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Radical Polymerization of *N*-(Alkyl-substituted phenyl)maleimides: Synthesis of Thermally Stable Polymers Soluble in Nonpolar Solvents

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ABSTRACT: To synthesize thermally stable vinyl polymers soluble in organic solvents, radical polymerization of 16 kinds of *N*-(alkyl-substituted phenyl)maleimides (RPhMI) was investigated. The yield and molecular weight of the polymers obtained decreased with an increase in both number and bulkiness of the alkyl substituents in the ortho position but increased when these substituents were introduced into meta and para positions. It was found that the resulting polymers were soluble in common organic solvents including benzene, although unsubstituted poly(*N*-phenylmaleimide) was soluble only in polar solvents, and that they showed an excellent thermal stability as well as poly(*N*-phenylmaleimide); i.e., no weight loss was observed below 370 °C in nitrogen. These RPhMI monomers were readily copolymerized with styrene and methyl methacrylate, and their reactivities were also dependent on the position, number, and bulkiness of the substituents introduced.

Introduction

In previous papers,[1-3] dialkyl fumarates (DRF), 1,2-disubstituted ethylene, with bulky ester alkyl groups were found to polymerize readily in the presence of a radical initiator to give high molecular weight polymers consisting of a poly(substituted methylene) structure. The polymerization reactivities of DRFs increased with increased bulkiness of the ester alkyl groups, i.e., tertiary > secondary > primary esters. Recently, some *N*,*N*,*N*′,*N*′-tetraalkylfumaramides and alkyl *N*,*N*-diethylfumaramates were observed to homopolymerize with a radical initiator.[4]

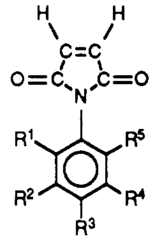
Maleimide and its N-substituted derivatives are also one of 1,2-disubstituted ethylenes. Their radical polymerization and copolymerization behavior and thermal properties of the polymers have been extensively studied by many workers.[5-16] Especially, the polymer of *N*-phenylmaleimide (**1**) has been reported to be superior in thermal stability,[12-17] but it is soluble only in a few polar organic solvents. On the other hand, poly(*N*-alkylmaleimide)s were soluble in many organic solvents including nonpolar solvents such as benzene,[13-16] although their thermal stabilities were lower than that of **1**. Therefore, we intended to introduce a substituent into the phenyl ring of **1** to improve its solubility. Some derivatives with polar para substituents have been already prepared and polymerized to clarify the substitution effects on polymerization reactivities.[7] In contrast, a systematic study on the polymerization of ortho- and meta-substituted derivatives has been scarcely reported.

In this article, *N*-(2-alkylphenyl)- or *N*-(2,6-dialkylphenyl)maleimides (**2**), *N*-(3-alkylphenyl)- or *N*-(3,5-dialkylphenyl)maleimides (**3**), and *N*-(4-alkylphenyl)maleimides (**4**) (Chart I) are prepared, and the effects of the alkyl substituents on the radical polymerization and copolymerization reactivities and on the properties of the polymers, i.e., solubility and thermal property, are examined and discussed.

Experimental Section

Monomers. **1** was commercially available and used after sublimation. Other maleimides were prepared from the reaction of maleic anhydride and the corresponding anilines according to the methods described in the literature,[18] followed by recrystallization or sublimation.

Chart I



RPhMI

RPhMI	R^1	R^2	R^3	R^4	R^5
1	H	H	H	H	H
2a	CH_3	H	H	H	H
2b	C_2H_5	H	H	H	H
2c	i-C_3H_7	H	H	H	H
2d	CH_3	H	H	H	CH_3
2e	C_2H_5	H	H	H	C_2H_5
2f	i-C_3H_7	H	H	H	i-C_3H_7
2g	CH_3	H	CH_3	H	CH_3
2h	Cl	H	H	H	H
3a	H	CH_3	H	H	H
3b	H	CF_3	H	H	H
3c	H	C_2H_5	H	H	H
3d	H	CH_3	H	CH_3	H
4a	H	H	CH_3	H	H
4b	H	H	C_2H_5	H	H
4c	H	H	n-C_4H_9	H	H

***N*-Phenylmaleimide (1)**: mp 90 °C; ^{13}C NMR ($CDCl_3$) δ 169.2 (C=O), 133.7 (C=C), 131.1, 128.7, 127.5, 125.8 (Ar). ***N*-(2-Methylphenyl)maleimide (2a)**: yield 42%; mp 72.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.08–7.33 (m, Ar, 4 H), 6.75 (s, CH=, 2 H), 2.12 (s, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.4 (C=O), 134.1 (C=C), 136.3, 130.9, 129.9, 129.2, 128.5, 126.7 (Ar), 17.6 (CH_3). ***N*-(2-Ethylphenyl)maleimide (2b)**: yield 43%; mp 60 °C; ^{1}H NMR ($CDCl_3$) δ 6.87–7.28 (m, Ar, 4 H), 6.64 (s, CH=, 2 H), 2.41 (q, $J = 7.4$ Hz, CH_2, 2 H), 1.10 (t, $J = 7.4$ Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.8 (C=O), 134.2 (C=C), 142.3, 129.6, 129.2, 128.9, 126.8 (Ar), 24.3 (CH_2), 14.2 (CH_3). ***N*-(2-Isopropylphenyl)maleimide (2c)**: yield 48%; mp 99 °C; ^{1}H NMR ($CDCl_3$) δ 6.80–7.40 (m, Ar, 5 H), 6.70 (s, CH=, 2 H), 2.70 (sept, $J = 6.6$ Hz, CH, 1 H), 1.16 (d, $J = 6.6$ Hz, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.0 (C=O), 134.3 (C=C), 147.3, 129.9, 128.9, 128.6, 126.7 (Ar), 28.7 (CH), 23.6 (CH_3). ***N*-(2,6-Dimethylphenyl)maleimide (2d)**: mp 107 °C; ^{1}H NMR ($CDCl_3$) δ 7.19 (t, $J = 7.7$ Hz, Ar, 1 H), 7.10 (d, $J = 7.7$ Hz, Ar, 2 H), 6.72 (s, CH=, 2 H), 2.07 (s, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.2 (C=O), 133.9 (C=C), 136.7, 129.1, 128.1

(Ar), 17.5 (CH_3). **_N_-(2,6-Diethylphenyl)maleimide (2e)**: mp 74.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.32 (t, J = 7.6 Hz, Ar, 1 H), 7.16 (d, J = 7.6 Hz, Ar, 2 H), 6.79 (s, CH=, 2 H), 2.39 (q, J = 7.4 Hz, CH_2, 4 H), 1.13 (t, J = 7.4 Hz, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.1 (C=O), 134.1 (C=C), 142.7, 129.8, 127.9, 126.6 (Ar), 24.5 (CH_2), 14.4 (CH_3). **_N_-(2,6-Diisopropylphenyl)maleimide (2f)**: yield 76%; mp 117.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.1–7.6 (m, Ar, 3 H), 6.70 (s, CH=, 2 H), 2.60 (sept, J = 6.6 Hz, CH, 2 H), 1.13 (d, J = 6.6 Hz, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 170.4 (C=O), 134.1 (C=C), 147.4, 130.1, 128.2, 123.8 (Ar), 29.2 (CH), 23.9 (CH_3). **_N_-(2,4,6-Trimethylphenyl)maleimide (2g)**: yield 57%; mp 102.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.80 (s, Ar, 2 H), 6.61 (s, CH=, 2 H), 2.21 (s, *p*-CH_3, 3 H), 2.00 (s, *o*-CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.4 (C=O), 134.1 (C=C), 139.1, 136.3, 129.0, 126.4 (Ar), 20.9 (CH_3), 17.6 (CH_3). **_N_-(2-Chlorophenyl)maleimide (2h)**: mp 76 °C; ^{1}H NMR ($CDCl_3$) δ 7.1–7.5 (m, Ar, 4 H), 6.70 (s, CH=, 2 H); ^{13}C NMR ($CDCl_3$) δ 168.7 (C=O), 134.3 (C=C), 132.9, 130.6, 130.2, 128.9, 127.6 (Ar). **_N_-(3-Methylphenyl)maleimide (3a)**: yield 41%; mp 35 °C, bp 134 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.10–7.31 (m, Ar, 4 H), 6.73 (s, CH=, 2 H), 2.36 (s, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.3 (C=O), 133.8 (C=C), 138.8, 130.9, 128.6, 128.5, 126.5, 123.0 (Ar), 21.0 (CH_3). **_N_-[3-(Trifluoromethyl)phenyl]maleimide (3b)**: yield 56%; mp 67 °C, bp 117 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ 7.39–7.49 (m, Ar, 4 H), 6.62 (s, CH=, 2 H). **_N_-(3-Ethylphenyl)maleimide (3c)**: yield 56%; mp 85.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.0–7.3 (m, Ar, 4 H), 6.69 (s, CH=, 2 H), 3.39 (q, J = 7.4 Hz, CH_2, 2 H), 1.24 (t, J = 7.4 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.5 (C=O), 134.1 (C=C), 145.4, 131.1, 128.9, 127.6, 125.6, 123.4 (Ar), 28.7 (CH_2), 15.3 (CH_3). **_N_-(3,5-Dimethylphenyl)maleimide (3d)**: yield 67%; mp 94.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.87 (s, Ar, 1 H), 6.79 (s, Ar, 2 H), 6.59 (s, CH=, 2 H), 1.23 (s, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.6 (C=O), 134.0 (C=C), 138.8, 129.8, 124.0 (Ar), 21.2 (CH_3). **_N_-(4-Methylphenyl)maleimide (4a)**: yield 49%; mp 154 °C; ^{1}H NMR ($CDCl_3$) δ 7.56 (d, J = 8.6 Hz, Ar, 2 H), 7.50 (d, J = 8.6 Hz, Ar, 2 H), 7.06 (s, CH=, 2 H), 2.67 (s, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.5 (C=O), 133.9 (C=C), 137.7, 129.5, 128.4, 125.8 (Ar), 20.9 (CH_3). **_N_-(4-Ethylphenyl)maleimide (4b)**: yield 73%; mp 65 °C; ^{1}H NMR ($CDCl_3$) δ 7.07 (s, Ar, 4 H), 6.58 (s, CH=, 2 H), 2.59 (q, J = 7.4 Hz, CH_2, 2 H), 1.19 (t, J = 7.4 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.6 (C=O), 134.1 (C=C), 144.1, 128.5, 126.0 (Ar), 28.6 (CH_2), 15.4 (CH_3). **_N_-(4-_n_-Butylphenyl)maleimide (4c)**: yield 82%; mp 41.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.06 (s, Ar, 4 H), 6.59 (s, CH=, 2 H), 2.57 (t, J = 6.9 Hz, NCH_2, 2 H), 1.2–1.7 (m, $NCH_2CH_2CH_2$–, 4 H), 0.94 (t, J = 6.0 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.4 (C=O), 133.9 (C=C), 142.5, 128.8, 125.7 (Ar), 35.1 (CH_2), 33.3 (CH_2), 22.2 (CH_2), 13.8 (CH_3).

Styrene (St) and methyl methacrylate (MMA) were purified by ordinary methods and distilled before use.

Other Reagents. 2,2′-Azobis(isobutyronitrile) (AIBN) as an initiator was recrystallized twice from ethanol. Solvents were used after purification by ordinary methods.

Polymerization Procedures. Polymerizations were carried out in benzene or in *N*,*N*-dimethylformamide (DMF) in the presence of AIBN in a sealed glass tube with shaking in a thermostated bath. After a given time, the polymerization mixture was poured into a large amount of methanol or a mixture of methanol and water to precipitate the polymer, which was filtered, washed with methanol or methanol/water, and then dried in vacuo at room temperature. The yield was determined gravimetrically. The polymers thus obtained were purified by a reprecipitation method from benzene or DMF solution into methanol.

Copolymerizations were carried out similarly. The composition of the copolymer was determined by elemental analysis or ^{1}H NMR spectroscopy, and then the monomer reactivity ratios were determined by nonlinear least-squares procedure.[19]

Viscosity and Molecular Weight. Intrinsic viscosities were determined in benzene, chloroform, or DMF at 30 °C by using an Ubbelohde viscometer. Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF), where molecular weight was calibrated with standard polystyrene.

Spectral Measurements. ^{1}H and ^{13}C NMR spectra were recorded on Hitachi R-24B (60-MHz), JEOL JNM-FX60Q (60-MHz), or GX400 (400-MHz) spectrometers with deuterochloroform and tetramethylsilane as a solvent and an internal standard, respectively. UV–vis spectra were taken in purified ethanol with a quartz cell of 1-cm thickness by means of a Shimadzu UV-160. IR spectra were determined in ethanol with a Shimadzu FTIR-4300.

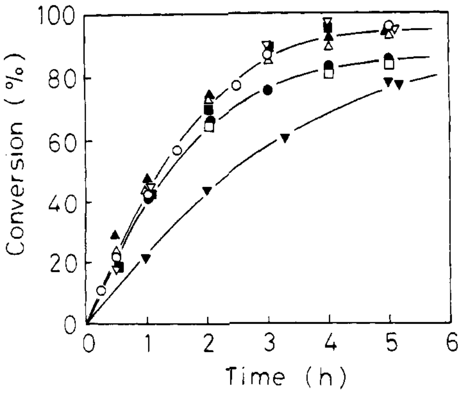


Figure 1. Time–conversion relations of radical polymerization of 1, 3, and 4 in benzene at 60 °C, [RPhMI] = 1.0 mol/L, [AIBN] = 5.0 × 10^{-3} mol/L: (▼) **1**, (○) **3a**, (□) **3b**, (△) **3c**, (▽) **3d**, (●) **4a**, (■) **4b**, (▲) **4c**.

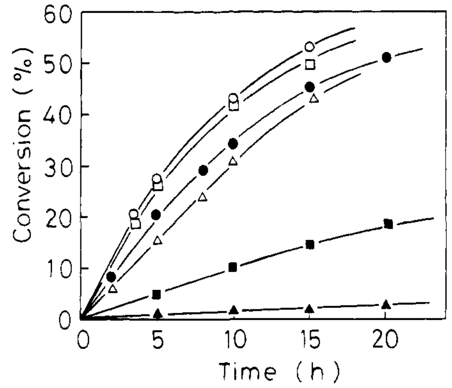


Figure 2. Time–conversion relations of radical polymerization of 2 in benzene at 60 °C, [RPhMI] = 1.0 mol/L, [AIBN] = 5.0 × 10^{-3} mol/L: (○) **2a**, (□) **2b**, (△) **2c**, (●) **2d**, (■) **2e**, (▲) **2f**.

Thermogravimetric Analysis. Thermogravimetric analysis was carried out by using 1.6 mg of the polymer sample in a nitrogen stream with a heating rate of 10 °C/min.

Results and Discussion

Polymerization Reactivity. Radical polymerization of RPhMIs bearing various nuclear substituents was carried out with AIBN in benzene at 60 °C. The time–conversion relations obtained are shown in Figures 1 and 2. The yield, [η], $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ of the resulting polymers are also listed in Table I.

The polymerization of **1**, **2h**, **3b**, and **4a** proceeded in a heterogeneous system because the polymers produced were insoluble in benzene used as solvent, but the other polymerization systems were performed apparently in a homogeneous system. In these polymerizations, the reactivities of RPhMIs were found to change significantly with the number, position, and bulkiness of their nuclear substituents.

The introduction of alkyl groups into meta or para positions of the phenyl nucleus in RPhMI enhanced the polymerization reactivities; e.g., **3** and **4** gave higher polymer yields and $\bar{M}_n$ than **1**. However, the substitution at the ortho positions decreased the reactivities, depending on the bulkiness of alkyl groups introduced. Such an effect was more remarkable in the polymerization of 2,6-disubstituted derivatives; i.e., **2f** gave an oligomer soluble in methanol with low yield. The R_p decreased with the introduction of the bulky substituents at 2- or 2,6-

Table I
Radical Polymerization of RPhMIs in Benzene and in DMF at 60 °C for 5 h[a]

			in benzene				in DMF		
RPhMI	substituent	σ_p or σ_m	yield, %	$[\eta]$,[b] dL/g	$\bar{M}_n$[c] × 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]	yield, %	$\bar{M}_n$[c] × 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]
1	none	0	78.9	0.10[d]	*e*	*e*	12.3	0.46	1.84
2a	2-CH_3	−0.17	27.6	0.17	3.34	1.86	8.6	0.49	3.01
2b	2-C_2H_5	−0.15	26.2	0.096	1.70	1.57	6.3	0.50	2.27
2c	2-*i*-C_3H_7	−0.15	15.3		1.13	2.22			
2d	2,6-$(CH_3)_2$	−0.34	20.4	0.098	1.87	1.57	1.1	0.13	2.01
2e	2,6-$(C_2H_5)_2$	−0.30	5.0	0.040	0.91	1.16	0.68	0.11	1.32
2f	2,6-(*i*-$C_3H_7)_2$	−0.30	0.82[f]		0.33	1.11			
2g	2,4,6-$(CH_3)_3$	−0.51	25.3	0.070	1.12	1.57	2.7	0.40	2.07
2h	2-Cl	0.23	42.4	0.22[d]	*e*	*e*	4.5	*e*	*e*
3a	3-CH_3	−0.07	95.7		*e*	*e*	19.0	1.49	1.99
3b	3-CF_3	0.43	84.3		*e*	*e*	8.0	0.32	2.22
3c	3-C_2H_5	−0.07	92.8	0.40[g]	7.31	3.25[h]	20.8	1.74	2.00
3d	3,5-$(CH_3)_2$	−0.14	94.3		*e*	*e*	15.3	1.95	3.94
4a	4-CH_3	−0.17	84.8[i]	0.28[g]	*e*	*e*	19.1	1.39	2.88
4b	4-C_2H_5	−0.15	94.8[j]	0.31[g]	4.38[j]	3.06[j]	20.4	1.54	2.16
4c	4-*n*-C_4H_9	−0.16	95.6	0.36[g]	6.19	3.10	20.7	1.95	1.98

[a] [Monomer] = 1.0 mol/L, [AIBN] = 5.0 × 10^{-3} mol/L. [b] Determined in benzene at 30 °C. [c] By GPC in THF. [d] In DMF at 30 °C. [e] Insoluble in THF. [f] Soluble in methanol. [g] In chloroform at 30 °C. [h] This large $\bar{M}_w/\bar{M}_n$ was ascribed to its high conversion. The narrow molecular weight distribution around 2 was obtained for the initial stage of the polymerization: polymerization time 0.5 h, polymer yield 23.7% $\bar{M}_w/\bar{M}_n$ = 1.96. Similar results are also obtained for poly(**4b**) and poly(**4c**). [i] [**4a**] = 0.3 mol/L. [j] Polymerized for 4 h.

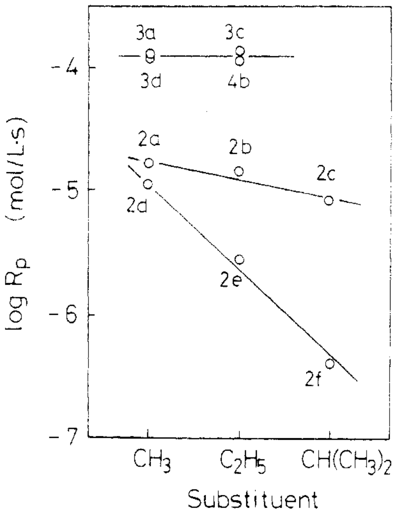


Figure 3. Dependence of the alkyl substituents on the initial polymerization rates (R_p) of RPhMIs. Polymerization conditions are identical with those in Figures 1 and 2.

positions, but it was independent of the bulkiness of the substituents at other positions (Figure 3). Similar tendencies by the ortho substituents were reported for radical polymerizations of phenyl methacrylates and *N*-phenylmethacrylamides.[20]

To compare the reactivities under homogeneous polymerization conditions, DMF was used as a solvent instead of benzene. The results are also shown in Table I. The polymer yields for all maleimides decreased, when compared with those in benzene, and all polymers obtained were of relatively low molecular weight. In the cases of **2d**, **2e**, and **2g**, a pronounced decrease in reactivity was observed for polymerization in DMF, relative to those in benzene. It seems that chain transfer to DMF occurs significantly and reinitiation by the resulting radical might be slow, resulting in the decrease of both yield and $\bar{M}_n$ of the polymers.

The decreasing order of polymer yield and $\bar{M}_n$ was identical with that observed in the polymerization in benzene. It is obvious from Table I that the introduction of electron-donating substituents at meta or para positions tends to enhance an apparent polymerization reactivity and that the introduction of an electron-withdrawing trifluoromethyl group decreased the reactivity. These findings were in accordance with the previous results for radical polymerization of the derivatives with polar substituents in para positions.[7] From the results of the polymerization of **2**, it may be concluded that the steric effect of the ortho substituent, which decreases its monomer reactivity, is more important than the polar effect.

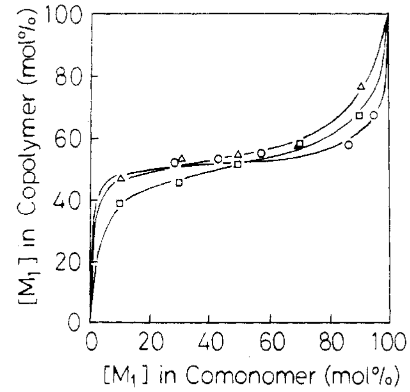


Figure 4. Comonomer–copolymer composition curves for the copolymerization with St in benzene at 60 °C: (○) **1**, (□) **2d**, (△) **2e**.

Copolymerizations with St and MMA. The nuclear substituents of RPhMIs are expected to affect reactivities in not only the homopolymerization but also copolymerization. Therefore, radical copolymerizations of RPhMIs (M_2) with St and MMA (M_1) were attempted. The comonomer–copolymer composition curves for these copolymerizations are shown in Figures 4 and 5. The monomer reactivity ratios determined and the Q_2 and e_2 values calculated are summarized in Table II.

It is well-known that many maleimide derivatives undergo alternating copolymerization with St regardless of the kind of N-substituents.[21] RPhMIs used in this study were also found to copolymerize alternatingly with St. The copolymerization of **1** with St proceeded rapidly, i.e., about 10 times faster than those of **2**. For example, the copolymerization rates of **1**, **2d**, and **2e** with St were 31.7, 3.64, and 3.33 × 10^{-6} mol/L·s, respectively ($[M_1] = [M_2] = 0.175$ mol/L, [AIBN] = 1 × 10^{-3} mol/L in benzene at 60 °C). Moreover, the copolymerization rate of **2e** was lower than that of **2d**, indicating that the reactivity decreased with an increase in the bulkiness of the substituent. The relative

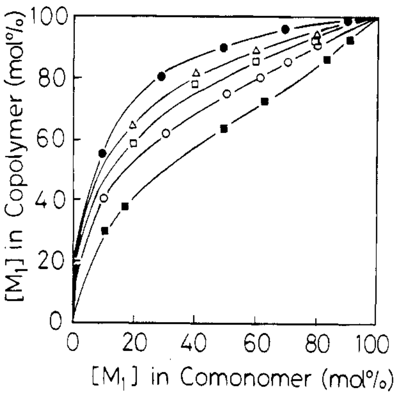


Figure 5. Comonomer–copolymer composition curves for the copolymerization with MMA in benzene at 60 °C: (○) 2a, (□) 2d, (△) 2e, (●) 2f, (■) 3a.

Table II
Radical Copolymerization of RPhMI (M_2) with St or MMA (M_1) in Benzene at 60 °C

M_1	M_2	r_1	r_2	$1/r_1$	Q_2[a]	e_2[a]
St	**1**	0.07	0.01	14		
	2d	0.14	0.08	7.2		
	2e	0.19	0.02	5.3		
MMA	**1**	0.91[b]	0.30[b]	1.10	1.29	1.54
	2a	2.22	0.09	0.45	0.55	1.65
	2d	3.62	0.07	0.28	0.33	1.57
	2e	4.78	0.05	0.21	0.25	1.59
	2f	10.9	0.02	0.092	0.11	1.56
	2h	2.10	0.10	0.48	0.58	1.64
	3a	1.18	0.22	0.84	1.00	1.56
	3b	1.57	0.10	0.64	0.81	1.75
	3d	1.63	0.28	0.61	0.65	1.30
	4a	0.83[b]	0.34[b]	1.20	1.40	1.53
	5[c]	1.35	0.24	0.71	0.80	1.44
	6[d]	2.50	0.17	0.40	0.44	1.35

[a] With $Q_1 = 0.74$ and $e_1 = 0.40$ for MMA. [b] Recalculated by the nonlinear least-squares method from the data in the literature.[7] [c] N-Cyclohexylmaleimide.[15] [d] N-Unsubstituted maleimide.[21]

reactivity of **2** toward a polystyryl radical ($1/r_1$) was also observed to decrease as shown in Table II.

The reactivities of RPhMIs toward the poly(MMA) radical decreased when the bulkier alkyl groups were introduced in the ortho position, similar to the copolymerization with St. The apparent Q_2 values for **2**, which were calculated from those of MMA ($Q_1 = 0.74$ and $e_1 = 0.40$), were small as compared with **1**, although e_2 values were similar to each other. This lowering in the Q_2 values should be interpreted as an expression of the steric hindrance to both resonance stabilization and propagation by introduction of ortho substituents.[22]

The relative reactivities of RPhMIs toward the electron-accepting poly(MMA) radical were plotted against Hammett's substituent constants. The results are shown in Figure 6, in which the straight line relationship ($\rho = -0.18$) reported for para-substituted derivatives[7] is also indicated. Similar results were also observed for other five-membered cyclic imides from unsaturated dibasic acids.[23]

It is noted that the plots for meta-substituted compounds obtained here were deviated slightly to the lower side from the line. Moreover, the pronounced decrease in reactivities was observed for ortho-substituted derivatives, as is seen in Figure 6, strongly indicating that the steric effect of these ortho substituents played an important role beyond their polar and resonance effects.[24]

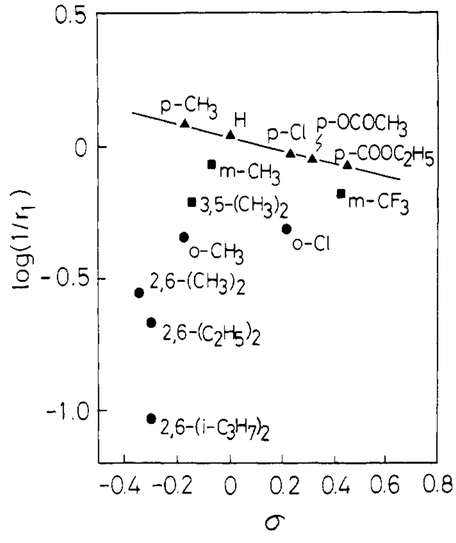


Figure 6. Hammett's plot of relative reactivity ratios of RPhMIs toward a poly(MMA) radical at 60 °C: (●) ortho-substituted RPhMIs, (■) meta-substituted RPhMIs, (▲) para-substituted RPhMIs.[7]

Table III
Spectral Data of RPhMIs

	UV[a]			^{13}C NMR[b]	
RPhMI	λ_{max}, nm (ϵ, L/mol·cm)	ϵ at 400 nm, L/mol·cm	IR[a] $\nu_{C=O}$, cm^{-1}	$\delta_{C=O}$, ppm	δ_{alkyl}, ppm
1	~280[c] (940)	29.8	1722	169.2	
2a	262.5 (930), ~285[c] (620)	5.9	1720	169.4	17.6
2b	262.5 (860), ~285[c] (570)	4.4	1720	169.8	24.3, 14.2
2c	262.0 (850), 287.5 (560)	3.8	1720	170.0	28.7, 23.6
2d	265.0 (870), 290.0 (500)	1.7	1720	169.2	17.5
2e	264.5 (880), 290.5 (500)	1.4	1718	170.1	24.5, 14.4
2f	264.0 (770), 291.5 (450)	1.2	1718	170.4	29.2, 23.9
2g	266.5 (670), ~285[c] (490)	6.9		169.4	20.9, 17.6
2h	~285[c] (1640), ~270[c] (1560)	2.9		168.7	
4a	~275[c] (2940)	57.7		169.5	20.9

[a] In ethanol. [b] In $CDCl_3$. [c] Shoulder.

To examine further the decreased polymerization reactivity by the ortho substituents, the effect of the substituents on the structure of RPhMI monomers was investigated. From molecular model of **2**, it is clear that the repulsion between the alkyl substituents in the phenyl nucleus and the carbonyl groups in the maleimide ring of **2** is important and that the phenyl group cannot keep a coplanar structure with the maleimide ring. It is expected that the repulsion increases with the bulkiness of the substituents and that the greater effect is expected in the 2,6-disubstituted monomer rather than the monosubstituted one.

In the UV spectra of **2** (Table III), the shift of absorption bands and the decreased absorption coefficients were observed. They are correlated with conformational change between the maleimide and phenyl rings because of the increment of steric hindrance by the introduction of ortho substituents. Moreover, the absorbance at the visual region decreased with an increase in bulkiness and the number of the ortho substituents. The apparent color of RPhMIs changed from yellow to colorless. The shift of the wavenumber of carbonyl stretching vibration in the IR region was also detected. In ^{13}C NMR spectra, however, an upfield shift by steric compression between the ortho substituent and the carbonyl group was not observed.

The twist of the phenyl groups should lead to a reduction in the polymerization reactivity because of the following

Table IV
Solubility of Poly(RPhMI)s[a]

polymer[b]	DMF	DMSO	AcAn	TFA	NBz	Actn	Chlo	Bz	THF	EtAc	CTC
poly(**1**)	s	s	i	s	s	i	i	i	i	i	i
poly(**2a–g**)[c]	s	s	s	s	s	s	s	s	s	s	i[d]
poly(**2h**)	s	s	i	s	s	i	i	i	i	i	i
poly(**3a**)	sw	sw	i	s	sw	sw	s	sw	sw	sw	i
poly(**3b**)	sw	sw	i	i	sw	i	i	i	i	i	i
poly(**3c**)	s	sw	sw	s	s	s	s	s	s	s	i
poly(**3d**)	sw	sw	i	s	sw	i	sw	sw	sw	i	i
poly(**4a**)	s	i	i	s	s	i	s	i	i	i	i
poly(**4b**)	s	i	i	s	s	i	s	sw	s	sw	i
poly(**4c**)	s	i	i	sw	s	sw	s	sw	s	sw	i

[a] s, soluble; sw, swelling; i, insoluble. DMF, dimethylformamide; DMSO, dimethyl sulfoxide; AcAn, acetic anhydride; TFA, trifluoroacetic acid; NBz, nitrobenzene; Actn, acetone; Chlo, chloroform; Bz, benzene; THF, tetrahydrofuran; EtAc, ethyl acetate; CTC, carbon tetrachloride. [b] Prepared for polymerization in benzene at 60 °C. [c] Except for poly(**2f**), which was soluble in all solvents because of its low molecular weight. [d] Except for poly(**2c**) and poly(**2g**).

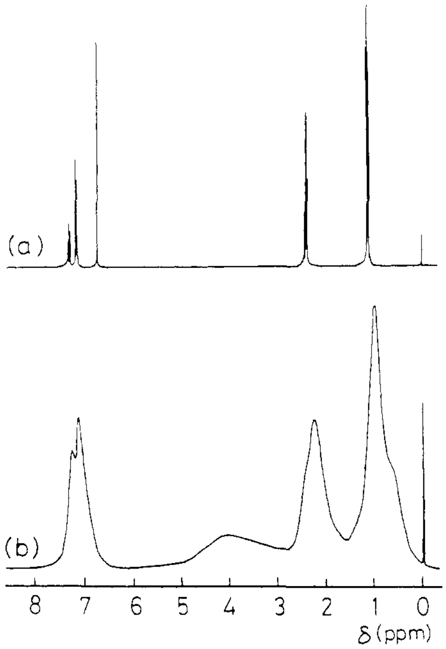


Figure 7. ^{1}H NMR spectra of **2e** (a) and poly(**2e**) (b) in $CDCl_3$.

two reasons: One is the lowering of monomer reactivity by the prohibition of resonance between the imide ring and a phenyl group, and another is steric hindrance of the alkyl groups at a position that is located near the reacting center, i.e., the carbon-to-carbon double bond, by the perpendicular orientation of the phenyl ring. The fact that the Q_2 values of **2** were much lower than those of *N*-cyclohexylmaleimide (**5**) and N-unsubstituted maleimide (**6**), which have no stabilizing moiety, might suggest that the latter factor, i.e., the direct steric hindrance of the propagation reaction, is also significant.

Characterization of the Polymers. The solubility of poly(RPhMI)s was summarized in Table IV. All polymers were colorless and insoluble in methanol, cyclohexane, and *n*-hexane. The polymers from **2** except for poly(**2h**) were soluble in many organic solvents. Poly(**2c**) and poly(**2g**) were soluble even in carbon tetrachloride, although other poly(**2**)s were insoluble. Poly(**2h**) had a solubility similar to poly(**1**) rather than other poly(**2**)s. The polymers bearing a *m*-methyl group, i.e., poly(**3a**) and poly(**3d**), were observed to be swelled in benzene in THF. The introduction of an ethyl group resulted in formation of soluble polymer. Poly(**3b**) was insoluble in all solvents examined, although it swelled slightly in DMF, dimethyl sulfoxide, and nitrobenzene. All poly(**4**)s were soluble in DMF, nitrobenzene, and chloroform. Poly(**4**)s substituted by ethyl and *n*-butyl groups were also soluble in THF.

The copolymers of **2**–**4** with St or MMA were also colorless powders and soluble in many organic solvents. The copolymer of **3b** with MMA was soluble in DMF, although its homopolymer of **3b** was insoluble.

In the ^{1}H NMR and ^{13}C NMR spectra of poly(**2e**), the absorption due to a carbon-to-carbon double bond in the monomer disappeared (Figure 7), indicating that radical polymerization of **2e** proceeded via an opening of the double bond (vinyl polymerization) to give a semiflexible poly(substituted methylene).[3,25] Similar results were also observed for the other RPhMIs. These polymethylenes had some features different from ordinary flexible vinyl polymers; i.e., they did not melt below their decomposition temperature, as is stated later. Transparent and brittle films of poly(RPhMI)s could be obtained by casting of their chloroform solution.

Thermal Stability of the Polymers. Poly(RPhMI)s showed good thermal stabilities; e.g., they did not show any change in appearance after heating below 300 °C in air. Poly(**1**) and methyl- or trifluoromethyl-substituted derivatives of poly(RPhMI)s underwent decomposition without softening and melting, when they were heated in vacuo from room temperature to above 400 °C. The polymers bearing an ethyl or *n*-butyl group were softened, accompanying their decomposition. The change in the molecular weight of the polymer after thermal treatment was investigated. After poly(**2d**) was heated isothermally at 340 °C in vacuo for 30 min, no change was observed in appearance, solubility, and molecular weight and its distribution. The polymer recovered after being heated at 360 °C turned slightly yellow and partly insoluble in THF. The $\bar{M}_n$ of the THF-soluble fraction of the polymer was found to decrease from 1.4 × 10^4 to 1.2 × 10^4 by GPC. When it was heated at 340 °C in air, a colored and insoluble polymer was recovered.

Furthermore, thermogravimetric analysis (TGA) was carried out in a nitrogen stream from room temperature to 500 °C. As shown in the thermograms (Figure 8), all polymers had no weight loss below about 370 °C. The *initial decomposition temperatures* (T_{init}), the maximum decomposition temperature (T_{max}), the half weight loss temperature (T_{50}), and the residual weight at 500 °C are summarized in Table V. The decomposition temperatures of poly(RPhMI)s were higher than those for poly(**1**), indicating that these polymaleimides have excellent thermal stability. The effect of alkyl substituents on the stability was in the following order in position: *o*- or *p*-methyl > *m*-methyl > none. That in the alkyl group was as follows: methyl > ethyl > none, although their difference was relatively small.

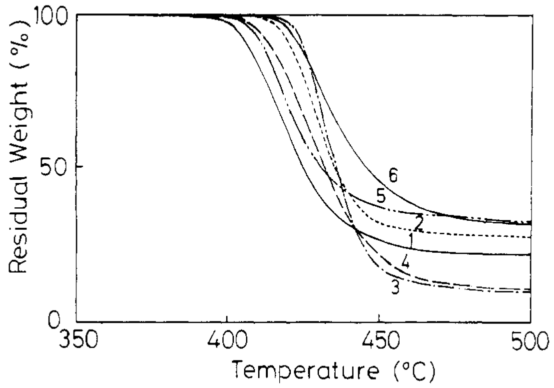


Figure 8. Thermogravimetric analysis in a nitrogen stream: (1) poly(**1**), (2) poly(**2a**), (3) poly(**2d**), (4) poly(**2e**), (5) poly(**3a**), (6) poly(**4a**). Heating rate: 10 °C/min.

Table V
Results of Thermogravimetric Analysis[a]

polymer	T_{init}, °C	T_{max}, °C	T_{50}, °C	residue at 500 °C, %
poly(**1**)	364	422	425	21.5
poly(**2a**)	392	427	435	27.2
poly(**2d**)	393	435	436	11.3
poly(**2e**)	378	432	432	12.0
poly(**2h**)	404	432	441	38.2
poly(**3a**)	388	418	431	33.1
poly(**3b**)	369	427	425	10.5
poly(**4a**)	402	422	446	31.8

[a] In a nitrogen stream with a heating rate of 10 °C/min.

Conclusions

Radical polymerization and copolymerization reactivities of *N*-(alkyl-substituted phenyl)maleimides were revealed to depend on the position, number, and bulkiness of the alkyl substituents; i.e., the introduction of alkyl groups into the ortho position decreased the yield and molecular weight of the polymers obtained in homopolymerization by steric hindrance and also decreased the relative reactivities of the monomers in copolymerization with styrene or methyl methacrylate. The meta and para substitutions induced increase of homopolymerization reactivity because of the introduction of electron-donating alkyl groups, but the slight decrease of the relative reactivity in copolymerization by a steric factor was observed in the meta substitution. The polymers produced were soluble in common organic solvents including benzene, chloroform, and THF. These alkyl-substituted polymers showed an excellent thermal stability as well as poly(*N*-phenylmaleimide).

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Registry No. 1, 941-69-5; 1 (homopolymer), 25101-57-9; (**1**)(St) (alternating copolymer), 115794-14-4; (1)(MMA) (copolymer), 32554-23-7; **2a**, 4067-01-0; **2a** (homopolymer), 35283-95-5; (**2a**)(MMA) (copolymer), 38744-39-7; **2b** (homopolymer), 129265-95-8; **2c** (homopolymer), 129265-96-9; **2d**, 1206-49-1; **2d** (homopolymer), 127377-32-6; (**2d**)(St) (alternating copolymer), 129266-05-3; (**2d**)(MMA) (copolymer), 117955-61-0; **2e**, 38167-72-5; **2e**, 129265-97-0; (**2e**)(St) (alternating copolymer), 129266-06-4; (**2e**)(MMA) (copolymer), 117955-60-9; **2f**, 56746-12-4; **2f** (homopolymer), 129265-98-1; (**2f**)(MMA) (copolymer), 129266-07-5; **2g**, 55862-98-1; **2g** (homopolymer), 129265-99-2; **2h**, 1203-24-3; **2h** (homopolymer), 37452-83-8; (**2h**)(MMA) (copolymer), 38807-39-5; **3a**, 20299-79-0; **3a** (homopolymer), 129285-51-4; (**3a**)(MMA) (copolymer), 129266-08-6; **3b**, 53629-19-9; **3b** (homopolymer), 129266-00-8; (**3b**)(MMA) (copolymer), 129266-09-7; **3c**, 129265-92-5; **3c** (homopolymer), 129266-01-9; **3d**, 65833-09-2; **3d** (homopolymer), 129266-02-0; (**3d**)(MMA) (copolymer), 129266-10-0; **4a**, 1631-28-3; **4a** (homopolymer), 25989-85-9; (**4a**)(MMA) (copolymer), 129266-11-1; **4b**, 76620-00-3; **4b** (homopolymer), 129266-03-1; **4c**, 65833-02-5; **4c** (homopolymer), 129266-04-2; (**5**)(MMA) (copolymer), 105469-99-6; (**6**)(MMA) (copolymer), 29061-91-4; St, 100-42-5; MMA, 80-62-6.