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Polymerization and copolymerization of *N*-cyclododecylmaleimide

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Homopolymerizations and copolymerizations of *N*-cyclododecylmaleimide (CDMI) were performed at 60°C in the presence of azobisisobutyronitrile (AIBN) as an initiator in tetrahydrofuran. The initial rate of polymerization was $R_p = k[\text{AIBN}]^{0.50}[\text{CDMI}]^{3.4}$, where k is the rate constant. Overall activation energy (E) and frequency factor (A) were 19.2 kcal mol^{-1} and 2.0×10^9 s^{-1}, respectively. The monomer reactivity ratios in the copolymerization of CDMI (M_1) with styrene (ST; M_2) or methyl methacrylate (MMA; M_2) and Alfrey–Price Q, e values were determined as: $r_1 = 0.10$, $r_2 = 0.102$, $Q_1 = 1.77$, $e_1 = 1.34$ in CDMI–ST system; $r_1 = 0.19$, $r_2 = 1.31$, $Q_1 = 0.91$, $e_1 = 1.58$ in CDMI–MMA system. The thermostabilities of the polymers and copolymers were investigated by differential scanning calorimetry and thermogravimetric analysis.

(Keywords: *N*-cyclododecylmaleimide; radical polymerization; characterization)

INTRODUCTION

The syntheses and polymerizations of *N*-substituted maleimides (RMIs) have been extensively studied by many workers[1]. RMI is a 1,2-disubstituted ethylene-type monomer and has a cyclic structure with two carbonyl groups. Therefore RMI shows characteristic polymerizability and copolymerizability. In particular, the main chain of RMI polymer is rigid, so that RMIs can become important reagents to improve the thermal stability of common vinyl polymers and resins[2]. *N*-Cyclohexylmaleimide (CHMI) is especially useful as a heat-resistant reagent for common vinyl polymers[3]. Application of *N*-phenylmaleimide (PhMI) and *N*-(*p*-hydroxyphenyl)-maleimide to acrylonitrile–butadiene–styrene (ABS)[4] and phenol resin[5], respectively, has also been investigated. RMI bearing functional groups, i.e. a carboxyl group in the *N*-substituent, has been reported in some extensive applications[6]. Polymerization reactivities of RMI bearing perfluoroalkyl groups[7] and long-chain alkyl groups[8] as *N*-substituent have been studied lately. However, there have been no reports on the polymerizabilities of *N*-cyclododecylmaleimide (CDMI) and the thermostabilities of the polymers and copolymers obtained from CDMI. CDMI has a cyclic structure as *N*-substituent, and is hydrophobic and bulkier than the cyclohexyl group. From the standpoint of transparent polymers and copolymers, CHMI polymer and the copolymer are better than PhMI.

In this article we describe the radical and anionic polymerizations of CDMI and the radical copolymerizations of CDMI with styrene (ST) and methyl methacrylate (MMA). The polymerization behaviour of CDMI was discussed, and compared with RMIs reported so far. Thermostabilities for CDMI polymers and the copolymers were also described, as compared with CHMI–ST, CHMI–MMA, PhMI–ST and PhMI–MMA copolymers.

EXPERIMENTAL

CDMI monomer

CDMI was synthesized from maleic anhydride (MAn) and cyclododecylamine (CDA), as shown in *Scheme 1*.

N-*Cyclododecylmaleamic acid (CDMA).* Maleic anhydride (98.1 g, 1.0 mol) was dissolved in 300 ml of dry benzene. A solution of CDA (183.3 g, 1.0 mol) in dry benzene (300 ml) was added dropwise to it at about 5°C for 3 h. Then the mixture was stirred at room temperature for 2 h. The resulting product was filtered and washed with cold benzene, and then dried. It was recrystallized from methanol/water (1/1) to obtain pure CDMA: yield 98%, m.p. 203–204°C.

I.r. spectrum (KBr disk; wavenumber (cm^{-1})): 3210, 3050, 2910, 2840, 1710, 1635, 1580, 1540, 1510, 1460, 1410, 1295, 1130, 845, 630.

^{1}H n.m.r. (chemical shift δ (ppm) from tetramethylsilane (TMS) in deuterated dimethylsulfoxide (DMSO-d_6)): 9.03 (d, 1H, $J = 8.25$ Hz, NH), 6.48 (d, 1H,

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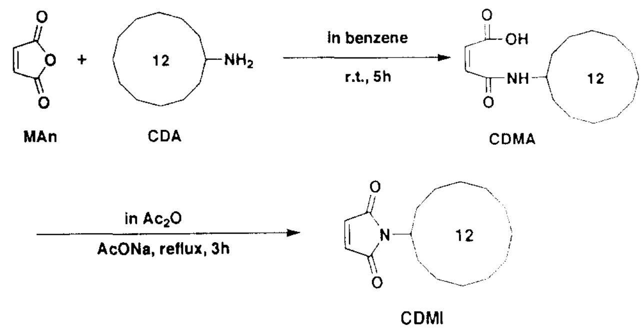

Scheme 1

J = 12.87 Hz, =CH–CON), 6.31 (d, 1H, J = 12.54 Hz, =CH–COO), 4.03 (s, 1H, CH in cyclododecyl), 1.70–1.41 (m, 22H, other protons in cyclododecyl).

^{13}C n.m.r. (δ (ppm) from TMS in DMSO-d_6): 165.26 (1C, N–C=O), 164.73 (1C, O–C=O), 133.03 (1C, =$\underline{C}$–CO–N), 131.84 (1C, =$\underline{C}$–CO–OH), 45.39 (1C, N–C in cyclododecyl), 29.46, 23.33, 23.11, 22.90, 22.65 and 21.33 (11C, other carbons in cyclododecyl).

Elemental analysis (%): calculated for $C_{16}H_{27}NO_3$, H 9.67, C 68.29, N 4.98; found, H 9.62, C 68.11, N 5.06.

CDMI. A mixture of CDMA (28.1 g, 0.1 mol), acetic anhydride (200 ml) and sodium acetate (1.5 g) was refluxed for 3 h. After the reaction, the mixture was stood at room temperature overnight. The precipitating product (A) was filtered. The filtrate was neutralized with sodium bicarbonate solution to give solid product (B), which was filtered. The mixture of A and B was washed with water repeatedly till the washed solution indicated no acidity. The product (A and B) was filtered, washed with water and dried. Then crude CDMI was isolated by column chromatography on alumina, using benzene as an eluent. It was purified by recrystallization three times from cyclohexane: yield 72%, m.p. 155–156°C.

I.r. spectrum (KBr disk; wavenumber (cm^{-1})): 2900, 2850, 1760, 1695, 1650, 1395, 1370, 1130, 845, 690.

^1H n.m.r. (chemical shift δ (ppm) from TMS in deuterated chloroform ($CDCl_3$)): 6.62 (s, 1H, CH=CH), 4.30–4.20 (m, 1H, CH in cyclododecyl), 2.05–1.32 (m, 22H, other protons in cyclododecyl).

^{13}C n.m.r. (δ (ppm) from TMS in $CDCl_3$): 171.26 (2C, C=O), 133.82 (2C, –CH=CH–), 46.86 (1C, N–C in cyclododecyl), 28.14, 24.16, 23.97, 22.62, 22.52 and 22.44 (11C, other carbons in cyclododecyl).

Elemental analysis (%): calculated for $C_{16}H_{25}NO_2$, H 9.57, C 72.97, N 5.32; found; H 9.68, C 73.01, N 5.43.

Comonomer and other materials

CHMI and PhMI were synthesized from MAn and the corresponding amine, according to the method reported by Searle[9]: PhMI m.p. 91°C and CHMI m.p. 89.0°C. ST and MMA were purified by the usual methods[10]. Azobisisobutyronitrile (AIBN) and solvents, i.e. toluene (TOL), tetrahydrofuran (THF), benzene (BEN), dioxane (DOX), dimethylformamide (DMF) and methanol were purified by the usual methods[11]. Commercially available n-butyllithium (n-BuLi) and 2,5-dimethyl-2,5-di(t-butylperoxy)hex-3-yne (PH2,5B) were used without further purification.

Polymerization procedure

Radical bulk and solution polymerizations of CDMI were carried out in a sealed glass tube with the initiator at 60 or 160°C. After polymerization for given time, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. The polymer was filtered, purified by reprecipitation from the THF solution into excess methanol, and dried under reduced pressure for 2 days.

Anionic polymerization of CDMI was performed with n-BuLi in THF, TOL or DMF at 0°C under nitrogen atmosphere. Polymerization was terminated with a few drops of methanol using a syringe. The solution was poured into a large amount of methanol. The obtained polymer was purified by the same procedure as that of radical polymerization.

Radical copolymerizations of CDMI with ST or MMA were performed with AIBN in benzene at 60°C in a sealed tube. After the prescribed time, the contents of the tube were poured into excess methanol to precipitate the copolymer. The copolymer was reprecipitated twice from the THF solution into excess methanol, and then filtered and dried in vacuum. The composition of the copolymer was determined from ^1H n.m.r. spectra and nitrogen analysis.

Radical polymerization and copolymerization of PhMI (or CHMI) were performed under the same conditions and procedure as CDMI.

Measurements

270.05 MHz ^1H n.m.r. and 67.80 MHz ^{13}C n.m.r. spectra were obtained with a JNM EX-270 FT-NMR (JEOL Ltd). Molecular weights of polymers and copolymers were measured by gel permeation chromatography (g.p.c.) on Shimadzu LC 3A equipped with data processor, using THF (1.2 ml min^{-1}) as the eluent, u.v. detector (254 nm) and Shimadzu polystyrene gel HGS-15-20-40. Diagrams of t.g.-d.t.a., t.g.-d.s.c. and d.s.c. were obtained with Rigaku Thermal Analysis and Shimadzu DSC-50 (Shimadzu Ltd) apparatus. X-ray spectra were obtained with a Shimadzu XD-3 apparatus.

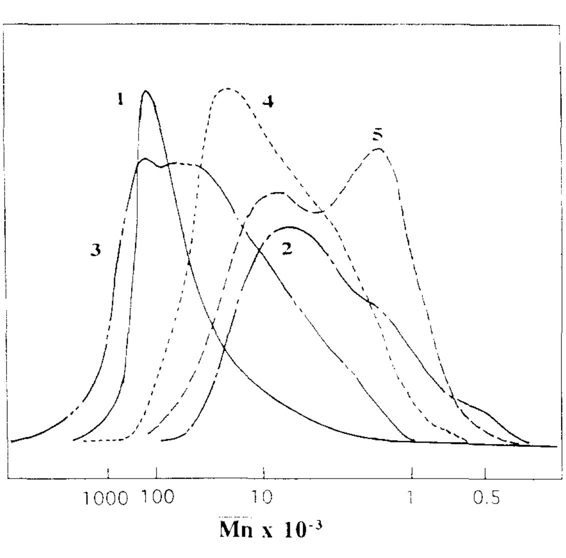

Figure 1 G.p.c. curves for the polymers obtained with AIBN at 60°C in (1) benzene (run 8 in *Table 1*), (2) toluene (run 5 in *Table 1*), (3) in bulk (run 19 in *Table 2*) and with n-BuLi at 0°C in (4) THF (run 21 in *Table 2*) and (5) toluene (run 25 in *Table 2*)

Table 1 Radical solution polymerizations of CDMI

Run	CDMI ($\times 10\,\mathrm{mol\,l^{-1}}$)	Initiator ($\times 10^2\,\mathrm{mol\,l^{-1}}$)	Polym. solvent[a] (ml)	Polym. temp. (°C)	Polym. time (h)	Convn. (%)	$\overline{M}_n$[b] ($\times 10^{-3}$)	$\overline{M}_w$[b] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$
1	9.49	AIBN(1.0)	THF(2)	60	24	39.6	1.4	2.0	1.36
2	6.33	AIBN(1.0)	THF(3)	60	24	87.2	1.5	1.9	1.31
3	6.34	AIBN(2.0)	THF(3)	60	24	21.2	1.8	2.2	1.30
4	9.51	AIBN(1.0)	TOL(2)	60	24	93.3	2.1	31.0	14.15
5	6.34	AIBN(1.0)	TOL(3)	60	24	92.3	3.9	13.1	3.31
6	9.51	AIBN(2.0)	TOL(2)	60	24	94.1	4.1	19.3	4.69
7	6.34	AIBN(2.0)	TOL(3)	60	24	90.6	3.2	12.8	3.89
8	19.0	AIBN(0.5)	BEN(1)	60	24	98.6	35.7	169.4	4.74
9	9.50	AIBN(0.5)	BEN(2)	60	24	98.6	25.5	125.0	4.91
10	9.49	AIBN(1.0)	BEN(2)	60	24	98.6	20.6	108.4	5.26
11	6.33	AIBN(1.0)	BEN(3)	60	24	94.2	13.1	79.6	6.09
12	9.48	AIBN(2.0)	BEN(2)	60	24	98.1	15.6	96.3	6.14
13	6.34	AIBN(2.0)	BEN(3)	60	24	97.4	10.5	68.3	6.51
14	9.48	AIBN(1.0)	DOX(2)	60	24	88.2	9.2	14.3	1.54
15	6.34	AIBN(1.0)	DOX(3)	60	24	82.5	5.0	7.5	1.51
16	9.50	AIBN(2.0)	DOX(2)	60	24	86.5	6.7	10.3	1.55
17	6.34	AIBN(2.0)	DOX(3)	60	24	81.7	4.9	7.2	1.47

[a] TOL, toluene; THF, tetrahydrofuran; BEN, benzene; DOX, dioxane
[b] By g.p.c.

Table 2 Radical bulk and anionic polymerizations of CDMI

Run	CDMI ($\times 10\,\mathrm{mol\,l^{-1}}$)	Initiator[a] (mol%)	Polym. solvent[b] (ml)	Polym. temp. (°C)	Polym. time (h)	Convn. (%)	$\overline{M}_n$[c] ($\times 10^{-3}$)	$\overline{M}_w$[c] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$
18	1.90[d]	PH2,5B(3.0)	None	160	25	100	12.4	90.0	7.3
19	1.90[d]	PH2,5B(5.7)	None	160	25	100	11.9	94.7	7.9
20	38.0	n-BuLi(2.6)	THF(5.0)	0	21	42.0	3.4	7.2	2.1
21	38.0	n-BuLi(5.2)	THF(5.0)	0	21	94.3	3.2	18.1	5.6
22	25.3	n-BuLi(4.0)	DMF(7.5)	0	25	99.2	2.2	19.5	3.8
23	25.3	n-BuLi(7.9)	DNF(7.5)	0	25	98.5	2.7	2.3	8.3
24	15.2	n-BuLi(2.6)	TOL(15.0)	0	24	10.7	2.5	4.5	1.8
25	15.2	n-BuLi(5.2)	TOL(15.0)	0	24	57.0	2.0	9.4	4.7

[a] PH2,5B, 2,5-dimethyl-2,5-di(t-butylperoxy)hex-3-yne; n-BuLi, n-butyllithium
[b] THF, tetrahydrofuran; DMF, *N*,*N*-dimethylformamide
[c] By g.p.c.
[d] $\times 10^3$ mol

RESULTS AND DISCUSSION

Homopolymerization of CDMI

The results of radical and anionic polymerizations are summarized in *Tables 1* and *2*. All polymerizations proceeded in a homogeneous system. The polymers were white powders. The yield and number-average molecular weight ($\overline{M}_n$) of the polymers obtained in benzene were quantitative and the highest. This may be due to the fact that no chain-transfer reaction took place in benzene because the latter is a non-polar solvent. With low concentration of the initiator, the polymer yields were higher, but the polydispersities were relatively large.

Figure 1 shows g.p.c. curves for polymers obtained with AIBN or n-BuLi. In radical and anionic polymerizations of CDMI, generally, solvent effects were significantly observed. The g.p.c. curve of polymer obtained with AIBN in benzene indicated a sharp peak at high $\overline{M}_n$. But the g.p.c. curve of the polymer obtained with AIBN in toluene showed two peaks at relatively low $\overline{M}_n$. This may result from differences in the occurrence of chain transfer in the solvents, as described above. This phenomenon was observed on anionic polymerizations in THF and toluene, as shown in *Figure 1* (curves 4 and 5). The fact that molecular-weight distributions were affected by using solvents may be attributable to solubility of the polymer in the solvent. In the polymerization at high temperature, where it was necessary to use a catalyst with longer half-life (PH2,5B with half-life over 100 h at 100°C), yields were much better, but polydispersity was broader.

^{1}H and ^{13}C n.m.r. spectra for CDMI polymers obtained from the radical and anionic polymerizations are shown in *Figure 2*. In the ^{1}H n.m.r. spectra, signals

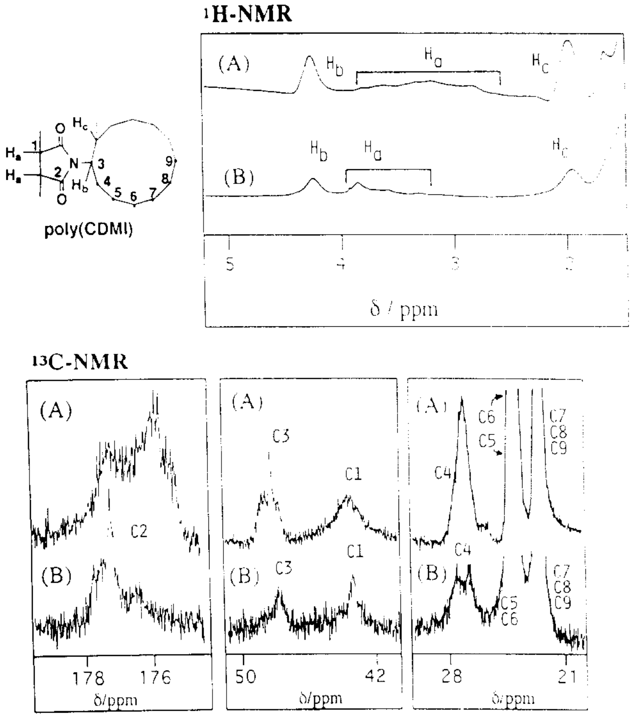

Figure 2 ¹H and ¹³C n.m.r. spectra for poly(CDMI) obtained with (A) AIBN (run 2 in *Table 1*) and (B) n-BuLi (run 22 in *Table 2*)

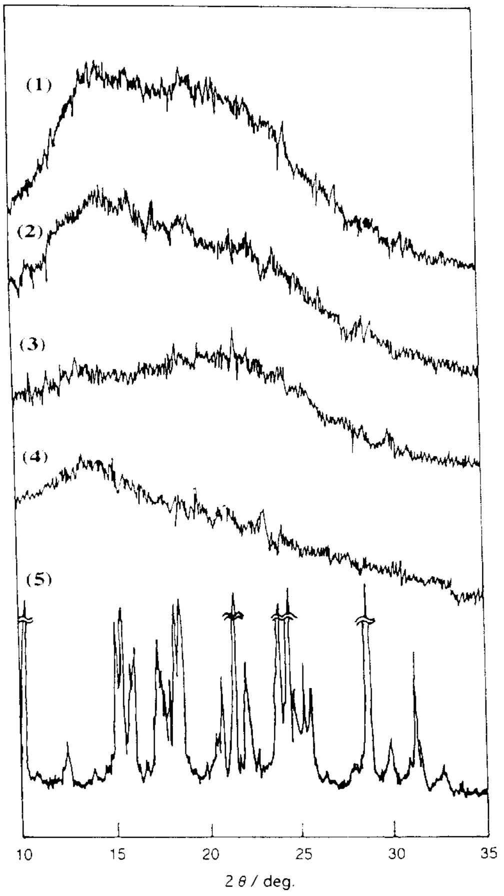

Figure 3 X-ray diffraction diagrams for (1) poly(CDMI) obtained with AIBN (run 2 in *Table 1*), (2) poly(CDMI) obtained with n-BuLi (run 22 in *Table 2*), (3) poly(CDMI-*co*-ST) (run 2 in *Table 4*), (4) poly(CDMI-*co*-MMA) (run 12 in *Table 4*) and (5) CDMI monomer

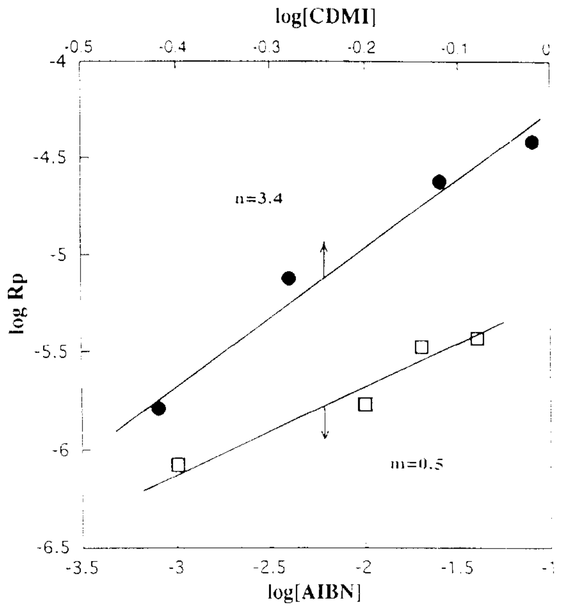

Figure 4 Effects of CDMI monomer and AIBN concentrations on the rate of polymerization in THF at 60°C

assigned to the methine of the main chain in CDMI polymer obtained with AIBN were observed in the range from 3.8 to 2.5 ppm, which had a peak maximum at about 3.2 ppm. On the other hand, signals due to the methine protons in the polymer obtained with n-BuLi were detected from 3.9 to 3.2 ppm, which showed a peak maximum at 3.8 ppm. In addition, the region of the signals in the polymer obtained with AIBN was broader than that obtained with n-BuLi. This tendency was also observed in the ¹³C n.m.r. spectra. The signals due to C2, C3 and C1 in the polymer obtained with AIBN were broader than those in the polymer obtained with n-BuLi. The tendency of signals due to C4 was the opposite. This may be due to different structures of the main chain in the polymers obtained with AIBN and n-BuLi. Anionic polymerization could be more stereo-regularly controlled than radical polymerization because of the bulky and hydrophobic *N*-cyclododecyl group.

X-ray diffraction (X.r.d.) diagrams for poly(CDMI) and CDMI monomer are shown in *Figure 3*. In X.r.d. for poly(CDMI) obtained with AIBN, two broad peaks were observed at about 15° and 21°. In X.r.d. for poly(CDMI) obtained with n-BuLi two broad peaks were also observed at about 15° and 22°. However, both poly(CDMI)s were found to be not crystalline but almost amorphous. In X.r.d. for poly(CDMI-*co*-ST) and poly(CDMI-*co*-MMA), similar tendencies were detected.

Polymerizations were performed with a constant concentration of CDMI monomer and various concentrations of AIBN in benzene at a constant polymerization temperature (60°C) for various periods of time. Polymerizations were carried out in benzene at 60°C with various monomer concentrations and constant AIBN concentration. The polymerization curves were drawn on the basis of these results. From the slope of each curve, being initially linear, the initial rate of polymerization, R_p, could be calculated. The relationship between log R_p and log[AIBN] is shown in *Figure 4*. The exponent of AIBN concentration (m) was determined as 0.50 from

Table 3 Rates (R_p), rate constants (k), overall activation energies (E) and frequency factors (A) for the radical polymerization of N-substituted maleimides

Monomer	$R_p = k[\text{AIBN}]^m[\text{M}]^n$ m	n	k (60°C)	E (kcal mol^{-1})	A (s^{-1})	Ref.
CDMI	0.50	3.4	4.57×10^{-4}	19.2	2.0×10^{9}	This work
BZMI[a]	0.54	2.7	1.32×10^{-4}	24.1	6.6×10^{12}	15
CHMI	0.80	2.3	1.86×10^{-3}	22.2	6.4×10^{11}	15
n-NHI[b]	0.80	2.5	9.91×10^{-4}	22.8	9.5×10^{11}	15
PhMI	0.80	1.2	–	25.2	8.3×10^{14}	16
NMI[c]	0.55	1.6	8.25×10^{-5}	24.4	8.5×10^{11}	17
FMI[d]	0.64	2.1	1.62×10^{-2}	26.4	3.4×10^{15}	17

[a] N-Benzylmaleimide
[b] N-n-Hexylmaleimide
[c] N-1-Naphthylmaleimide
[d] N-2-Fluorenylmaleimide

the slope of this line. This indicates that CDMI can satisfy the ordinary 1/2 power rule, and that bimolecular termination may occur. The m for RMI reported so far was 0.6 to 0.9 even in a homogeneous polymerization system, and generally greater, as shown in *Table 3*. This can be explained by monomolecular termination due to resonance stabilization, as reported by Yamada *et al.*[12,13]. In our experiments the monomer concentrations were relatively low and 0.95 to 0.38 mol l^{-1} because of the poor solubility of the monomer. Thus the initiator efficiency may be slightly lower than the general values[14]. Consequently, there may be a possibility that the n value happened to be in fair agreement with 0.50.

According to the same procedure for determining m, the relation between $\log R_p$ and log[CDMI] (where [CDMI] is the monomer concentration) is plotted in *Figure 4*. The exponent of monomer concentration (n) was determined as 3.4 from the slope of this line. The reason why n was greater than 1 may result from a polymerization process with practically aggregated form of CDMI monomers. There has been no practical evidence for the formation of CDMI monomer aggregate. However, CDMI has both strong polarity because of the two carbonyl groups of the maleimide ring and hydrophobic character due to the N-cyclododecyl group. In addition, CDMI monomer has very poor solubility. Thus it is considered that CDMI monomers can easily aggregate[12,13,15–17]. The n (=3.4) for CDMI is greater than those (n = 1.0 to 2.7) for other RMI[15–17], as shown in *Table 3*. This suggests that the hydrophobic character of the N-cyclododecyl group of CDMI is stronger than for other RMIs.

Polymerization was performed in benzene with constant CDMI monomer and AIBN concentration at 50, 60, 70 and 80°C. R_p was calculated from the relation between time and conversion. The rate constants (k) at 50, 70 and 80°C were calculated from the rate equation at 60°C:

$$R_p = k[\text{AIBN}]^{0.50}[CDMI]^{3.4}$$

Overall activation energy (E) and frequency factor (A) of the polymerization were obtained as 19.2 kcal mol^{-1} and 2.0×10^9 s^{-1}, respectively, from the relation between $\log k$ and $1/T$, as shown in *Figure 5*. This value is smaller than those for other RMI[15–17], and equal to those for vinyl monomer[18], as shown in *Table 3*. The reason for the smaller E cannot be explained exactly from only the hydrophobic character of N-cyclododecyl groups in CDMI. This may be attributable not only to the hydrophobic character but also to steric hindrance of the bulky N-cyclododecyl group. It is considered that the polymerization rate, especially propagation rate constant, was scarcely influenced by the polymerization temperature, and that termination hardly took place because of the bulky N-cyclododecyl group.

Radical copolymerization of CDMI with ST or MMA

The copolymerization of CDMI (M_1) with ST (M_2) or MMA (M_2) was carried out in benzene at 60°C by using AIBN as the initiator. The polymerizations were homogeneous throughout. The results are summarized in *Table 4*. When the concentration of CDMI in monomer feeds in both systems increased, the yields of copolymer increased. The copolymer–composition curve obtained above is shown in *Figure 6*. It is well known that the copolymerization of RMI with ST is practically alternating. In the CDMI–ST and CDMI–MMA systems, similar tendencies were observed as reported previously[15,17]. In the copolymerization systems the bulky N-cyclododecyl group cannot play an important role.

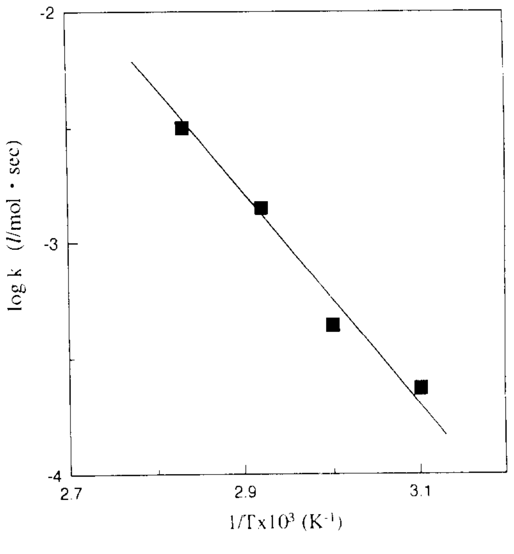

Figure 5 Relationship between $\log k$ and $1/T$ for the polymerization of CDMI initiated by AIBN in THF at various temperatures

Table 4 Radical copolymerization of CDMI (M_1) with ST (M_2) or MMA (M_2) in benzene (6 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polym. time (min)	Convn. (%)	N-anal. (%)	M_1 in copolymer (mol%)	$\overline{M}_n$[b] ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$
1	ST	10.0	30	5.9	3.25	38.32	4.9	2.96
2	ST	20.0	30	7.9	3.36	40.42	9.8	2.51
3	ST	29.6	30	11.9	3.52	43.63	12.5	2.39
4	ST	49.6	30	13.4	3.80	49.74	14.0	2.77
5	ST	68.9	30	23.1	4.09	56.83	16.9	2.70
6	ST	78.4	30	23.5	4.15	58.41	15.1	2.66
7	ST	89.3	30	21.2	4.46	67.36	7.4	3.52
8	MMA	10.0	60	8.1	1.02	8.28	4.7	2.11
9	MMA	19.8	60	8.0	1.64	14.52	4.5	2.17
10	MMA	29.8	60	8.3	2.12	20.12	4.2	2.22
11	MMA	49.6	60	8.9	2.88	30.92	3.6	2.65
12	MMA	69.4	60	12.1	3.80	48.67	3.6	2.71
13	MMA	79.9	60	15.6	4.43	65.46	3.5	2.80
14	MMA	88.2	60	20.6	4.55	69.40	3.1	2.72

[a] [AIBN] = 1.0×10^{-2} mol l^{-1}; $M_1 + M_2 = 1.0$ g

[b] By g.p.c.

The monomer reactivity ratios (r_1, r_2) calculated by the Tüdös–Kelen method[19] and Alfrey–Price[20] Q, e values are shown in *Table 5*. Generally, it is well known that the Q values for RMI calculated from the copolymerization of RMI with ST are abnormal because of the formation of a charge-transfer (CT) complex[21].

We have not been able to prove the existence of a CT complex by u.v. measurements of a mixture of the two monomers. However, a shift of the resonance signals of the protons in CDMI was observed in the n.m.r. spectra in the presence of excess ST. The data were treated according to the Hanna–Ashbaugh relation[22,23]:

$$\frac{1}{\Delta_{\mathrm{obs}}} = \frac{1}{K\Delta_{\mathrm{CTC}}} \times \frac{1}{[\mathrm{D}]_0} + \frac{1}{\Delta_{\mathrm{CTC}}} \qquad (1)$$

Table 6 shows chemical shift values from n.m.r. analysis of CDMI–ST CT complexes. Based on the concentration of monomers and the n.m.r. data shown in *Table 6*, the reciprocal of the change in chemical shift, $1/\Delta_{\mathrm{obs}}$, was plotted over the reciprocal of the concentration of ST, $1/[\mathrm{D}]_0$ (donor monomer). The complex formation constant (K) was calculated as 0.401 mol^{-1} from the slope and the intercept of the linear equation shown in *Figure 7*. These results strongly suggest that a CT complex is involved in the copolymerization of ST and CDMI.

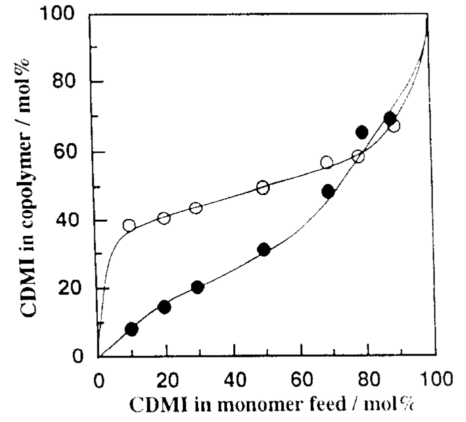

Figure 6 Copolymer–composition curves for (○) poly(CDMI-*co*-ST)s and (●) poly(CDMI-*co*-MMA)s

In our CDMI, the Q (=1.77) value for CDMI bearing cyclododecyl group generally indicated the higher one. It is thought that the Q value for CDMI calculated from

Table 5 Monomer reactivity ratio (r_1, r_2) and the Alfrey–Price Q, e values

M_1	M_2	r_1	r_2	Q_1	e_1	Ref.
CDMI	ST	0.10	0.102	1.77	1.34	This work
CDMI	MMA	0.19	1.306	0.91	1.58	This work
CHMI	ST	0.07	0.00	–	–	15
CHMI	MMA	0.13	2.29	0.50	1.50	15
n-HMI[a]	ST	0.08	0.00	–	–	15
n-HMI	MMA	0.17	2.02	0.56	1.43	15
BZMI[b]	ST	0.02	0.04	2.94	1.87	15
BZMI	MMA	0.14	1.54	0.79	1.63	15
NMI[c]	ST	0.0	0.15	–	–	17
NMI	MMA	0.036	1.89	0.75	2.0	17
FMI[d]	MMA	0.24	0.93	0.43	1.82	17
PhMI	ST	0.13	0.05	3.30	1.45	21
PhMI	MMA	0.30	0.98	1.18	1.51	21

[a] *N*-n-Hexylmaleimide

[b] *N*-Benzylmaleimide

[c] *N*-1-Naphthylmaleimide

[d] *N*-2-Fluorenylmaleimide

Table 6 Chemical shift values from n.m.r. analysis of CDMI–ST charge-transfer complexes, measured in $CDCl_3$

CDMI (mol%)	ST (mol%)	δ_{obs} (Hz)	Δ_{obs} (Hz)
0.025	0.000	1789.81	0.00
0.024	0.419	1779.26	10.55
0.026	0.770	1772.66	17.15
0.027	1.056	1766.39	23.42
0.027	1.972	1750.88	38.93

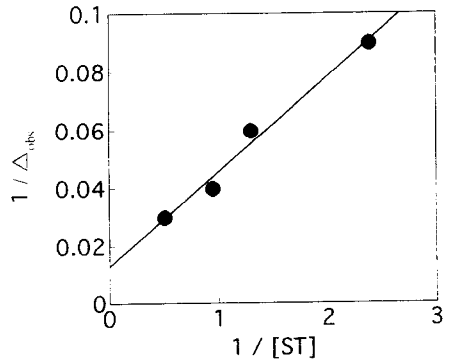

Figure 7 Plot of $1/\Delta_{\rm obs}$ vs. concentration of ST for determination of complex constant (K)

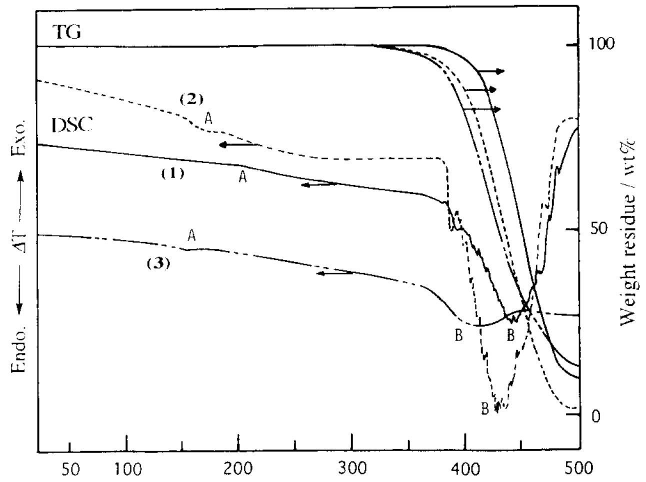

Figure 8 T.g.-d.s.c. curves for (1) poly(CDMI) (run 13 in *Table 1*), (2) poly(CDMI-*co*-ST) (run 1 in *Table 4*) and (3) poly(CDMI-*co*-MMA) (run 11 in *Table 4*) at a heating rate of $10^{\circ}{\rm C\,min^{-1}}$ in nitrogen

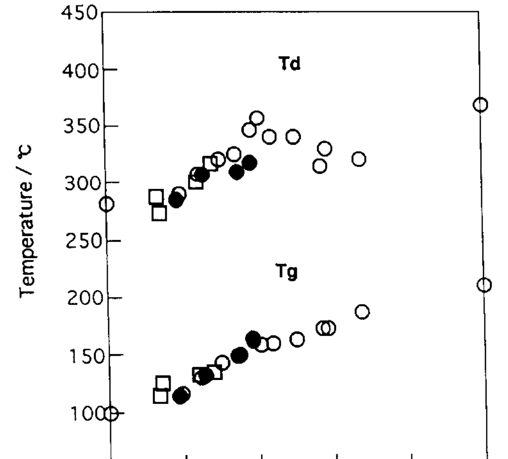

Figure 9 Relationships between CDMI content (mol%) in copolymer and T_g and T_d: (○) poly(CDMI-*co*-ST)s, (●) poly(CHMI-*co*-ST)s and (□) poly(PhMI-*co*-ST)s

the CDMI–MMA system is reasonable, as compared with other RMI Q values. The e value for CDMI was determined to be 1.46, which is an average one calculated from ST and MMA systems.

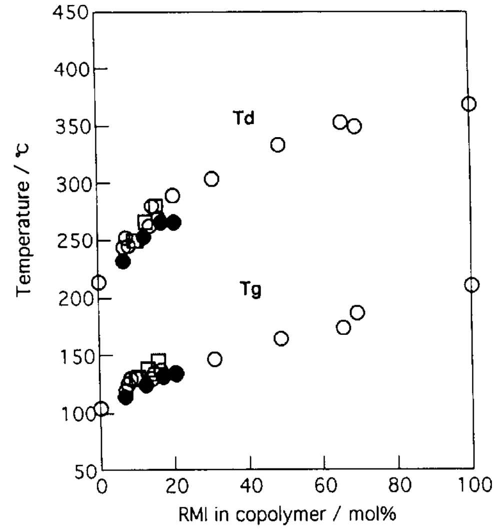

Figure 10 Relationships between CDMI content (mol%) in copolymer and T_g and T_d: (○) poly(CDMI-*co*-MMA)s, (●) poly(CHMI-*co*-MMA)s and (□) poly(PhMI-*co*-MMA)s

Molecular-weight distributions for both poly(CDMI-*co*-ST) and poly(CDMI-*co*-MMA) exhibited one peak, as well as that of the CDMI polymer obtained with AIBN in benzene (run 8) shown in *Figure 2*. Generally $\overline{M_n}$ for the copolymers were higher than those for poly(CDMI) shown in *Tables 1* and *2*. The $\overline{M_n}$ distribution revealed a peak maximum for $\overline{M_n}$ when the ratio of RMI/ST in the monomer feeds is about 1/1. In the CDMI–MMA system, the yields were much lower than those for poly(CDMI-*co*-ST)s. But the $\overline{M_n}$ for poly(CDMI-*co*-MMA) linearly decreased with an increase of CDMI monomer feed and were much lower than those for poly(CDMI-*co*-ST)s. This tendency can also be recognized in other RMI studied so far[15,17,24,25]. Characteristic observation could not be observed in the CDMI copolymerizations despite interaction among carboxyl groups in CDMI, polymerization solvent and hydrophobic character of N-cyclododecyl group.

Typical diagrams of thermogravimetric (t.g.) and differential scanning calorimetric (d.s.c.) analysis for CDMI homopolymer and copolymers are shown in *Figure 8*. In a t.g.-d.s.c. curve for poly(CDMI), one endothermic peak due to a glass transition temperature (T_g) (A in *Figure 8*) and some large peaks (B in *Figure 8*) due to melting and decomposition were observed. In t.g.-d.s.c. curves for both poly(CDMI-*co*-ST) and poly(CDMI-*co*-MMA), similar tendencies were observed.

Figures 9 and *10* show the dependence of CDMI content (mol%) in poly(CDMI-*co*-ST)s and poly(CDMI-*co*-MMA)s on T_g, and initial degradation temperature (T_d). T_d indicates the temperature at which the decomposition of copolymer starts. In both relationships, T_g and T_d increased with the CDMI content in the copolymers. T_g and T_d for poly(CDMI) were 210 and 369°C, respectively. Matsumoto *et al.*[8] reported that T_g for N-n-alkylmaleimide (nRMI) corresponded to the number of carbon atoms in the N-alkyl groups, e.g. from 97°C for poly(N-n-octadecylmaleimide) ($n = 18$) to 185°C for poly(N-n-butylmaleimide) ($n = 4$). Similar tendencies were reported by Barrales-Rienda *et al.*[21,26]. However, the T_g for CDMI was much higher than that

(T_g = 117°C)[8] for poly(*N*-n-dodecylmaleimide) (n = 12) bearing a linear long alkyl chain as *N*-substituent. T_g for poly(CDMI-*co*-ST)s and poly(CDMI-*co*-MMA)s were 116 to 187°C and 120 to 187°C, respectively. T_d for poly(CDMI-*co*-ST)s and poly(CDMI-*co*-MMA)s were 290 to 320°C and 244 to 350°C, respectively. It is necessary to evaluate thermostabilities for CDMI–ST, CDMI–MMA, CHMI–ST, CHMI–MMA, PhMI–ST, and PhMI–MMA copolymers obtained under the same conditions. Thus, these CHMI and PhMI copolymers were prepared under the same conditions as CDMI copolymers. In the CDMI–ST copolymers containing less than 40 mol% of CDMI, the thermostabilities of the copolymers indicated tendencies similar to those for the CHMI–ST and PhMI–ST copolymers, as shown in *Figure 9*. As can be seen from *Figure 10*, in the CDMI–MMA copolymers containing less than 20 mol% of CDMI, the thermostabilities of the copolymers showed similar tendencies to those for the CHMI–MMA and PhMI–MMA copolymers.

CONCLUSIONS

N-Cyclododecylmaleimide (CDMI) was newly synthesized from maleic anhydride and cyclododecylamine.

Homopolymerization of CDMI was performed with radical and anionic initiators in several solvents or in bulk to obtain the polymer. The yields and $\overline{M}_n$ of the polymers obtained in benzene were quantitative and the highest ($\overline{M}_n = 3.5 \times 10^4$).

The initial rate of polymerization was $R_p = k[\text{AIBN}]^{0.50}[\text{CDMI}]^{3.4}$, where k is the rate constant. Overall activation energy (E) and frequency factor (A) were 19.2 kcal mol^{-1} and 2.0×10^9 s^{-1}, respectively.

The monomer reactivity ratios in the copolymerization of CDMI (M_1) with styrene (ST; M_2) or methyl methacrylate (MMA, M_2) and Alfrey–Price Q, e values were determined as $r_1 = 0.10$, $r_2 = 0.102$, $Q_1 = 1.77$, $e_1 = 1.34$ in CDMI–ST system, and $r_1 = 0.19$, $r_2 = 1.31$, $Q_1 = 0.91$, $e_1 = 1.58$ in CDMI–MMA system.

Glass transition temperature (T_g) and initial degradation temperature (T_d) for poly(CDMI) were 210 and 369°C, respectively.

T_g for poly(CDMI-*co*-ST)s and poly(CDMI-*co*-MMA)s were 116 to 187°C and 120 to 187°C, respectively. T_d for poly(CDMI-*co*-ST)s and poly(CDMI-*co*-MMA)s were 290 to 320°C and 244 to 350°C, respectively.

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