

## Polymerization and Copolymerization of *N*-(4-Carboxyphenyl)maleimide

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**ABSTRACT:** Homopolymerization and copolymerization of *N*-(4-carboxyphenyl)maleimide (CPMI) were performed at 70°C in the presence of azobisisobutyronitrile (AIBN) as an initiator in tetrahydrofuran. The initial rate of polymerization was  $R_p = k[\text{AIBN}]^{0.65} [\text{CPMI}]^{2.4}$ , where  $k$  is an over-all rate constant. The monomer reactivity ratios ( $r_1, r_2$ ) in the polymerization of CPMI ( $M_1$ ) with styrene (ST,  $M_2$ ), or with methyl methacrylate (MMA,  $M_2$ ) and Alfrey-Price  $Q, e$  values were determined as  $r_1 = 0.019, r_2 = 0.23, Q_1 = 0.67, e_1 = 1.53$  for the CPMI-ST system;  $r_1 = 0.24, r_2 = 1.08, Q_1 = 1.09, e_1 = 1.56$  for the CPMI-MMA system.

**KEY WORDS** *N*-(4-carboxyphenyl)maleimide / Radical Polymerization / Initial Rate / Copolymerization / Styrene / Monomer Reactivity Ratio /  $Q, e$  Values /

There have been many reports on polymerizations and copolymerizations of *N*-substituted maleimides (RMI)<sup>1</sup>. RMI is an important reagent to improve the thermal stability of common vinyl polymers and resins.<sup>2</sup> *N*-Cyclohexylmaleimide is especially useful for heat resistant reagents of common vinyl polymers.<sup>3</sup> Application of *N*-phenylmaleimide and *N*-(*p*-hydroxyphenyl)maleimide to ABS<sup>4</sup> and phenol resin,<sup>5</sup> respectively, has also been investigated. RMI including functional groups, *i.e.*, a carboxyl group in *N*-substituent have been reported as a thermoplastic matrix composite,<sup>6</sup> heat resistant and transparent copolymer,<sup>7,8</sup> controllable thermoplastic coatings,<sup>9</sup> and electrodeposition coatings.<sup>10</sup> However, there have been few reports on fundamental parameters related to homopolymerization reactivity and copolymerization behavior for RMI containing a carboxyl group. Only one report could be found on the copolymerization of acrylonitrile with *N*-(*p*-carboxyphenyl)maleimide (CPMI).<sup>11</sup> However, in that article, no homopolymerization behavior was de-

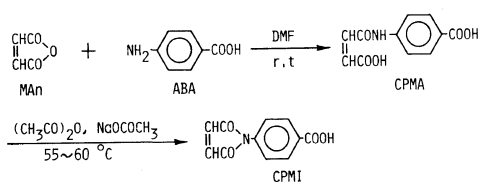
scribed. The determination of copolymerization reactivity of CPMI with styrene (ST) and methyl methacrylate (MMA) has been required since RMI is effective for the improvement of heat resistant poly (ST) and poly (MMA).

In this article we describe the radical polymerization of CPMI and copolymerizations of CPMI with ST and MMA. The characteristic polymerization behavior of CPMI is discussed, compared with PMI including no functional groups. Thermostabilities of CPMI monomer, the polymers, and the copolymers are also described.

### EXPERIMENTAL

#### *Preparation of CPMI Monomer*

CPMI was prepared from maleic anhydride and *p*-amino-benzoic acid (ABA), according to the method reported by Reo<sup>12</sup>, with some modification (see Scheme 1). Maleic anhydride (98.1 g, 1.0 mol) and ABA (137.1 g, 1.0 mol) were dissolved in *N,N*-dimethylformamide (DMF; 320 ml), and then the mixture was



Scheme 1.

stirred at room temperature for 5 h under nitrogen atmosphere. The resulting solution was poured into a large amount of water to precipitate crude *N*-(4-carboxyphenyl)-maleamic acid (CPMA). The crude CPMA was filtrated, dried, and then recrystallized three time from water to obtain pure CPMA (yield 98%). A mixture of CPMA (43.5 g; 0.2 mol), acetic anhydride (100 ml) and sodium acetate (2.5 g) was stirred at 55–60°C for 2 h. The reaction mixture was poured into a large amount of water to give crude CPMI. The crude CPMI was filtered, washed with water, dried, and recrystallized three times from methanol–water (6:1) mixture solution; yield 85%, mp. 244°C (lit.<sup>12</sup> mp 208–210°C).

IR spectrum (KBr disk), wavenumber ( $\text{cm}^{-1}$ ): 3150, 2980, 2300, 1770, 1700, 1640, 1600, 1390, 1370, 1200, 820, 690.

<sup>1</sup>H NMR (chemical shift,  $\delta$ , ppm from tetramethylsilane in dimethyl sulfoxide-*d*<sub>6</sub> (DMSO) [see hydrogen position (a to g) as shown in Figure 3: 13.45–12.78 (s, 1H, g), 8.03 (d,  $J=8.24$  Hz, 2H, e and f), 7.49 (d,  $J=8.24$  Hz, 2H, c and d), 7.22 (s, 2H, a and b).

<sup>13</sup>C NMR ( $\delta$ , ppm in DMSO-*d*<sub>6</sub>): 169.39 (C3, C4), 166.55 (C11), 135.43 (C10), 134.74 (C1, C2), 129.80 (C8, C9), 129.56 (C5), 126.03 (C6, C7) (see carbon numbers in Figure 4).

Elemental analysis (%): Calculated for C<sub>11</sub>H<sub>7</sub>NO<sub>4</sub>: H=3.25%, C=60.83%, N=6.45%; Found: H=3.24%, C=60.53%, N=6.22%.

#### Comonomer and Other Materials

ST and MMA were purified by the usual methods. AIBN and solvents such as tetrahydrofuran (THF), cyclohexanone (CHO),

ethyl methyl ketone (MEK), ethyl acetate (EA), dioxane (DOX), DMF, DMSO, dichlorobenzene (DCB), and methanol were purified by the usual methods. Commercially available 2,5-dimethyl-2,5-di(*t*-butylperoxy)hex-3-yne (PH25B) was used without further purification.

#### Polymerization Procedure

Radical solution polymerization of CPMI was carried out in a sealed glass tube with the initiator at 60 to 150°C. After polymerization for a given time, the contents were poured into a large amount of methanol to precipitate the polymer. The polymer was filtered, purified by reprecipitation from THF/methanol, and dried under reduced pressure for 2 days.

Radical copolymerizations of CPMI with ST or MMA were performed with radical initiators in THF at 70°C in a sealed tube. After a prescribed time, the contents were poured into a large amount of methanol to precipitate the copolymer. The copolymer was reprecipitated twice from THF/methanol, and then filtered, dried in vacuum. The composition of the copolymer was determined by nitrogen analysis.

#### Determination of Polymerization Rate ( $R_p$ )

Polymerization rates ( $R_p$ ) were determined by using high performance liquid chromatograph (HPLC) with UV detector (254 nm). That is, yield of polymer was estimated from the concentration of monomer consumption calculated from a HPLC calibration curve for CPMI. The HPLC apparatus used was a Shimadzu LC 3A, operated with Shimadzu Zorbax ODS column in a mixture solution of methanol and water (50/50) at 60°C. The flow rate was 1.2 ml min<sup>-1</sup>.

#### Measurements

199.5 MHz <sup>1</sup>H NMR and 50.1 MHz <sup>13</sup>C NMR, and 100 MHz <sup>1</sup>H NMR spectra were obtained with a JEOL FX-200 and a JEOL JNM-MH-100. Molecular weights of polymers and copolymers were measured by gel

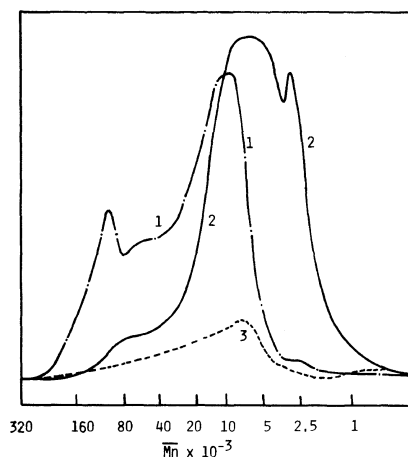
permeation chromatography (GPC) on Shimadzu LC 3A equipped with data processor, using DMF as the eluent and Shimadzu polystyrene gel HGS-20. Diagrams of TG-DSC and X-ray diffraction were obtained with Rigaku Thermal Analysis and Shimadzu XD-3 apparatus, respectively.

## RESULTS AND DISCUSSION

### Homopolymerization of CPMI

The results of radical solution homopolymerization are summarized in Table I. All polymerizations proceeded in heterogeneous system. That is, a part of the polymer precipitated in the solvent. Yields are those for the polymers insoluble in methanol. Polymerization solvents influence both yields of polymers and their number-average molecular weights ( $M_n$ ). The polymerization in DMF or DMSO gave only trace of polymers insoluble in methanol. Figure 1 shows GPC chart for (1) CPMI polymer insoluble in methanol and for (2) the product soluble in methanol (obtained from polymerization of CPMI in THF at 60°C for 15 h) (run 1). The  $M_n$  for poly (CPMI) was

higher than that for poly(*N*-carboxymethyl)-maleimide (CMMI),<sup>13</sup> which was obtained from the polymerization of CMMI with AIBN in THF at 60°C for 42 h, as shown in Figure 1. But polymers obtained in the polymerization of CPMI in THF show greater polydispersity [(weight average molecular weight ( $M_w$ ))/ $M_n$ ]



**Figure 1.** Molecular weight distributions for the polymer obtained with AIBN at 60°C in THF (run 1): (1) poly(CPMI) insoluble in methanol, (2) poly(CPMI) soluble in methanol, and (3) poly(CMMI) obtained from polymerization of CMMI with AIBN at 60°C in THF.

**Table I.** Radical homopolymerization of CPMI in various solvents

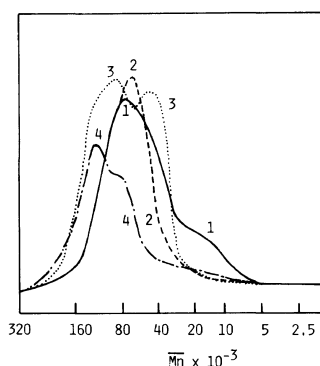
Run No.	[CPMI]	Initiator	Solvent <sup>a</sup>	Polym. time	Temp.	Yield	N-Analysis	$\bar{M}_n^b$	
	$\times 10^3 \text{ mol}$							$\times 10^2 \text{ mol l}^{-1}$	ml
1	2.46	AIBN (4.8)	THF (8)	15	60	14.3	5.8	1.2	4.4
2	2.32	AIBN (6.0)	THF (8)	0.2	70	9.2	—	5.7	9.1
3	2.38	AIBN (1.0)	THF (8)	24	70	12.0	—	—	—
4	2.45	AIBN (1.0)	DMF (2)	24	70	0	—	—	—
5	2.44	AIBN (1.0)	DMS (2)	24	70	0	—	—	—
6	2.37	AIBN (3.0)	DOX (8)	24	70	56.1	6.2	3.6	1.6
7	2.38	AIBN (3.0)	DCB (8)	24	70	0	—	—	—
8	2.36	AIBN (3.0)	CHO (8)	24	70	59.5	5.6	4.4	1.4
9	2.35	AIBN (3.0)	MEK (8)	24	70	81.2	6.1	3.5	1.5
10	2.45	AIBN (3.0)	EA (8)	24	70	81.9	6.4	6.4	1.5
11	2.37	PH25B (2.4)	DCB (5)	0.5	150	64.6	4.2	7.2	1.1
12	2.32	PH25B (2.2)	CHO (5)	0.5	150	54.7	4.9	1.8	2.3
13	2.36	PH25B (2.4)	MEK (5)	24	120	81.6	5.6	4.2	1.4
14	2.39	PH25B (2.6)	EA (5)	24	120	93.6	5.8	4.2	1.4

<sup>a</sup> THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; DOX, dioxane; DCB, dichlorobenzene; CHO, cyclohexanone; MEK, methyl ethyl ketone; EA: ethyl acetate.

<sup>b</sup> By GPC.

than those in other solvents, as shown in Table I and Figure 2. This may be attributed to the solubility of the polymer in the solvent. In polymerization at high temperature, where it was necessary to use the catalyst with longer half-life, PH25B (half-life, over 100 h at 100°C), yields were much better.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of polymers obtained from the polymerization of CPMI in ethyl acetate (EA) at 70°C (run 10) are shown in Figures 3 and 4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra

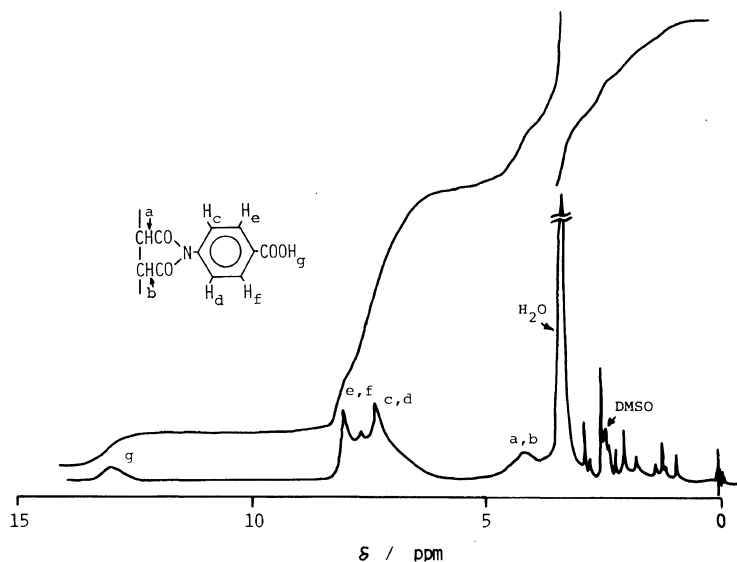


**Figure 2.** Molecular weight distributions for the polymers: (1) poly(CPMI) (run 6), (2) poly(CPMI) (run 11), (3) poly(CPMI-co-ST) (run S-3), and (4) poly(CPMI-co-MMA) (run M-3).

for the CPMI polymers obtained in EA at 120°C (run 14) or in DCB at 150°C are similar to those for the polymer obtained at 70°C. In  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, some signals were observed at high magnetic field. In  $^1\text{H}$  NMR, an integration value for phenyl groups at about 6 to 8 ppm was twice that for other signals. These signals and integration values suggest the addition of a radical at the growing chain end or a hydrogen radical of the carboxyl group in the polymer to a CPMI monomer took place.

X-Ray diffraction (XRD) diagrams for poly(CPMI) (run 10) and CPMI monomer are shown in Figure 5. In XRD for poly(CPMI), four peaks were observed at about 16.2, 23.1, 26.2, and 29.5 deg. Poly(CPMI) was found to be not crystalline but amorphous.

Polymerizations were performed with the constant concentration of CPMI monomer ( $2.9 \times 10^{-1} \text{ mol l}^{-1}$ ) and various concentrations of AIBN at a constant polymerization temperature (70°C) for various periods of time. Yield of polymer was calculated from consumption of CPMI monomer, by using HPLC. Time-conversion curves were drawn on the basis of these results. From the slope of each curve, the initial rate of polymerization,  $R_p$ ,



**Figure 3.**  $^1\text{H}$  NMR spectrum for poly(CPMI) (run 10).

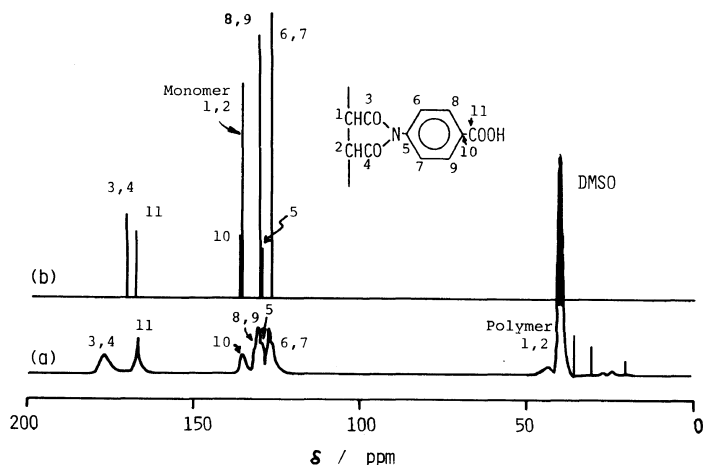


Figure 4.  $^{13}\text{C}$  NMR spectrum for (a) poly(CPMI) (run 10) and (b) CPMI monomer.

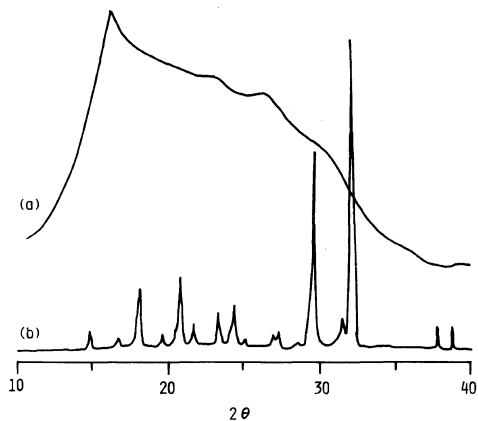


Figure 5. X-Ray diffraction diagrams for (a) poly(CPMI) (run 10) and (b) CPMI monomer.

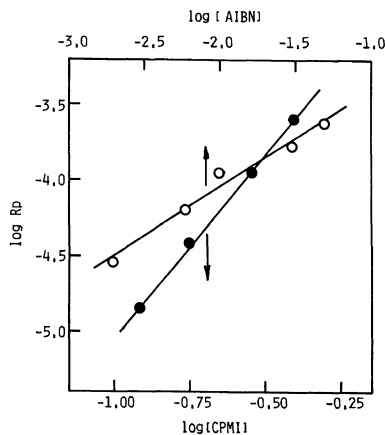


Figure 6. Effects of CPMI monomer and AIBN concentrations on the rate of polymerization in THF at  $70^\circ\text{C}$ .

could be calculated.  $R_p$  was determined at various AIBN concentrations. The relation between  $\log R_p$  and  $\log[\text{AIBN}]$  is shown in Figure 6. The dependence of AIBN concentration ( $m$ ) was determined as 0.65 from the slope of this line. This indicates that polymerization of CPMI does not satisfy the ordinary  $1/2$  power rule, and that both monomolecular and bimolecular terminations may occur simultaneously. This may be attributable to "occlusion" of a radical at the polymer end because of the heterogeneous polymerization system. The  $m$  for RMI reported so far was 0.6 to 0.9 even in

a homogeneous polymerization system, and generally greater than 0.5, as shown in Table II. This can be explained from monomolecular termination due to resonance stabilization, as reported by Yamada *et al.*<sup>14</sup>

Polymerizations were carried out at  $70^\circ\text{C}$  at various monomer concentrations. The concentration of the initiator AIBN ( $1.0 \times 10^{-2} \text{ mol l}^{-1}$ ) was constant.  $R_p$  was calculated from the slope of an initial straight line in time-conversion curves. According to the same procedure for determining  $m$ , the relation

between  $\log R_p$  and  $\log [\text{CPMI}]$ , (where  $[\text{CPMI}]$  is the monomer concentration), is plotted in Figure 6. The dependence of monomer concentration ( $n$ ) was determined as 2.4 from the slope of this line. The reason that  $m$  was greater than 1 may be attributable to the heterogeneous system due to precipitation of the polymer in the solvent. In addition, this may result from polymerization with the practically aggregated form of CPMI mono-

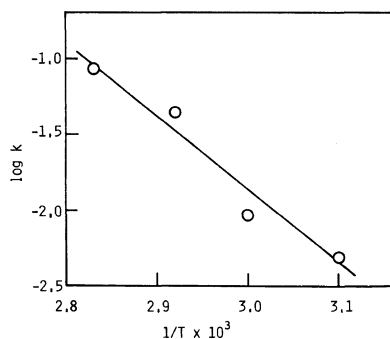
mers because of the strong polarity for carboxyl groups of maleimide ring. The  $n$  ( $=2.4$ ) for CPMI is similar to those ( $n=1.0$  to  $2.7$ ) for other RMI,<sup>15-17</sup> as shown in Table II. This may be reduced to a hydrogen bond between the monomers due to a carboxyl group located at the para of phenyl group.

Polymerization was performed at constant CPMI monomer and AIBN concentrations at 50, 60, 70, and 80°C. From the results,  $R_p$  was obtained. The rate constants ( $k$ ) at 50, 60, and 80°C were calculated from the rate equation at 70°C:  $R_p = k[\text{AIBN}]^{0.65}[\text{CPMI}]^{2.4}$ . Figure 7

**Table II.** Homopolymerization parameters of *N*-substituted maleimides (RMI)

RMI (R)	$R_p =$ $k[\text{AIBN}]^m[\text{M}]^n$		$E$ kcal mol <sup>-1</sup>	Ref
	$m$	$n$		
-C <sub>6</sub> H <sub>4</sub> COOH	0.65	2.4	22.6	
-CH <sub>2</sub> OH	0.81	1.2	25.9	15
-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	0.54	2.7	24.1	16
-C <sub>6</sub> H <sub>5</sub>	0.8	1.2	25.2	15
-C <sub>6</sub> H <sub>4</sub> OH	0.95	1.0	29.1	17
-C <sub>6</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	0.8	1.4	29.1	17
MMA <sup>a</sup>	0.5	1.0	19.9	18
PhII <sup>b</sup>	0.6	1.2	19.5	19
ClPhII <sup>c</sup>	0.5	1.1	16.1	19

<sup>a</sup> Methyl Methacrylate. <sup>b</sup> *N*-(Phenyl)itaconimide.  
<sup>c</sup> *N*-(4-Chlorophenyl)itaconimide.



**Figure 7.** Relationship between  $\log k$  and  $1/T$  for polymerization of CPMI initiated by AIBN in THF at various temperatures.

**Table III.** Copolymerization of CPMI ( $M_1$ ) with ST ( $M_2$ ), or MMA ( $M_2$ ) in THF at 60°C<sup>a</sup>

Run <sup>b</sup> No.	$M_1$ in monomer	Yield <sup>c</sup> %	N <sup>d</sup> %	$M_1$ in copolymer	$\bar{M}_n^e$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
	mol%			mol%		
S-1	20.3	60.47	3.34	33.9	7.56	1.2
S-2	40.3	82.16	3.98	43.6	7.57	1.2
S-3	49.6	76.47	4.12	45.9	6.11	1.2
S-4	59.9	48.58	4.05	44.7	6.78	1.2
S-5	79.3	20.64	4.48	52.2	0.90	5.5
M-1	20.2	23.03	1.95	16.7	9.83	1.0
M-2	39.2	7.02	3.16	30.7	10.26	1.1
M-3	50.5	1.78	3.57	36.4	9.22	1.1
M-4	59.5	1.83	4.05	44.7	6.78	1.2
M-5	75.7	trace	—	—	—	—

<sup>a</sup>  $[\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ; THF = 8 ml;  $M_1 + M_2 = 1.0 \text{ g}$ ; polymerization time = 24 h.

<sup>b</sup> Run No. S-1 to S-5 = CPMI-ST; M-1 to M-5 = CPMI-MMA.

<sup>c</sup> Yield of the polymer insoluble in methanol.

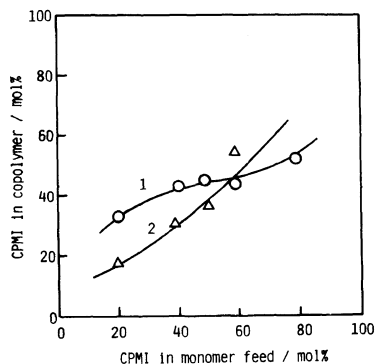
<sup>d</sup> Elemental analysis of polymers.

<sup>e</sup> By GPC.

shows the relation between  $\log k$  and  $1/T$ . Over-all activation energy ( $E$ ) of the polymerization was obtained as  $22.6 \text{ kcal mol}^{-1}$ . This value is smaller than those for other RMI, and higher than those for vinyl monomer<sup>18</sup> and *N*-substituted itaconimide,<sup>19</sup> as shown in Table II. But, the  $E$  value cannot be simply compared with those for other RMI because of the heterogeneous system in the polymerization of CPMI.

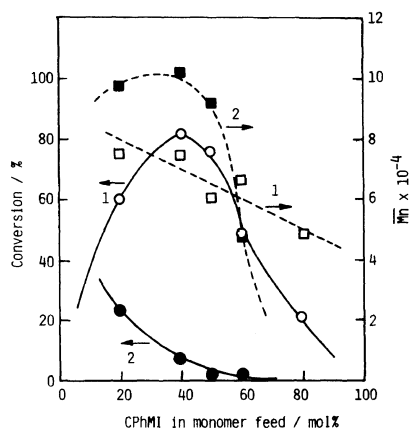
### Radical Copolymerization

The copolymerization of CPMI ( $M_1$ ) with ST ( $M_2$ ) or MMA ( $M_2$ ) was performed in THF at  $70^\circ\text{C}$  by using AIBN as the initiator. The polymerization systems were heterogeneous throughout. The results are summarized in Table III. When the concentration of CPMI in



**Figure 8.** Copolymer-composition curves for (1) copolymerization of CPMI with ST and (2) of CPMI with MMA.

monomer feeds in CPMI-MMA system increased, the yield of copolymer extremely decreased. At 80 mol% of CPMI in monomer feed, the yield was a trace. The copolymer-composition curves obtained above the results are shown in Figure 8. It is known that the copolymerization of RMI with ST is a practically alternating one.<sup>14-17</sup> But, in the copolymerization of CPMI with ST, the alternating character decreased. This could be observed in the polymerization of *N*-carboxymethylmaleimide (CMMI) with ST.<sup>13</sup> On the other hand, it is known that the copolymerization of RMI with MMA is ideal along an azeotropic line.<sup>16</sup> In the CPMI and MMA



**Figure 9.** Effects of CPMI concentration in monomer feeds on conversion ( $\circ$ ,  $\bullet$ ), and  $M_n$  ( $\square$ ,  $\blacksquare$ ) of the copolymer: (1) poly (CPMI-*co*-ST)s and (2) poly (CPMI-*co*-MMA)s.

**Table IV.** Copolymerization parameters of *N*-Substituted Maleimides (RMI)

RMI ( $M_1$ )	$M_2$	$r_1$	$r_2$	$Q_1$	$e_1$	Ref
-C <sub>6</sub> H <sub>4</sub> COOH	ST	0.019	0.23	0.67	1.53	
	MMA	0.24	1.08	1.09	1.56	
-CH <sub>2</sub> OH	ST	0.06	0.01	11.3	1.92	15
	MMA	0.27	1.66	0.31	1.30	15
- <i>n</i> -C <sub>4</sub> H <sub>9</sub>	ST	0.06	0.025	5.20	1.75	22
	MMA	(-0.10)	1.41	—	—	23
-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	ST	0.02	0.04	2.94	1.87	16
	MMA	0.14	1.54	0.79	1.63	16
-C <sub>6</sub> H <sub>4</sub> COOC <sub>2</sub> H <sub>5</sub>	ST	0.1	0.02	6.3	1.79	24

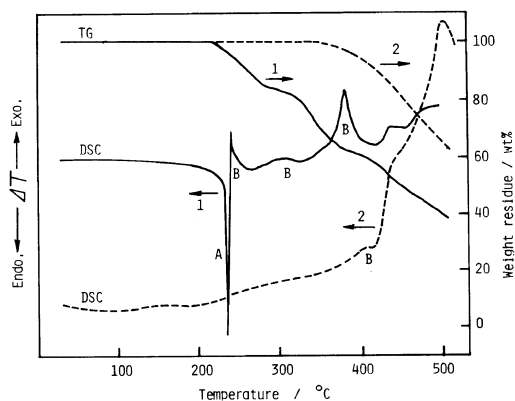
system, a similar tendency was detected.

The monomer reactivity ratios ( $r_1$ ,  $r_2$ ) calculated by the Kelen-Tüdös method<sup>20</sup> and Alfrey-Price<sup>21</sup>  $Q$ ,  $e$  values are shown in Table IV. Generally,  $Q$  values for PMI calculated from the copolymerization of RMI with ST are abnormal one because of the formation of a charge transfer(CT) complex. But the  $Q$  ( $=0.67$ ) value for CPMI containing carboxyl group indicated normal and reasonable value, as shown in Table IV. So,  $Q$  values was determined as 0.88, which was an average value of 0.67 and 1.09 calculated from CPMI-ST and CPMI-MMA system, respectively. The  $e$  value

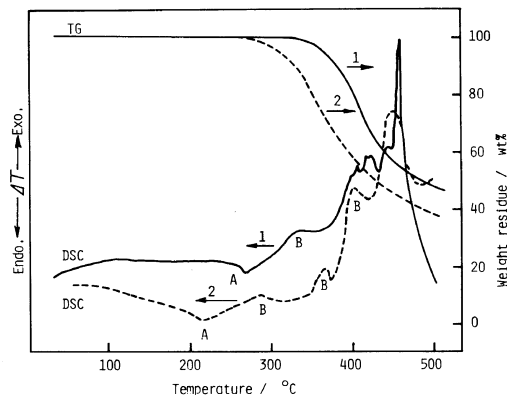
for CPMI was determined as 1.55 (an average of 1.53 and 1.56), which was similar to those for other RMI.

Molecular weight distributions for both poly(CPMI-co-ST) and poly(CPMI-co-MMA) exhibited two peaks, as shown in Figure 2. This may be ascribed to the heterogeneous polymerization system. Figure 9 gives the effects of [CPMI] in monomer feed on conversion and  $M_n$  for copolymers.  $M_n$  of poly(CPMI-co-ST) almost linearly decreased with increase of CPMI monomer feed. This tendency was not observed in other poly(RMI-co-ST)s investigated so far. That is,  $M_n$  distribution revealed a maximum peak for  $M_n$  when the ratio for RMI/ST in the monomer feeds was 1/1. On the other hand, in the CPMI-MMA system, the yields were much lower than those for poly(CPMI-co-ST)s. But  $M_n$  for poly(CPMI-co-MMA) was higher than those for poly(CPMI-co-ST). This too was not recognized for RMI studied so far.

Diagrams of a thermogravimetric (TG) and a differential scanning calorimetric (DSC) analysis for CPMI monomer, homopolymer and copolymers are shown in Figures 10 and 11. In a TG-DSC curve for CPMI monomer, one endothermal (A) and some exothermal (B) peaks were observed due to melting and degradation of CPMI monomer, respectively. The CPMI monomer melted simultaneously and decomposed. There were no softening points ( $T_m$ ) for the poly(CPMI). Only the initial degradation temperatures ( $T_d$ ) were observed as 328 to 356 °C. In TG-DSC curves for the CPMI-ST and CPMI-MMA copolymers, one endothermal (A) and some exothermal (B) peaks were observed based on melting and degradation, respectively.  $T_m$  and  $T_d$  were as follows:  $T_m=258$  to  $298$  °C,  $T_d=318$  to  $346$  °C for poly(CPMI-co-ST)s;  $T_m=199$  to  $248$ ,  $T_d=252$  to  $298$  for poly(CPMI-co-MMA)s. These  $T_m$  were reconfirmed by measurement with the ordinary capillary melting point methods.



**Figure 10.** TG-DSC curves for (1) CPMI monomer and (2) poly(CPMI) (run 8) at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in nitrogen.



**Figure 11.** TG-DSC curves for (1) poly(CPMI-co-ST) (run S-3) and (2) poly(CPMI-co-MMA) (run M-3) at a heating rate of  $10^{\circ}\text{C/min}$  in nitrogen.



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