Polymerization and Copolymerization of *endo*-*N*-Cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide

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ABSTRACT: *endo*-*N*-Cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHN or *endo*-CHN), one of the norbornene derivatives, was prepared from *N*-cyclohexylmaleimide (CHMI) and cyclopentadiene (CPD) according to the Diels–Alder reaction. Yields of homopolymers were about 10 wt%. No CHN could be polymerized in bulk without radical catalysts under 250°C. But at 250°C for 6 h, *endo*-CHN was converted to *exo*-CHN in a 75 mol% yield. The polymerization of CHN over 300°C for 1 h gave the polymer in about 100% yield. The molecular weights ($\bar{M}_w$) of polymer insoluble in methanol were 1500 to 2000 and the $\bar{M}_w$ of the polymer soluble in methanol was about 700. It was found that the polymer consisted of a mixture among CHN, CHMI and an adduct(II) obtained from CHN and CPD.

KEY WORDS *N*-Cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide / Norbornene Derivative / Radical Polymerization / Copolymerization / Monomer Reactivity Ratio / *Q,e* Values / Thermostability /

There have been many reports on the polymerizations of norbornene and its derivatives. It is known that norbornene is polymerized by cationic and Ziegler–Natta catalysts to give the vinylene-type polymer and ring-opened-type polymer, respectively.[1] *N*-Phenyl-5-norbornene-2,3-dicarboximide (I), one of the norbornene derivatives, was polymerized by radical initiators to yield a polymer of about 800 in molecular weight.[2] A ^{13}C NMR study was carried out on the polymers obtained from I in bulk without radical catalysts.[3] Recently *N*-cyclohexylmaleimide (DHMI) was found to be useful for an improvement of the thermostabilities of the common vinyl polymers.[4] In this article, *endo*-*N*-cyclohexylbicyclo[2.2.1]-hept-2-ene-5,6-dicarboximide (CHN or *endo*-CHN) containing a DHMI group at 2,3-positions in norbornene, was polymerized with and without catalysts in bulk and in solvents at high temperatures. Copolymerizations of CHN with styrene (ST), methyl methacrylate

(MMA), or vinyl acetate (VAC) were performed with radical initiators at high temperatures. In addition, several ionic polymerizations of CHN were performed with cationic, anionic and the Ziegler–Natta catalysts.

EXPERIMENTAL

Monomers

CHN Monomer. CHN was prepared from CHMI and cyclopentadiene (CPD) according to the Diels–Alder reaction. CPD (6.7 ml, 0.11 mol) was added dropwise to a solution of CHMI (17.6 g, 0.1 mol) in toluene (60 ml), and then the mixture was stirred for 2 h at room temperature. The precipitate was filtered, recrystallized from cyclohexane–chloroform (4 : 1) to obtain a pure CHN in 53% yield. mp 158—159°C, IR (cm^{-1}): 1620 (C=C), 1701 (C=O); ^{1}H NMR (δ, ppm in CDCl$_3$) [see hydrogen position (a to f) as shown in Scheme 1]: 6.10 (m, 2H, a), 3.75 (m, 1H, d), 3.35 (m,
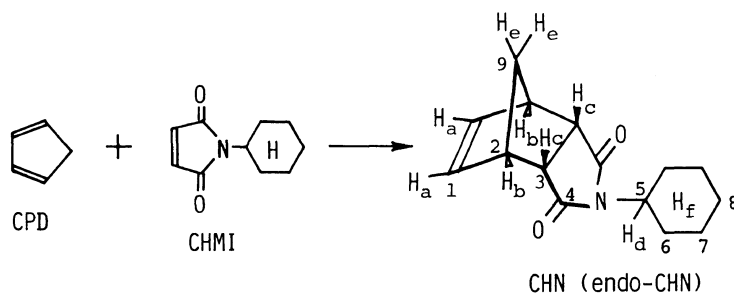
Scheme 1.

2H, c), 3.15 (m, 2H, b), 2.05—1.22 (m, 12H, e and f). ^{13}C NMR (δ, ppm in CDCl$_3$) [see carbon numbers (1 to 9) shown in Scheme 1]: 177.6 (C4), 134. 1(C1), 51.7 (C5), 51.1 (C9), 45.0 (C3), 44.9 (C2), 28.6 (C6), 25.7 (C7), 24.9 (C8). *Elemental analysis* (%). Calcd for C$_{14}$H$_{19}$O$_2$N: H=7.81%, C=73.44%, N=5.71%; Found: H=7.84%, C=73.17%, N=5.85%.

exo-CHN. CHN was heated in a sealed glass tube under vacuum for 6 h at 250°C. A small amount of homopolymer was removed from the reaction mixture with a column chromatographic method using an activated alumina as a packing. *exo*-CHN was extracted from the reaction mixture with cyclohexane. The solvent was distilled thoroughly under reduced pressure and then the residue of the crude *exo*-CHN was recrystallized from methanol three times to obtain a pure *exo*-CHN in 65% yield. mp 130—132°C. IR (cm^{-1}): 1623 (C=C), 1695 (C=O); ^{1}H NMR (δ, ppm in CDCl$_3$) [reference to hydrogen positions (a' to f') shown in Scheme 1]: 6.28 (m, 2H, a'), 3.94 (m, 1H, d'), 3.25 (m, 2H, c'), 2.61 (m, 2H, b'), 2.16—1.17 (m, 12H, e' and f'). ^{13}C NMR (δ, ppm in CDCl$_3$) [reference to carbon numbers (1 to 9) in Scheme 1]: 178.0 (C4'), 137.8 (C1'), 51.6 (C5'), 47.4 (C9'), 45.4 (C3'), 42.6 (C2'), 28.3 (C6'), 25.4 (C7'), 24.6 (C8'). *Elemental analysis* (%). Calcd for C$_{14}$H$_{19}$O$_2$N: H=7.81%, C=73.44%, N=5.71%; Found: H=7.80%, C=72.73%, N=5.70%.

Comonomer and Materials

ST, MMA, and VAC were purified by the usual methods. 2,2'-Azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), aluminum trichloride and solvents were purified by the usual methods. Commercially available 1,1-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane (PH3M), 2,5-dimethyl-2,5-di(*t*-butylperoxyl)-hex-3-yne (PH25B), and anionic and cationic catalysts were used without further purification.

Polymerization Procedures

Radical polymerizations of CHN in bulk or in solvents were carried out in a sealed-glass tube with or without the initiator at 120 to 350°C. After polymerization for a given time, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. In bulk polymerization, a small amount of tetrahydrofuran (THF) was added to the tube, and the THF solution was poured into a large amount of methanol. The polymer was filtered and dried under reduced pressure for 2 days.

Radical copolymerizations of CHN with styrene (ST), methyl methacrylate (MMA), or vinyl acetate (VAC) were achieved with the radical initiator in benzene or in bulk at 70 to 170°C in a sealed glass tube. After the prescribed time, the product was poured into a large amount of methanol and purified by reprecipitation, using a THF–methanol solution, and dried in vacuum. Composition of the copolymer was determined from nitrogen

analysis.

Solution ionic polymerizations of CHN were performed with cationic, anionic or Zieglar–Natta catalysts in various solvents at different temperatures. All operations of polymerization procedures were attained under nitrogen atmoshpere using a polyethylene bag.

Measurements

199.5 MHz ^{1}H NMR and 50.1 MHz ^{13}C NMR spectra were obtained with a JEOL FX-200. The molecular weights of the polymers and copolymers were measured by gel permeation chromatography (GPC) on Shimadzu LC 3A equipped with data processor, using THF as the solvent and Shimadzu polystyrene gels HGS-20-15-10 or by a vapor pressure osmometer (VPO) on Corona 114 using the vapor of benzene. Diagrams of TG and DSC were obtained with Rigaku Thermal analysis apparatus.

RESULTS AND DISCUSSION

Radical Polymerizations

The results of radical homopolymerizations in bulk and in solvents are summarized in Table I. Homopolymerization of CHN with PH3M as a catalyst in chlorobenzene (CB) at 120°C gave the polymer in an about 10% yield with a $\bar{M}_w$ of 2300 to 3000. But under 110°C, the yields were zero even if radical catalyts were used. At 120°C the yields in the polymerizations with PH3M (half-life, 18 min at 120°C) were better than those with other catalysts. At 170°C in bulk polymerizations with PH25B (half-life, 12 min at 170°C) the yields were better than those with PH3M. Thus, the yields may be related to the half-life of the catalysts. In addition, the polymerizations required over 10 mol% catalyst to obtain the polymers in enough yields. No CHN could be polymerized in bulk without the radical initiators under 250°C. However at 250°C for 6 h,

Table I. Radical homopolymerizations of CHN at high temperatures

Run No.	CHN mmol	Initiator mmol	Solvent[b] ml	Temp °C	Time h	Yield[c] wt%	$N^{[d]}$ %	$\bar{M}_n{}^{[e]}$ ×10^{-3}	$\bar{M}_w/\bar{M}_n{}^{[e]}$	$\bar{M}_w{}^{[f]}$ ×10^{-3}
1-1	8.33	PH3M (0.87/20 min)[a]	CB (4)	120	1.0	11.0	5.34	2.9	1.1	2.11
1-2	4.29	PH3M (0.44)	CB (2)	120	1.0	7.1	—	3.0	1.4	—
1-3	4.21	PH3M (0.24/20 min)[a]	CB (2)	120	1.0	9.3	5.55	2.8	1.5	2.19
1-4	4.69	PH3M (0.24)	CB (2)	120	1.0	9.3	—	2.3	1.4	—
2-1	4.11	PH3M (0.44)	—	170	1.0	6.5	—	3.7	1.6	3.28
2-2	4.19	PH3M (0.18/10 min)[a]	—	170	1.0	6.9	—	2.3	1.5	—
3-1	4.18	PH25B (0.25)	—	170	1.0	11.2	5.46	4.5	2.4	3.26
3-2	4.38	PH25B (0.21/10 min)[a]	—	170	1.0	2.4	—	2.4	1.7	—
4-1	20.30	PH25B (0.20)	—	170	2.0	9.0	5.15	2.4	1.1	2.25
4-2	20.30	PH25B (0.20)	—	170	4.0	7.0	5.17	2.6	1.0	2.43
4-3	21.00	PH25B (0.20)	—	170	6.0	7.0	5.45	2.5	1.1	2.31
5	4.06	BPO (0.4)	—	230	6.0	9.6	5.21	1.9	2.6	1.85
6-1	21.00	—	—	250	2.0	—	—	—	—	—
6-2	21.00	—	—	300	2.0	48.8	5.59	1.1	1.0	1.61
6-3	21.00	—	—	350	2.0	47.1	5.29	0.98	1.0	1.31

[a] The catalyst was added in 4 portions over 20 or 10 min to a preheated solution of CHN, followed by heating for an additional 40 or 50 min at 120 or 170°C.

[b] CB = monochlorobenzene.

[c] Yield of the polymer insoluble in methanol.

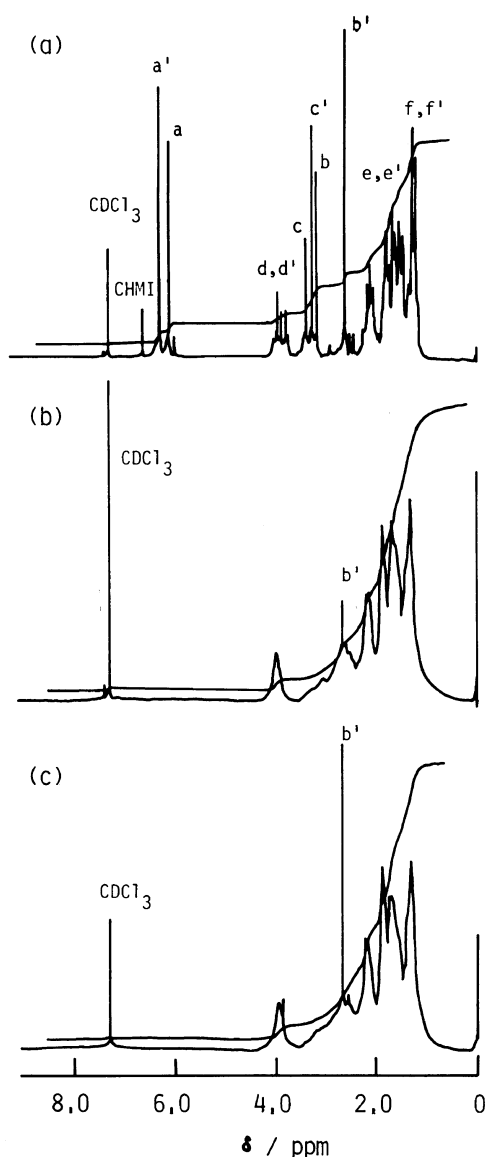[d] Elemental analysis of polymers.

[e] By GPC.

[f] By VPO.

T. Oishi, Y. Morioka, and M. Fujimoto

Figure 1. 199.5 MHz ^{1}H NMR spectra of CHN polymerized for 2 h at (a) 250 (b) 300 and (c) 350°C.

Figure 2. 50.1 MHz ^{13}C NMR spectra of CHN polymerized for 2 h at (a) 250 (b) 300 and (c) 350°C.

CHN was converted to *exo*-CHN in a 75% yield, judging from the NMR spectra, as shown in Scheme 2(a). ^{1}H NMR and ^{13}C NMR spectra of the reaction mixture at 250, 300, and 350°C are shown in Figures 1 and 2. In the polymerization at 250°C for 2 h, the yield of polymer was zero as shown in Table I. Each integration value of three signales at 6.28

(a′), 3.25 (c′), and 2.61 (e′) ppm in *exo*-CHN was similar to 3/5 of each of the corresponding three signals in CHN. Thus the reaction mixture obtained may have been a mixture of CHN–*exo*-CHN (2:3). This behavior was also confirmed by HPLC. In Figure 1(a) and 2(a), the peaks of the double bond of CHMI and an adduct (II) obtained from CHN and CPD prepared in retro-Diels–Alder reaction can be
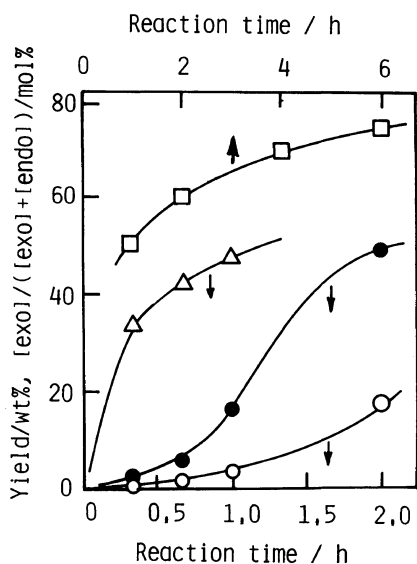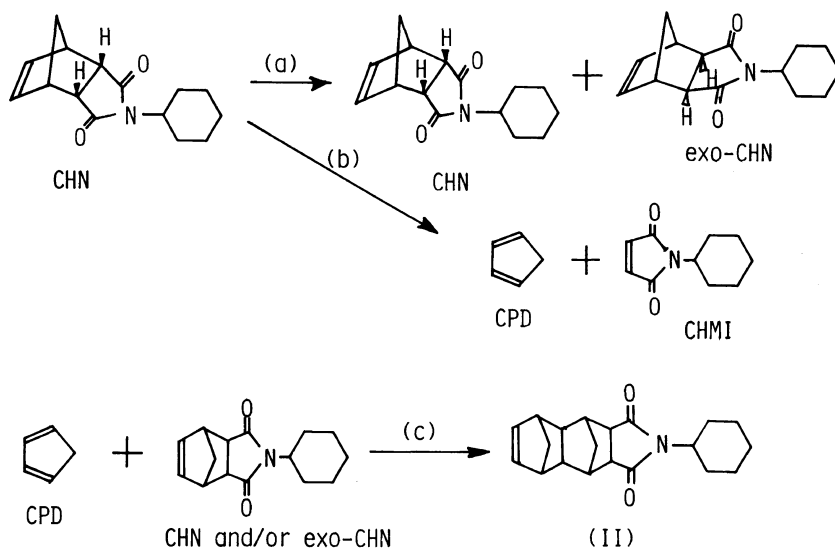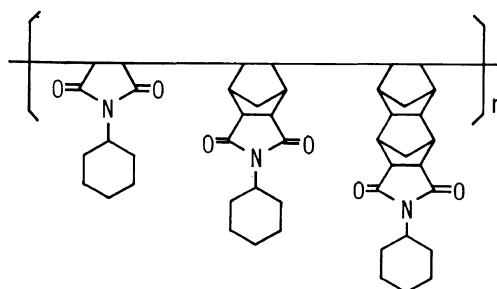
Scheme 2.

Figure 3. Relationships between yields of polymer insoluble in methanol or mole fraction of *exo*-CHN and reaction time for polymerization of CHN in bulk at different temperatures: (□), 250; (○), 280; (●), 300; (△), 320°C.

Scheme 3.

observed. This suggests that three reactions might occur as shown in Scheme 2. In Figures 1(b), (c) and 2(b), (c), no peaks of double bonds can be observed, which indicates that different kinds of monomers could not exist in the reaction mixture but that all were polymerized. Figure 3 shows the relation between conversions of *exo*-CHN and reaction times at 250°C. The polymerization of CHN over 300°C for 1 h gave the polymers quantitatively. The molecular weights $(\bar{M}_w)$ of the polymer insoluble in methanol were 1500 to 2000 and the $\bar{M}_w$ of the polymer soluble in methanol was about 700. It was found that the polymer obtained consists of a mixture among CHN, *N*-cyclohexylmaleimide (CHMI) and an adduct(II) obtained from CHN and CPD prepared in retro-Diels-Alder reaction because of high temperatures as shown in Schemes 2 and 3. The relationship between the conversion of the polymer insoluble in methanol and reac-

tion time is shown in Figure 3. The rate of polymerization (R_p) was calculated from the slope of the initial straight line in Figure 3. The over-all activation energy was then determined as 20.3 kcal mol^{-1}, which was less than that (22.2 kcal mol^{-1})[5] in the polymerization of CHMI in THF at 60°C.

Radical Copolymerizations

Radical copolymerizations of CHN with ST, MMA, or VAC were performed in bulk [170°C, PH25B (0.04 g)] and in benzene [70°C, BPO $(1.01 \times 10^{-2}$ mol l^{-1}), benzene (5 ml); 120°C, PH25B (0.06 g), benzene (1.5 ml)]. All copolymerizations proceeded homogeneously throughout. The yields of copolymers in all systems decreased with increasing CHN concentration in monomer feeds. In CHN–ST systems, the yields were 22.3 to 2.1% for 24 h at 70°C; 65.8 to 0.8% for 20 h at 120°C and 6.7 to 1.3% for 2 h at 170°C. In CHN–MMA systems, the yields were 56.5 to 2.2% for 24 h at 70°C; 52.5 to 7.4% for 20 h at 120°C, and 10.5 to 3.3 for 10 to 20 h at 170°C. In CHN–VAC systems, the yields were almost trace for 24 h at 70°C; 34.2 to 0% for 20 h at 120°C, and 7.5 to 9.5% for 4 to 16 h at 170°C. Copolymer-composition curves are shown in Figure 4. In solution the polymerizations of CHN with ST and MMA in benzene at 70 and 120°C, and the content of CHN in polymer were very low. In bulk at 170°C, the copolymerizabilities were better than other systems. The monomer reactivity ratios (r_1, r_2) calculated according to the Integration method by Mayo and Lewis[6] and the Alfrey–Price[7] Q, e values were obtained for the bulk copolymerization at 170°C as follows: $r_1 = 0.07$, $r_2 = 5.43$, $Q_1 = 0.084$, $e_1 = 0.15$ in the CHN(M$_1$)–ST(M$_2$); $r_1 = 0.03$, $r_2 = 25.8$, $Q_1 = 0.04$, $e_1 = 0.91$ in the CHN(M$_1$)–MMA(M$_2$); $r_1 = 0.30$, $r_2 = 0.83$, $Q_1 = 0.02$, $e_1 = 0.95$ in the CHN(M$_1$)–VAC(M$_2$) system. Generally, the reactivity ratios $(r_1$ for CHN) were very small, which suggests that CHN has very low homopolymerizability. These tendencies were recognized in other norbornene de-
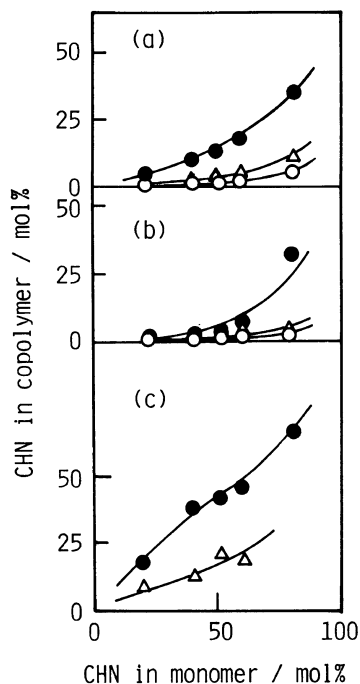

Figure 4. Copolymer–composition curves for (a) CHN–ST, (b) CHN–MMA, and (c) CHN–VAC systems: (O), in benzene (5 ml) at 70°C; (△), in benzene (1.5 ml) at 120°C; (●), in bulk at 170°C.

rivatives.[8–12] The average Q and e values of CHN in three systems were determined as $Q = 0.05$ and $e = 0.67$, respectively, which indicates CHN to be consistent with the structure having a non-resonance character. Compared with the Q and e values for other norbornene derivatives $(Q = 0.038$, $e = 0.26$ for 5-cyanobicyclo[2.2.1]hept-2-ene[8]; $Q = 0.059$, $e = 0.26$ for 5-carbomethoxybicyclo[2.2.1]-hept-2-ene,[9,10] the Q value (0.05) for CHN almost agreed with the reported values. The e value (0.67) was slightly larger than those for other norbornene derivatives.[8–10] The reason for this may be the electron-attracting character of the two carbonyl groups in the imide ring. The Q and e values for CHN were considerably smaller than those $(Q = 0.50$, $e = 1.50)$ for N-cyclohexylmaleimide (CHMI).[5] This may be understood from the fact that the reaction double bond of CHN is not conjugated with two

carbonyl groups. The number-average molecular weight $(\bar{M}_n)$ and polydispersity [weight-average molecular weight $(\bar{M}_w)/\bar{M}_n$] are $\bar{M}_n = 8.8 \times 10^3$ to 3.4×10^3, $\bar{M}_w/\bar{M}_n = 16.0$ to 1.6 in poly(CHN-co-ST)s; $\bar{M}_n = 2.0 \times 10^4$ to 7.4×10^3, $\bar{M}_w/\bar{M}_n = 7.0$ to 1.1 in poly(CHN-co-MMA)s; and $\bar{M}_n = 1.6 \times 10^4$ to 3.5×10^3, $\bar{M}_w/\bar{M}_n = 1.3$ to 1.1 in poly(CHN-co-VAC)s.

Ionic and Ziegler–Natta Polymerizations

There are many patents[13] for the polymerizations of norbornene derivatives with ionic and Ziegler–Natta catalysts. But no ionic polymerizations of norbornene derivatives having N-substituted dicarboximide at 5,6-position in norbornene could be carried out in the presence of an ionic or Ziegler Natta catalyst.

Anionic polymerizations of CHN were carried out with n-butyl lithium (n-BuLi) as the catalyst in THF or toluene at different temperatures (-78 to $28°C$). But no appreciable polymers could be obtained. In addition, only a CHN peak was observed in the HPLC charts of the reaction mixture. There were no polymers having low molecular weights and soluble in methanol of precipitant, judging from VPO measurement.

Cationic polymerizations of CHN were performed with $BF_3O(Et)_2$, $FeCl_3$, $AlCl_3$, or $MoCl_3$ as the catalyst in $CHCl_3$ at room temperature and $50°C$. However, no polymers could be obtained under these reaction conditions.

Polymerizations of CHN were accomplished in the presence of the Zieglar-Natta system catalyst, that is, $Al(Et)_3/TiCl_4 = 0.4$, 0.5, 1.0, 1.7; $Al(Et)_3/MoCl_5 = 5.0$, 9.8; $(Et)_2AlCl/TiCl_4 = 0.5$, 1.0, 2.0, 2.4, 2.6, 3.7; $(Et)_2AlCl/WCl_6 = 5.0$, 9.8 in 1,2-dichloroethane, benzene, toluene, or monochlorobenzene at room temperature to $60°C$ for 16 to 20 h. In all polymerizations, the yields were traces; that is, methanol of the precipitatnt became turbid on pouring the reaction mixture into it and consequently properties of the polymers could not

be measured. It is very difficult to explain the reason why the yields were low. Possibly, the steric hindrance of the N-cyclohexyl dicarboximide group at 5,6-position in norbornene may have been the cause.

Thermostabilities of the Polymers

Diagrams of a thermogravimetric (TG) and a differential scanning calorimetric (DSC) analysis are shown in Figures 5 and 6. Softening points (T_m) and initial degradation temperatures (T_d) of the polymers from the radical polymerizations were as follows: $T_m = 268$ to $306°C$ and $T_d = 334$ to $363°C$. It has been reported[4] that there is no T_m of N-cyclohexylmaleimide (CHMI) polymers and that the weight loss gradually increases with rise in temperature over $300°C$. Accordingly, the thermostabilities of CHN polymers were slightly worse than those of CHMI polymers from the viewpoint of softening points. But the weight loss of CHN polymers was almost equal to that of CHMI homopolymers. The thermostabilities of CHN–ST and CHN–MMA copolymers were worse than those of the corresponding CHMI–ST and CHMI–MMA copolymers.[4] The reason for this may
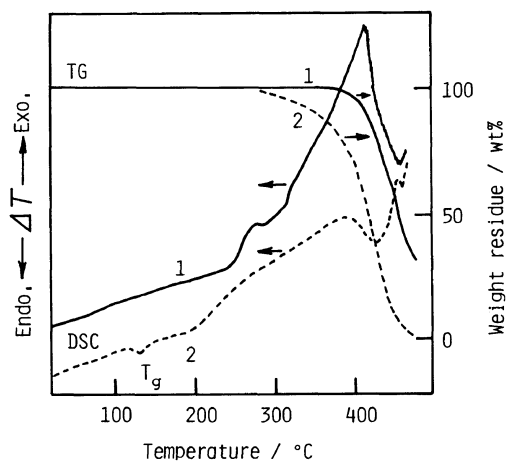
Figure 5. TG and DSC curves for (1) CHN homopolymer [run no. 6-3] and (2) CHN–ST copolymer [obtained from CHN (49.8 mol%) and ST with PH25B (0.041 g) in bulk at 170°C] at a heating rate of $10°C \, min^{-1}$ in nitrogen.

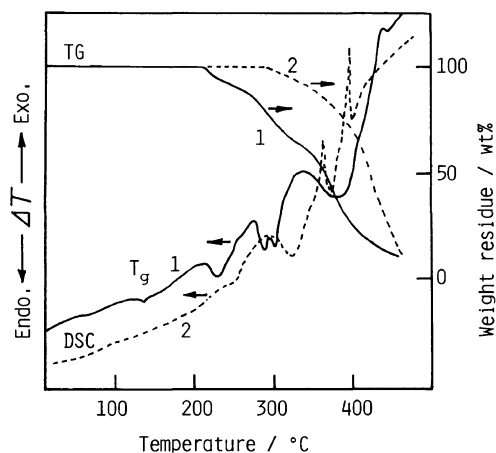T. OISHI, Y. MORIOKA, and M. FUJIMOTO

Figure 6. TG and DSC curves for (1) CHN–MMA copolymer [obtained from CHN (49.6 mol%) and MMA with PH25B (0.037 g) in bulk] and (2) CHN–VAC copolymer [obtained from CHN (49.4 mol%) and VAC with PH25B (0.12 g) in bulk at 170°C] at a heating rate of 10°C min^{-1} in nitrogen.

be that CHN–ST and CHN–MMA copolymers contain very small amounts of CHN units in the polymer side chains. However, the thermostabilities of CHN–VAC copolymers were much better than those of CHMI–VAC copolymers because of better copolymerizability of CHN with VAC. T_m and T_d of the copolymers were as follows: $T_m = 115$ to 130°C, $T_d = 210$ to 260°C for poly(CHN-co-ST)s; $T_m = 160$ to 180°C, $T_d = 220$ to 250°C for poly(CHN-co-MMA)s; $T_m = 240$ to 283°C for poly(CHN-co-VAC)s. The glass transition temperatures (T_g) were observed at 108 to 116°C for CHN–ST copolymers [obtained from CHN (20.0 to 49.8 mol% in monomer feeds) and ST in bulk at 170°C] and at 130 to 138°C for CHN–MMA copolymers as shown in Figures 5 and 6.

REFERENCES

1. T. Tsujino, T. Mitsueda, S. Kobayashi, and J. Furukawa, *Kogyo Kagaku Zasshi*, **67**, 1961 (1964); J. Furukawa, "Kobunshi Gosei," Kagakudoujin, Kyoto, 1986, p 102.
2. N. G. Gayload, M. Martan, and A. B. Deshpande, *J. Macromol. Sci.-Chem.*, **A19**, 537 (1983).
3. A. C. Wong and W. M. Ritchey, *Macromolecules*, **14**, 825 (1981).
4. M. Urushizaki, H. Aida, and H. Ukai, *Fukui Univ., Kougakubu Kenkyu Hokoku*, **30**, 97 (1982); T. Oishi, M. Momoi, M. Fujimoto, K. Sumida, and K. Doiuchi, *Mem. Fac. Eng., Yamaguchi Univ.*, **39**, 127 (1988).
5. T. Oishi and T. Kimura, *Kobunshi Ronbunshu*, **33**, 685 (1976).
6. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
7. T. Alfrey, Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
8. M. Imoto, T. Otsu, and T. Ito, *Kogyo Kagaku Zasshi*, **67**, 961 (1964).
9. J. M. Judge and C. C. Price, *J. Polym. Sci.*, **41**, 435 (1959); L. J. Young, *J. Polym. Sci.*, **54**, 411 (1961).
10. L. J. Young, Copolymerization Reactivity Ratios and Tabulation of Q–e values, in "Polymer Handbook," ed. by J. Brandrup and E. H. Imergut, John Wiley and Sons Inc., New York, N. Y., 1975, pp II-105 and II-387.
11. T. Ito, T. Otsu and M. Imoto, *Mem. Fac. Eng., Osaka City Univ.*, **7**, 87 (1965).
12. L. D. Mazo, A. I. Ezrielev, and E. S. Roskin, *Vysokmol. Soedin. Ser. B*, **10**, 615 (1968) (*Chem. Abstr.*, **69**, 107137b).
13. For examples: Nippon Kokai Tokkyo Koho 53-103000, 53-97099, 51-32547, 52-47899.