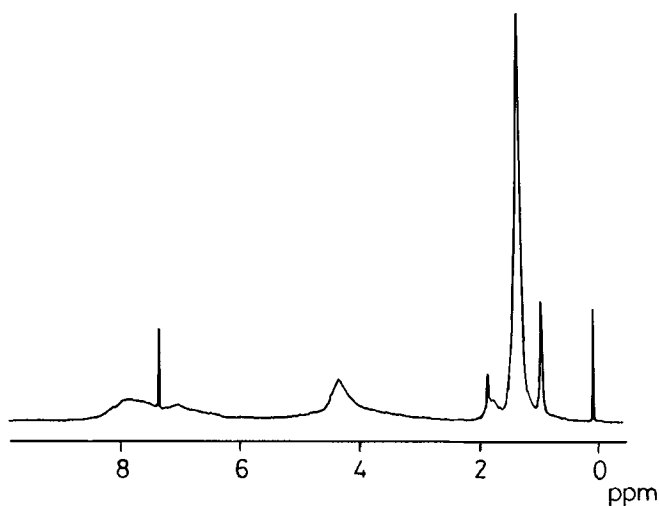


FIG. 5. <sup>1</sup>H-NMR spectrum of the polymer recovered from poly(OPMI) after reaction with dodecanol.

39% conversion in the case of poly(MPMI). However, it was found that transesterification of poly(OPMI) barely occurred under similar conditions. This was interpreted by the steric hindrance around the carbonyl group on the *N*-phenyl ring. It was also found that poly(MPMI) modified with a dodecyl group gave a transparent film of relative toughness from its chloroform solution, and that is different from the original poly(MPMI).

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