

NOTES

Anionic Polymerizations of *N*-Substituted Isomaleimide

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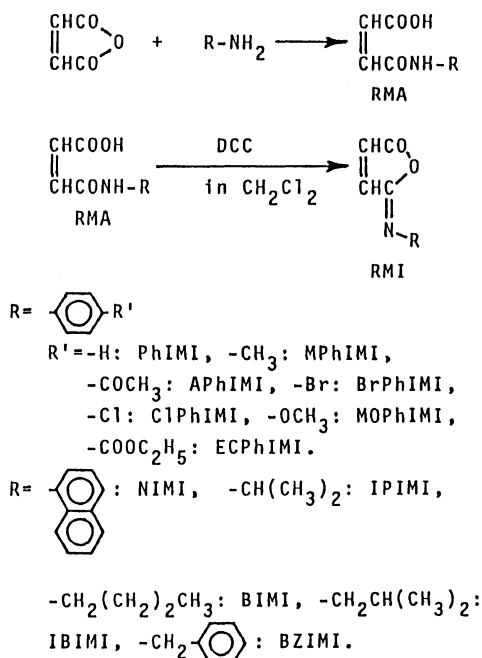
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In order to obtain more detailed information on the polymerization behavior of an unsaturated dibasic acid and its derivatives, particularly five-membered cyclic imides, we investigated the reactivities of *N*-substituted maleimide,¹⁻³ *N*-(4-substituted phenyl)isomaleimide,⁴⁻⁶ *N*-substituted itaconimide,^{7,8} *N*-substituted citraconimide,^{9,10} *N*-substituted isocitraconimide,¹¹ and alkyl *N*-(4-substituted phenyl)itaconamate.¹² It was found that *N*-(4-substituted phenyl)isomaleimide (RPhIMI) are capable of radical homopolymerization and the obtained homopolymers have both structure of maleimide and isomaleimide⁶ units and that RPhIMI has good radical copolymerizability with four common vinyl monomers, as reported in the previous papers.^{4,5} That is, the reactivities of RPhIMI in radical copolymerizations with the vinyl monomers were investigated in detail.⁴⁻⁶ In this note, anionic polymerizations of *N*-substituted isomaleimide (RIMI) and anionic copolymerization of RIMI with styrene (ST) or methyl methacrylate (MMA) are investigated.

EXPERIMENTAL

12 types of RIMI were synthesized according to the method by Cotter *et al.*,¹³ as shown in Scheme 1. *N*-Substituted maleamic acid



Scheme 1.

(RMA) was prepared from maleic anhydride and the primary amine in diethyl ether at 0—5°C. RMA was treated with *N,N'*-dicyclohexylcarbodiimide (DCC) in dichloromethane to give crude RIMI, which was recrystallized several times from ether-petroleum ether (1:1) or was distilled under reduced pressure in cases of alkyl isomaleimides. RIMI was identified on the basis of

Table I. Yields, melting points, and boiling points of *N*-substituted isomaleimides (RIMI)

RIMI	mp, [bp]	Yield ^a
	°C, [°C mmHg ⁻¹]	%
PhIMI	63	87
MPhIMI	70	63
APhIMI	122	49
BrPhIMI	102	48
ClPhIMI	97	66
ECPHIMI	62	65
MOPhIMI	77	75
NIMI	71	50
IPIMI	[63/7]	62
<i>n</i> -BIMI	[96/6]	57
IBIMI	[89/7]	58
BZIMI	49	46

^a Based on *N*-substituted maleamic acids.

the results of elemental analysis, IR and ¹H NMR spectra. Yields, melting points, and boiling points are shown in Table I.

ST, MMA, 2,2'-azobisisobutyronitrile (AIBN), toluene, tetrahydrofuran (THF), and methanol were purified by the usual methods. Commercial *n*-butyllithium (BuLi) (15% in *n*-hexane) was used without further purification.

Anionic homopolymerizations of RIMI were carried out with BuLi as an initiator at several temperatures. Toluene (10 ml) and RIMI were placed in a dry glass ampule under nitrogen. The solution was cooled to -78°C and then degassed under vacuum by the ordinary freeze-thaw technique. The catalyst solution was added to the solution using a syringe at a constant temperature. During the polymerization, the solution was magnetically stirred. The polymerization was terminated by the addition of a small amount of methanol and the polymer was precipitated in diethyl ether.

The anionic copolymerizations of RIMI with ST or MMA were carried out in the same way.

The radical homopolymerizations and copolymerizations of RIMI with ST or MMA were performed in the presence of AIBN as

an initiator in THF at 70°C, in the same procedure as described previously.⁴

The composition of the copolymer was calculated from nitrogen analysis. The monomer reactivity ratios (r_1, r_2) were determined according to the method by Fineman and Ross.¹⁴ The molecular weights of the polymers were measured by GPC as described previously.¹⁵ A vapor pressure osmometer (Corona Ltd.) was also used to estimate the molecular weights of homopolymers. In this apparatus, the vapor of benzene was used.

RESULTS AND DISCUSSION

Homopolymerization of RIMI

The results of anionic homopolymerization of RIMI are shown in Table II. Anionic homopolymerizations of RIMI were performed at temperature range from -78 to 50°C, but considerable amounts of polymer could be obtained for 8 h only at 20°C. In general, the molecular weights (\bar{M}_w) were similar to those of the radical polymerizations. It can be seen from Table II that the obtained homopolymers were oligomers having 2 to 5 degrees of polymerization. The reason for the low molecular weights may be attributable to the steric hindrance of *N*-substituents located in the neighborhood of the double bond of RIMI, as pointed out previously.⁴⁻⁶ The obtained polymers consisted of both the structure of isomaleimide and maleimide, as judged by IR and ¹H NMR spectra. In the IR spectra for homopolymers, as shown in Figure 1, the peaks of 5-membered imide ring were observed at 1710 and 1770 cm⁻¹, instead of the peaks for the lactone ring at 1790 cm⁻¹ (branches). In the ¹H NMR of the homopolymer, as shown in Figure 2, two peaks (δ values = 3.6 and 4.0 ppm in CDCl₃ using TMS as a standard) due to CH in the 5-membered isomaleimide ring were observed. If all the isomaleimide ring were converted to the maleimide ring, CH in the 5-membered ring would have indicated one peak at 3.6 ppm in ¹H NMR spectra (Figure

Table II. Anionic homopolymerizations of RIMI^a

RIMI	Conversion	Degree of polymerization ^b	Softening point	η_{sp}/c^c
	%		°C	dl g ⁻¹
PhIMI	11.7	3–4	102–152	—
MPhIMI	19.4	3–4	167–182	0.15
APhIMI	34.7	4–5	202–231	0.13
BrPhIMI	24.7	3–4	185–218	0.11
ClPhIMI	32.1	3–4	122–182	—
MOPhIMI	25.9	3–4	113–162	—
NIMI	9.1	—	171–192	—
IPIMI	12.5	5–6	138–174	0.11
<i>n</i> -BIMI	11.7	4–5	122–163	0.12
BZIMI	11.9	4–5	107–135	0.14

^a Concentration of monomer = 2.0 mol l⁻¹; toluene = 10 ml; initiator = *n*-BuLi (3.1 × 10⁻² mol l⁻¹); polymerization time = 8.0 h; polymerization temperature = 20°C.

^b By VPO.

^c In THF at 30°C.

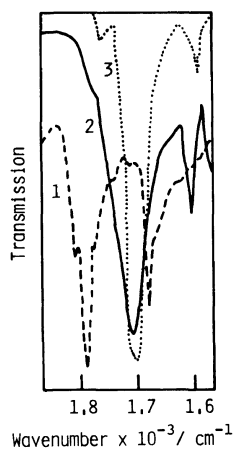


Figure 1. IR spectra for (1) PhIMI monomer (2) PhIMI homopolymer (3) *N*-phenyl maleimide (PhMI) homopolymer.

1). Thus the homopolymer may have the structure illustrated in Scheme 2. The polymers contained 35 to 45 mol% of RIMI units, as calculated from the NMR spectra.

Anionic Copolymerizations

Anionic copolymerizations of RIMI with ST or MMA were carried out in the presence of BuLi (3.1 × 10⁻² mol l⁻¹) at 20°C. The concentrations of RIMI (M₁) and ST (M₂) or MMA (M₂) in monomer feeds were changed

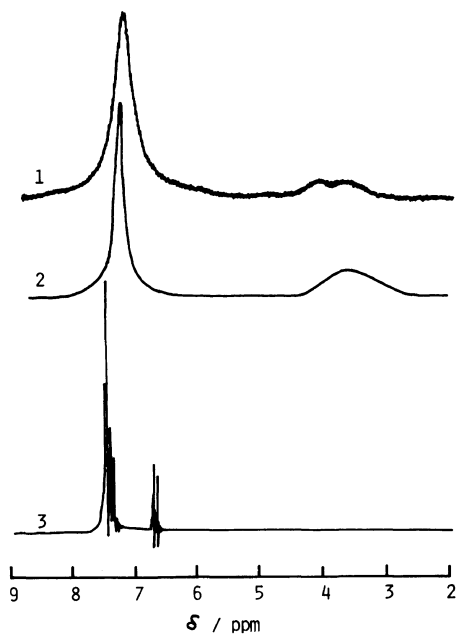
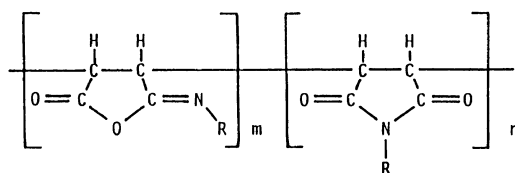


Figure 2. ¹H NMR spectra for (1) PhIMI homopolymer (2) *N*-phenyl maleimide (PhMI) homopolymer (3) PhIMI monomer.

so as to obtain the copolymer composition curves. The conversions of the copolymers were within 5 to 10% when polymerization time was 10 min. The copolymerization proceeded homogeneously throughout. Two typi-



Scheme 2.

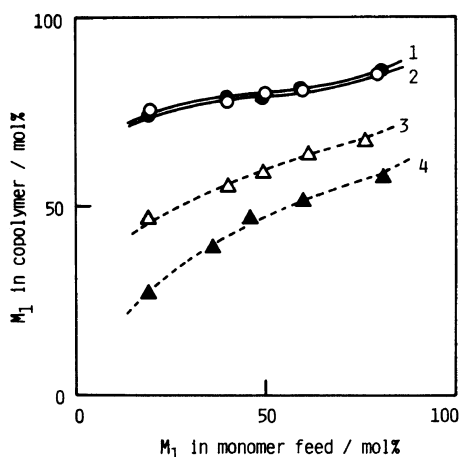


Figure 3. Copolymer composition curves for the RIMI (M_1) and ST (M_2) or MMA (M_2) systems: (1) ECPHIMI–ST (by anionic initiator); (2) ECPHIMI–MMA (by anionic initiator); (3) ECPHIMI–ST (by radical initiator); (4) ECPHIMI–MMA (by radical initiator).

cal types of copolymer composition curves for RIMI–ST and RIMI–MMA system are shown in Figure 3, in which typical composition curves in radical copolymerizations are also indicated (curves 3 and 4 in Figure 3). It can be seen from Figure 3, generally, that the reactivities in anionic copolymerizations were higher than those in the radical copolymerization. The copolymer–composition curves for RIMI with ST were similar to those for RIMI with MMA. Table III indicates the monomer reactivity ratios (r_1, r_2) for the copolymerizations of RIMI (M_1) with ST (M_2) or MMA (M_2). The monomer reactivity ratios in radical copolymerizations are also indicated in Table III. The values of r_1 were much larger than those of r_2 having almost zero within experimental error. This suggests that the relative reactivities ($1/r_2$) of the RIMI monomers toward an attack by a polystyryl anion were very high. On the other hand, the relative reactivities ($1/r_1$) of ST monomer toward an attack by a RIMI anion, especially of 4-substituted phenyl group, would not be correlated with the Hammett σ constants (ρ = almost zero). Thus, the reactivities appear to be much influenced

Table III. Anionic copolymerization parameters of RIMI

RIMI (M_1)	Comonomer (M_2)	Monomer reactivity ratios			
		r_1	r_2	(r_1) ^a	(r_2) ^a
PhIMI	ST	0.85 ± 0.1	0 ± 0.1	(0.26) ^b	(0.25) ^b
MPhIMI	ST	1.14 ± 0.09	0 ± 0.1	(0.01) ^b	(0.27) ^b
ClPhIMI	ST	0.89 ± 0.1	0 ± 0.1	(0.03) ^b	(0.22) ^b
ECPHIMI	ST	1.05 ± 0.08	0 ± 0.08	(0.56) ^b	(0.12) ^b
MOPHIMI	ST	0.60 ± 0.07	0 ± 0.08	(0.16) ^b	(0.16) ^b
NIMI	ST	1.08 ± 0.05	0 ± 0.09	(0.62) ^b	(0.08) ^b
IPIMI	ST	—	—	(0.13)	(0.54)
<i>n</i> -BIMI	ST	0.49 ± 0.05	0 ± 0.05	(0.11)	(0.40)
BZIMI	ST	1.26 ± 0.09	0 ± 0.08	(0.21)	(0.20)
MPhIMI	MMA	0.74 ± 0.07	0 ± 0.09	—	—
ECPHIMI	MMA	1.24 ± 0.09	0 ± 0.09	(0.40) ^b	(0.71) ^b
NIMI	MMA	0.55 ± 0.07	0 ± 0.09	(0.88) ^b	(2.13) ^b
IPIMI	MMA	0.65 ± 0.06	0 ± 0.09	(0.04)	(3.80)
<i>n</i> -BIMI	MMA	0.78 ± 0.08	0 ± 0.07	(0.06)	(2.85)
BZIMI	MMA	2.50 ± 0.2	0 ± 0.2	(0.18)	(4.30)

^a Monomer reactivity ratios for the radical copolymerizations.

^b See ref 4 and 5.

not by the polar character but by the steric hindrance of the *N*-substituents in the neighborhood of the double bond in RIMI. This tendency was recognized in the *N*-alkyl substituted isomaleimide systems. IR spectra for the RIMI-ST and RIMI-MMA system copolymers indicated the same patterns at a wave number range from 1600 to 1900 cm^{-1} as the homopolymers shown in Figure 1(2). In the ^1H NMR spectra for the copolymers, two signals were observed at 3.6 and 4.0 ppm. Thus the isomaleimide ring was apparently converted to the maleimide ring in 55 to 65 mol% yield. The weight average molecular weights \bar{M}_w of the obtained copolymers were 2.3×10^3 to 2.5×10^4 . \bar{M}_w of RIMI-ST copolymers were larger than those of RIMI-MMA copolymers.

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