

Polymerizations and Copolymerizations of *N*-Substituted Itaconimides

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Abstract

Homopolymerizations and copolymerizations of *N*-phenyl itaconimide (PhII), *N*-(4-chlorophenyl) itaconimide (ClPhII), *N*-(4-methylphenyl) itaconimide (MPhII), and *N*-1-naphthyl itaconimide (NII) were carried out at 60°C by using azobisisobutyronitrile (AIBN) as an initiator in tetrahydrofuran. The initial rates of the polymerization were $R_p = k[AIBN]^{0.6}[PhII]^{1.5}$, $R_p = k[AIBN]^{0.5}[ClPhII]^{1.1}$, $R_p = k[AIBN]^{0.5}[MPhII]^{1.0}$, and $R_p = k[AIBN]^{0.5}[NII]^{1.0}$, where k is rate constant. The over-all activation energies (E) and frequency factors (A) were $E = 19.5$ kcal/mol (PhII), 16.1 kcal/mol (ClPhII), 20.1 kcal/mol (MPhII), 17.5 kcal/mol (NII) and $A = 9.9 \times 10^9$ (PhII), 3.1×10^7 (ClPhII), 1.7×10^{10} (MPhII), 4.5×10^8 (NII). The reactivity ratios were determined as $r_1 = 0.08$, $r_2 = 0.05$; $r_1 = 0.14$, $r_2 = 0.15$; $r_1 = 0.24$, $r_2 = 0.16$; $r_1 = 0.35$, $r_2 = 0.08$ for the copolymerizations of PhII, ClPhII, MPhII and NII (M_1) with styrene (M_2), respectively. The Q and e values calculated from these reactivity ratios were $Q = 1.9$, $e = 1.6$ for PhII; $Q = 1.4$, $e = 1.2$ for ClPhII; $Q = 1.5$, $e = 1.0$ for MPhII; and $Q = 2.7$, $e = 1.1$ for NII.

1. Introduction

As studies on syntheses and polymerizations of α , β -unsaturated dibasic acid and its derivatives, the authors have synthesized various type of *N*-substituted maleimides and studied their polymerization properties¹⁻⁴).

To continue the previous study, the authors studied itaconic acid derivatives. From the polymerization reaction point of view, a linear polymer can be produced from itaconic acid by addition polymerization, and unsaturated polyester or polyamide by condensation reaction with two carboxylic acids, or substance containing two functional groups. Many studies have been carried out on the polymerization of itaconic acid and its derivatives⁵⁻⁸). However, in those studies its derivatives containing nitrogen have been synthesized only⁹⁻¹¹), not carried out on the polymerization.

Four types of *N*-substituted itaconimides containing nitrogen: *N*-phenyl itaconimide (PhII), *N*-(4-chlorophenyl) itaconimide (ClPhII), *N*-(4-methylphenyl) itaconimide (MPhII) and *N*-1-naphthyl itaconimide (NII) were synthesized and their homopolymerization rate equation studied; apparent activation energy, and frequency factor values obtained. Also, copolymerizations with styrene (St) and methyl methacrylate (MMA) were carried out, and the monomer reactivity ratios and Q , e values were calculated. Also, by comparison with the polymerization parameters obtained so far

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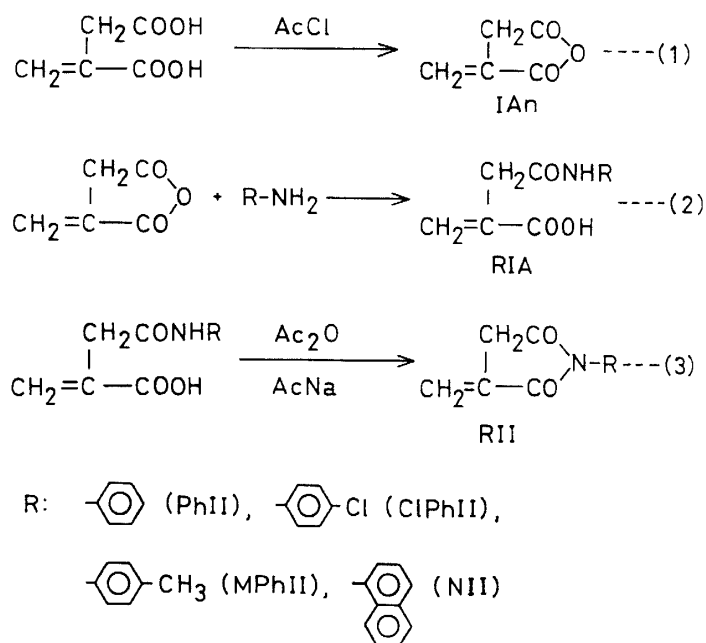
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of *N*-substituted maleimide in the five-number ring containing nitrogen, we considered whether or not these *N*-substituted itaconimides have unusual characteristics.

2. Experimental

2.1 Synthesis of monomers

Four types of *N*-substituted itaconimide were synthesized following processes (1), (2), and (3), according to the method of Akashi⁸, or Metha *et al.*¹².



Scheme 1

A mixture of 50 g (0.38 mol) of itaconic acid and 100 ml of acetyl chloride was refluxed for an hour. After refluxed for another 15 minutes, acetyl chloride and acetic acid produced were distilled away under reduced pressure (17 mmHg) in nitrogen atmosphere. Further, adding 60 ml of toluene to the mixture, they were completely distilled away. During distillation, the reaction temperature was maintained at under 80°C. Adding 100 ml of anhydrous ethyl ether to the sirupy residue, 32g of itaconic anhydride was obtained. It was recrystallized from ethyl ether. (mp 68–9°C, yield 74%)

Itaconic anhydride was dissolved in anhydrous ethyl ether solution of the same mol of the first amine was added dropwise for 1 hour. The solution agitated at 0–5°C for 2–3 hours. *N*-substituted itaconamic acid was obtained. (yield 80%)

Then, *N*-substituted itaconamic acid was dissolved in acetic anhydride and the ring closing reaction was carried out by dehydration in the presence of sodium acetate to produce *N*-substituted itaconimide. The products were recrystallized two times from ethanol.

They were identified by elemental analyses, their IR spectra and their NMR spectra.

Table 1 gives the results of the analyses of the *N*-substituted itaconimide monomers and polymers.

2.2 Monomers, initiator and solvents

Azobisisobutyronitrile (AIBN) was used as initiator. Tetrahydrofuran (THF) was used as solvent. In order to purify these compounds, commercial quality AIBN was recrystallized and the THF was dehydrated with sodium metal and distilled before use. The St and MMA monomers were purified by the usual methods before use.

2.3 Polymerization methods

2.3.1 *Homopolymerization.* All the polymerizations were solution processes carried out in closed containers. A specific weight of monomer was added to a tube and a specific amount of THF containing a certain amount of AIBN dissolved in it was then added. While cooling the above ingredients with a freezing mixture, nitrogen was introduced in the tube by the usual method, and then the tube was sealed. The polymerization was carried out while shaking the above-mentioned mixture in a thermostat set at a specified temperature. After a specified time, the tube was opened, and its contents poured into a large amount of methanol to precipitate the polymer produced. After the precipitate was filtered and thoroughly washed with methanol, the polymer was recovered by drying under reduced pressure.

2.3.2 *Copolymerization.* The copolymerization of *N*-substituted itaconimide with St and MMA was carried out using AIBN as an initiator, in THF at 60°C. The composition of the copolymers was obtained from nitrogen elemental analysis results.

2.4 Viscosity measurements

The reduced viscosity of the polymers was measured in THF at 30°C using an Ostwald viscometer.

2.5 Softening point measurements

These determinations were carried out following the general method for melting point measurements in a fused-salt bath containing a mixture of potassium nitrate and sodium nitrate.

3. Results and Discussion

3.1 Homopolymerization

In the homopolymerization of the four itaconimides, all polymerizations proceeded as a homogenized system throughout.

The polymerization of each monomer was carried out at a constant monomer concentration and a constant polymerization temperature (60°C) in the presence of AIBN initiator, using various polymerization times. The polymerization curves were drawn based on the above results. From the slope of initial period linear portion, the

initial rate of over all polymerization R_p was obtained. The R_p was measured for various AIBN concentrations. When the logarithms of these two values were plotted, the lines shown in Figure 1 were obtained. The exponent of the initiator concentration term (m) was measured from the slope of these lines. The results are shown in Table 2.

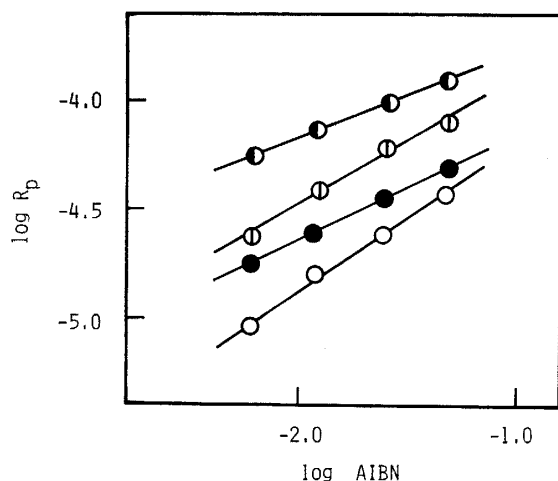


Fig. 1. Effect of the AIBN concentration on the rate of polymerization at 60°C.

- : $[\text{PhII}] = 3.21 \times 10^{-1} \text{ mol/l.}$
- : $[\text{ClPhII}] = 2.71 \times 10^{-1} \text{ mol/l.}$
- ⊙ : $[\text{MPhII}] = 2.99 \times 10^{-1} \text{ mol/l.}$
- ⦿ : $[\text{NII}] = 2.53 \times 10^{-1} \text{ mol/l.}$

Table 1. Elemental analyses of monomers and polymers.

Sample	mp (°C)	H (%)		C (%)		N (%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
PhII (M)	95.5–96.0	4.85	4.72	70.57	70.12	7.48	7.09
PhII (P) ^{a)}	—	4.85	5.08	70.57	70.98	7.48	7.39
ClPhII (M)	131–132	3.64	3.51	59.61	59.71	6.32	6.30
ClPhII (P) ^{b)}	—	3.64	4.01	59.61	60.24	6.32	6.59
MPhII (M)	125–126	5.51	5.44	71.63	71.07	6.96	6.89
MPhII (P) ^{c)}	—	5.51	5.68	71.63	72.07	6.96	6.74
NII (M)	124–124.5	4.67	4.54	75.94	76.00	5.90	6.13
NII (P) ^{d)}	—	4.67	4.98	75.94	75.86	5.90	6.08

(M): Monomer; (P): Polymer.

a) $[\text{PhII}] = 3.26 \times 10^{-1} \text{ mol/l.}$, $[\text{AIBN}] = 1.51 \times 10^{-2} \text{ mol/l.}$

b) $[\text{ClPhII}] = 4.01 \times 10^{-1} \text{ mol/l.}$, $[\text{AIBN}] = 1.51 \times 10^{-2} \text{ mol/l.}$

c) $[\text{MPhII}] = 5.42 \times 10^{-1} \text{ mol/l.}$, $[\text{AIBN}] = 1.51 \times 10^{-2} \text{ mol/l.}$

d) $[\text{NII}] = 4.10 \times 10^{-1} \text{ mol/l.}$, $[\text{AIBN}] = 1.51 \times 10^{-2} \text{ mol/l.}$

Then, the polymerizations were carried out at 60°C with the various monomer concentrations. The concentration of the initiator AIBN was constant. R_p was calculated from the time-conversion relationship. Using the same procedure as for determining m , the relation $\log R_p - \log [M]$ (where $[M]$ is the monomer concentration) was plotted in Figure 2. The exponent of the monomer concentration (n) was obtained from the slope of this line. The results are shown in Table 2.

The following are the polymerization rate equations for the four types of *N*-substituted itaconimides using the values for m and n from Table 2.

Table 2. Rate equations (R_p), rate constants (k), over-all activation energies (E) and frequency factors (A) for the radical polymerization of *N*-substituted itaconimides.

Monomer	$R_p = k[AIBN]^m[M]^n$		k 60°C	E (kcal/mol)	A sec ⁻¹	Reference
	m	n				
PhII	0.6	1.5	1.58×10^{-3}	19.5	9.9×10^9	—
CIPhII	0.5	1.1	8.83×10^{-4}	16.1	3.1×10^7	—
MPhII	0.5	1.0	1.28×10^{-3}	20.1	1.7×10^{10}	—
NII	0.5	1.0	2.29×10^{-3}	17.5	4.5×10^8	—
PhMI ^{a)}	0.80	1.2	—	25.2	8.3×10^{14}	13
NMI ^{b)}	0.55	1.6	8.25×10^{-5}	24.4	8.5×10^{11}	1
n-HMI ^{c)}	0.80	2.5	9.91×10^{-4}	22.8	9.5×10^{11}	3
MMA	0.5	1.0	—	19.9	3.7×10^9	14

 a) *N*-Phenyl maleimide.

 b) *N*-1-Naphthyl maleimide.

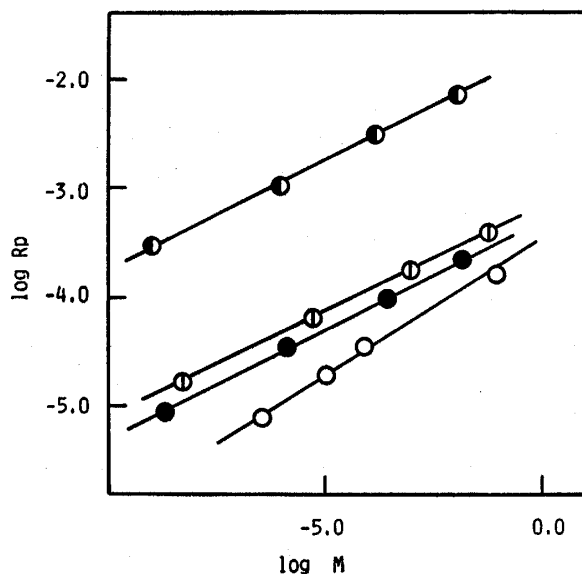
 c) *N*-n-Hexyl maleimide.


Fig. 2. Effect of the monomer concentration on the rate of polymerization at 60°C.

- : [M]=PhII,
[AIBN]= 2.50×10^{-2} mol/l.
- : [M]=CIPhII,
[AIBN]= 2.50×10^{-2} mol/l.
- ⊙: [M]=MPhII,
[AIBN]= 2.50×10^{-2} mol/l.
- ⦿: [M]=NII,
[AIBN]= 2.50×10^{-2} mol/l.

$$R_p = k[AIBN]^{0.6}[PhII]^{1.5} \quad (4)$$

$$R_p = k[AIBN]^{0.5}[CIPhII]^{1.1} \quad (5)$$

$$R_p = k[AIBN]^{0.5}[MPhII]^{1.0} \quad (6)$$

$$R_p = k[AIBN]^{0.5}[NII]^{1.0} \quad (7)$$

k : rate constant

As shown in Table 2, m is about 0.5. You can see that *N*-substituted itaconimides satisfy the ordinary 1/2 power rule, and that they occur the bimolecular termination. The authors¹⁻³⁾ have reported that in the homopolymerization rate equation of

N-substituted maleimides, m is 0.6–0.9, of considerable higher order than 0.5. *N*-Substituted maleimides may differ because of the simultaneous occurrence of monomolecular terminations and bimolecular terminations. But, *N*-substituted itaconimides did not show this tendency. Also, n is about 1 except for PhII. It seems that an ordinary radical addition reaction occurred in copolymerization of *N*-substituted itaconimides. In the case of PhII, the reason for this higher order may be, as pointed out in polymerization of *N*-substituted maleimides¹⁻⁴), a "cage effect".

Then, the polymerization was carried out at constant concentrations of monomers and AIBN, using different temperatures. From these results, the R_p 's were obtained, and they were substituted in rate equations (4), (5), (6), and (7), respectively, for the calculation of rate constants (k). Figure 3 shows the relationship between $\log k$ and

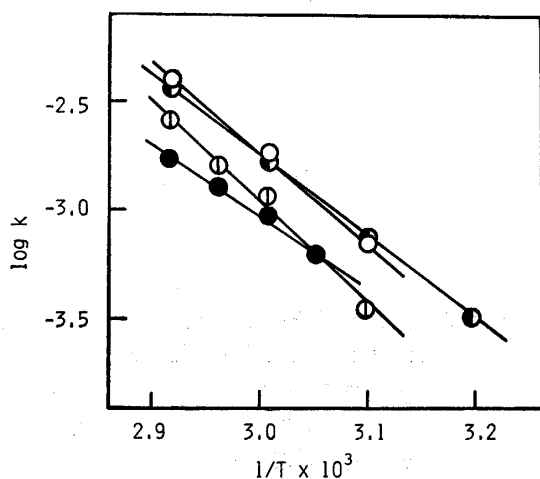


Fig. 3. Relationship between $\log k$ and $1/T$ for the polymerization of *N*-substituted itaconimides initiated by AIBN at various temperatures.

- : $[\text{PhII}] = 3.21 \times 10^{-1} \text{ mol/l}$,
 $[\text{AIBN}] = 2.50 \times 10^{-2} \text{ mol/l}$.
- : $[\text{ClPhII}] = 2.71 \times 10^{-1} \text{ mol/l}$,
 $[\text{AIBN}] = 2.50 \times 10^{-2} \text{ mol/l}$.
- ⊙: $[\text{MPhII}] = 2.99 \times 10^{-1} \text{ mol/l}$,
 $[\text{AIBN}] = 2.50 \times 10^{-2} \text{ mol/l}$.
- ◐: $[\text{NII}] = 2.53 \times 10^{-1} \text{ mol/l}$,
 $[\text{AIBN}] = 2.50 \times 10^{-2} \text{ mol/l}$.

$1/T$. From the slope of this straight line, the activation energy (E) was obtained. Also, using Arrhenius' equation, the frequency factor (A) was calculated. These values were shown in Table 2. To compare these results with those of *N*-substituted maleimides, the polymerization parameters of *N*-substituted maleimides containing five-number ring and MMA, one of the ordinary vinyl compounds, were shown in Table 2, too. As this table indicates, the E and A of *N*-substituted itaconimides measured by the authors are equal to those of MMA. The values, however, when compared with those of *N*-substituted maleimides, are considerably little. The reason for this difference may be as follows: The double bond of *N*-substituted maleimides is placed in five-number ring containing nitrogen, but one of *N*-substituted itaconimides is placed outside five-number ring containing nitrogen. Therefore, the double bond of *N*-substituted itaconimides may be not strongly influenced by carbonyl groups. Also, in comparison with the E and A for three types of *N*-substituted itaconimides, the order of those for *N*-substituted itaconimides is as follows:



Since the reason for this may be related to the e value, we would like to mention it in *Copolymerization*.

3.2 Copolymerization

The copolymerizations of *N*-substituted itaconimide (M_1) with St (M_2), and of *N*-substituted itaconimides (M_1) with MMA (M_2) were carried out at 60°C by using AIBN as initiator. The polymerizations were homogeneous throughout. The results of the polymerizations were shown in Table 3 and Table 4. The monomer-copolymer composition curves obtained from the above results were shown in Figure 4 and Figure 5. Table 3, 4 and Figure 4, 5 indicate that the copolymerization of *N*-substituted itaconimides with St or MMA occurred readily. It is known that the copolymerization of maleic anhydride and *N*-substituted maleimides with St is practically an alternating type process. But, in the *N*-substituted itaconimides-St system, it was found that the molar fraction of *N*-substituted itaconimides in the copolymer tends to increase, as the molar fraction of *N*-substituted itaconimides in the prepared monomer feed increases. On the other hand, in the *N*-substituted maleimides-MMA system, the process was practically an ideal copolymerization along azeotropic line. In the *N*-substituted itaconimides-MMA system, the process was similar to that of the *N*-substituted itaconimides-St system.

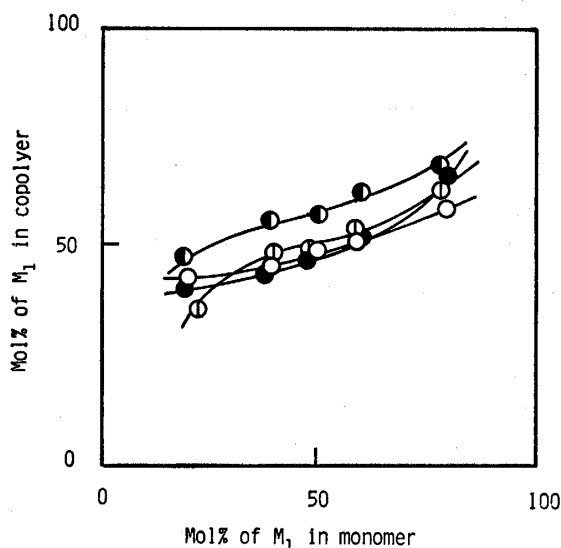
Table 3. Copolymerization of *N*-substituted itaconimide (M_1) with Styrene (M_2) in THF at 60°C.

Monomer	M_1 mol% in monomer	Time (min)	Conversion (%)	N-Analysis (%)	M_1 mol% in copolymer
PhII*	20.0	40	6.7	4.3	44.0
	40.1	15	4.0	4.5	45.2
	50.2	15	6.1	4.8	50.0
	60.0	15	7.6	5.0	52.1
	80.0	13	8.8	5.4	59.0
ClPhII*	19.9	20	4.9	3.8	43.3
	37.2	15	6.7	4.1	45.1
	49.3	15	6.8	4.2	48.9
	60.0	15	9.9	4.4	52.6
	80.7	10	7.1	5.2	68.9
MPhII*	14.4	15	2.6	3.6	35.7
	40.0	15	5.9	4.6	50.2
	49.0	10	7.3	4.6	50.2
	60.0	10	6.1	4.9	55.2
	78.8	10	8.2	5.2	64.3
NII*	19.5	10	3.9	4.0	47.9
	39.8	10	5.2	4.5	57.5
	49.7	10	6.9	4.5	57.5
	59.9	10	7.0	4.7	64.3
	78.9	10	9.7	5.0	70.2

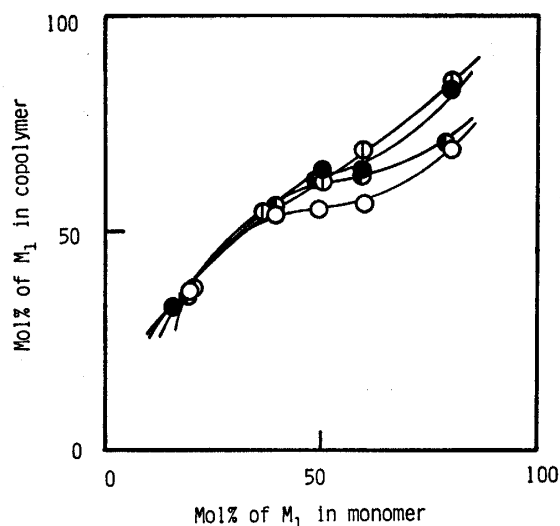
* [AIBN] = 2.5×10^{-2} mol/l, THF = 5 ml.

Table 4. Copolymerization of *N*-substituted itaconimide (M_1) with methyl methacrylate (M_2) in THF at 60°C.

Monomer	M_1 mol% in monomer	Time (min)	Conversion (%)	N-Analysis (%)	M_1 mol% in copolymer
PhII*	19.9	15	6.2	3.9	37.1
	39.9	10	6.5	5.1	54.0
	49.7	10	6.6	5.2	55.3
	60.0	8	4.9	5.3	56.7
	80.4	6	4.2	6.1	69.0
ClPhII*	15.0	20	10.4	3.3	33.2
	39.6	15	11.5	4.6	55.0
	50.2	15	11.1	5.1	65.1
	59.9	15	14.7	5.0	64.3
	79.8	10	5.2	5.9	83.1
MPhII*	20.0	15	9.0	3.8	37.4
	36.2	15	12.7	5.0	54.1
	50.0	10	10.9	5.3	61.4
	59.5	10	13.1	5.7	69.3
	80.0	10	15.0	6.4	85.3
NII*	19.9	10	9.9	3.4	36.2
	39.1	10	9.5	4.4	56.1
	48.7	10	17.0	4.7	61.0
	59.9	10	17.4	4.8	62.9
	77.9	10	18.2	5.0	70.8

* [AIBN] = 2.5×10^{-2} mol/l, THF = 5 ml.Fig. 4. Copolymer composition curves of *N*-substituted itaconimides (M_1) and St (M_2) in THF at 60°C.

○ : PhII-St. ● : ClPhII-St.
 ⊙ : MPhII-St. ⊙ : NII-St.

Fig. 5. Copolymer composition curves of *N*-substituted itaconimides (M_1) and MMA (M_2) in THF at 60°C.

○ : PhII-MMA. ● : ClPhII-MMA.
 ⊙ : MPhII-MMA. ⊙ : NII-MMA.

Table 5. Monomer reactivity ratios for *N*-substituted itaconimides (M_1) and vinyl monomers (M_2), and Q_1 , e_1 values of *N*-substituted itaconimides.

Monomer (M_1)	Monomer reactivity ratios				$Q_1^{a)}$	$e_1^{a)}$	Reference
	$M_2 = \text{St}$		$M_2 = \text{MMA}$				
	r_1	r_2	r_1	r_2			
PhII	0.08	0.05	0.26	0.46	1.9	1.6	—
ClPhII	0.14	0.15	1.05	0.28	1.4	1.2	—
MPhII	0.24	0.16	1.28	0.33	1.5	1.0	—
NII	0.35	0.08	0.42	0.02	2.7	1.1	—
PhMI ^{b)}	0.66 ^{c)}	0.02 ^{c)}	—	—	0.74 ^{e)}	1.75 ^{e)}	13
NMI ^{d)}	0.0	0.15	0.036	1.89	0.75 ^{e)}	2.0 ^{e)}	1
n-HMI ^{f)}	0.08	0.0	0.17	2.02	0.56 ^{e)}	1.43 ^{e)}	3

a) $M_2 = \text{St}$, $Q_2 = 1.0$, $e_2 = -0.8$.

b) *N*-Phenyl maleimide.

c) $M_2 = \text{Vinyl acetate}$, $Q_2 = 0.026$, $e_2 = -0.22$.

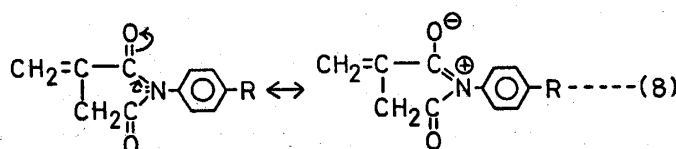
d) *N*-1-Naphthyl maleimide.

e) $M_2 = \text{MMA}$, $Q_2 = 0.74$, $e_2 = 0.40$.

f) *N*-n-Hexyl maleimide.

The monomer reactivity ratios, r_1 and r_2 were obtained by the Fineman-Ross method or the Integration method. Using these values, Q_2 and e_2 of St were assumed to be $Q_2 = 1$ and $e_2 = -0.8$, Q_2 and e_2 of MMA were assumed to be $Q_2 = 0.74$ and $e_2 = 0.4$, and the Q and e of *N*-substituted itaconimides were calculated. The copolymerization parameters were shown in Table 5. In Table 5, the Q and e values of *N*-substituted maleimides were also shown. As this table shows, the every Q value is high, when compared with the Q value of *N*-substituted maleimides, it is higher than that of *N*-substituted maleimides. The e values are high because of polarization of the carbonyl groups, too. However, they are lower than those of *N*-substituted maleimides. As this is mentioned later, the reason for this may be arisen from the difference of structure between *N*-substituted maleimides and *N*-substituted itaconimides, that is, it is probable that the double bond of the point of reaction is difference between "inside" and "outside" of five-number ring containing nitrogen.

Now, in order to compare with the Q and e value of PhII, ClPhII, and MPhII, we proposed the resonance structure as follows:



Scheme 2

That is, owing to the mobile lone electron pair of the nitrogen, the effects of substituent R may affect the double bond of the point of reaction in *N*-substituted itacon-

imides. That is to say, when the substituent R is Cl, the double bond become higher $\delta+$ because of the electron-withdrawing group of Cl. In the case of the substituent, CH_3 , the electron density of double bond may become lower $\delta+$, because of the electron donor of CH_3 group. As Table 5 indicates, the e value of ClPhII is 1.2, and of MPhII is 1.0. Therefore, these values are generally in fair agreement with a theory mentioned above. But, in the case of PhII, which was containing no substituent, the e value was higher than those of ClPhII and MPhII. The Q value was also similar tendency. The reason for those may be arised from another influence except for Inductive Effect presented above. The reason why the Q values for three types of N -substituted itaconimides are practically high may be that the double bond of the point of reaction is completely conjugated phenyl group according to the resonance structure as eq. (8). The Q value for NII, which containing more π electron system than phenyl group, is abnormally high.

Now let us consider the relation between the characteristics of homopolymerization and the Q and e value of N -substituted itaconimides. In general, it is known that the characteristics of homopolymerization for α, β -unsaturated dibasic acid such as maleic unhydride or N -substituted maleimides are affected the influence by the e value rather than the Q value¹⁻³). In other words, the homopolymerization reaction of monomer containing substituent to lower e value progresses readily. This means that the factor to inhabit the homopolymerization reaction is action of repulsion by the same $\delta+$ between the monomer and monomer. The author's monomers are considered, in the Table 2, the k constant for ClPhII is the smallest of all, and the characteristics of the homopolymerization is the worst of the author's monomers. However, the E and A value of ClPhII are lower than those of other N -substituted itaconimides, and the monomer having high Q value is likely to have high E and A value. The relation between these E, A values and Q, e values is not clarified so far. Since the polymerizations of N -substituted itaconimides have not satisfactorily carried out yet, the homopolymerizations and copolymerizations of N -(4-substituted phenyl) itaconimides will be studied more, and the relation between Q, e and E, A values will be clarified.

3.3 Properties of the polymers

Table 1 shows the results of elemental analyses of polymers. The results in Table 1 and the IR spectra of itaconimide polymers and monomers showed little difference between the monomers and polymers. Therefore, it was concluded that polymerizations had undergone a normal addition.

The reduced viscosity and the softening points are shown in Table 6. As shown in Table 6, the softening point of NII containing naphthyl group is the highest of all, but there is no large difference when compared with those for the N -substituted itaconimides containing phenyl substituents. Also, it was known that the softening point was higher than that for vinyl polymers in general. That is, they seem to be high because of the polarization of the carbonyl group. This tendency agreed with the case of N -substituted maleimides.

The four type polymers are white powder, and soluble in organic solvent such as

Table 6. Reduced viscosities and melting points of *N*-substituted itaconimide polymers.

Polymer	Melting points (°C)	η_{sp}/C $C=0.5$ g/dl in THF at 30°C
Poly-PhII ^{a)}	263~285	0.23
Poly-ClPhII ^{b)}	250~276	0.19
Poly-MPhII ^{c)}	269~280	0.20
Poly-NII ^{d)}	294~308	0.22

a) [PhII]=1.63 mol/l, [AIBN]= 1.51×10^{-2} mol/l.b) [ClPhII]=2.01 mol/l, [AIBN]= 1.51×10^{-2} mol/l.c) [MPhII]=2.71 mol/l, [AIBN]= 1.51×10^{-2} mol/l.d) [NII]=2.05 mol/l, [AIBN]= 1.51×10^{-2} mol/l.

THF, dioxane, chloroform, *N,N*-dimethylformamide, or *N,N*-dimethyl sulfoxide. Solubilities of *N*-substituted itaconimide-St or *N*-substituted itaconimide-MMA copolymers showed the similar tendency.

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