

Oligomerization and Copolymerization of *endo-N*-Cyclohexyl-9-oxabicyclo[2,2,1]hept-2-ene-5,6-dicarboximide

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ABSTRACT: *endo-N*-Cyclohexyl-9-oxabicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHO or endo-CHO), one of the norbornene derivatives, was prepared from *N*-cyclohexylmaleimide (CHMI) and furan (FN) according to the Diels-Alder reaction. The number average molecular weights (\bar{M}_n) of the polymers insoluble in methanol were 1100 to 2000, *i.e.*, the degree of polymerization was 4 to 8. The oligomers having \bar{M}_n below 1000 were soluble in methanol. Retro-Diels Alder reaction mainly took place in the bulk reaction of CHO over 140°C. CHO was copolymerized with styrene, methyl methacrylate and vinyl acetate in the presence of radical initiators. The monomer reactivity ratios and Alfrey-Price $Q-e$ values were determined.

KEY WORDS *N*-Cyclohexyl-9-oxabicyclo[2,2,1]hept-2-ene-5,6-dicarboximide / Radical Polymerization / Copolymerization / Monomer Reactivity Ratio / Q, e Values / Thermostability /

A number of polymerizations of norbornene and its derivatives have been investigated. 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 (PhN), one of the norbornene derivatives, was polymerized by radical initiators.² A ¹³C NMR study was carried out on polymers obtained from PhN in bulk without radical catalysts.³ However, there have been no reports on radical polymerization reactivity, particularly of the monomer reactivity ratios in copolymerizations of norbornene derivatives containing *N*-substituted maleimide groups.

Recently, *N*-cyclohexylmaleimide (CHMI) was found to be useful for improvement of the thermostabilities of the common vinyl polymers.⁴ In order to promote the applications of CHMI, the fundamental investigations have been made.⁵ For this purpose, polymerization and copolymerization of CHMI-cyclopenta-

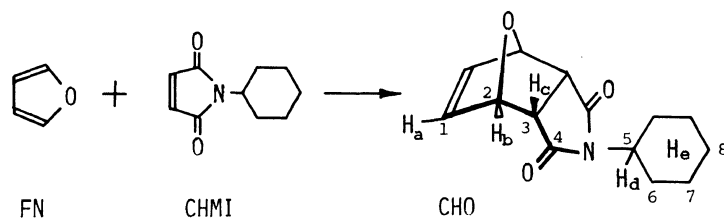
diene (CPD) Diels-Alder adduct, *endo-N*-cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHN) were investigated.⁶

In this article, *endo-N*-cyclohexyl-9-oxabicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHO or endo-CHO) containing a CHMI group at 5,6-positions in oxa-norbornene, was polymerized with and without catalysts in bulk and in solvents. Copolymerizations of CHO with styrene (ST), methyl methacrylate (MMA), or vinyl acetate (VAC) were performed, using radical initiators. In addition, several ionic polymerizations of CHO were performed with cationic, anionic and the Ziegler-Natta catalysts.

EXPERIMENTAL

Monomers

Endo-CHO monomer: CHO was prepared from CHMI⁷ and furan (FN) according to the Diels-Alder reaction, as shown in Scheme 1. FN (40.8 g, 0.2 mol) was added dropwise to a



Scheme 1.

solution of CHMI, mp. 79°C (35.2 g, 0.2 mol) in toluene (120 ml), and then the mixture was refluxed for 3 h. Toluene was distilled out under reduced pressure, and the residue was recrystallized from cyclohexane to obtain a pure CHO in 75.1% yield. mp 134–135°C, ^1H NMR (δ , ppm in CDCl_3) [see hydrogen position (a to e) as shown in Scheme 1]: 6.50 (s, 2H, a), 5.25 (s, 2H, b), 3.98–3.85 (m, 2H, d), 2.75 (s, 2H, c), 2.18–1.12 (m, 10H, e); ^{13}C NMR (δ , ppm in CDCl_3) [see carbon numbers (1 to 8) shown in Scheme 1]: 176.67 (C4), 136.97 (C1), 81.53 (C2), 52.53 (C5), 47.56 (C3), 29.28 (C6), 26.32 (C7), 25.45 (C8). Elemental analysis (%): Calculated for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}$: H=6.92, C=68.87, N=5.57; Found: H=6.93, C=68.30, N=5.66.

Comonomer and Materials

St, MMA, and VAC were purified by the usual methods. Benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), aluminium 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*-butylperoxy)hex-3-yne (PH25B), and anionic and cationic catalysts were used without further purification.

Polymerization Procedures

Radical polymerizations of CHO in bulk or in solvents were carried out in a sealed-glass tube with or without the initiator at 80 to 150°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 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 CHO with ST, MMA, or VAC were performed with the radical initiators in chlorobenzene or in bulk at 70 and 120°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. The composition of the copolymer was determined from nitrogen analysis.

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

Measurements

199.5 MHz ^1H NMR and 50.1 MHz ^{13}C NMR, and 100 MHz ^1H NMR spectra were obtained with a JEOL FX-200 and a JEOL JNM-MH-100. 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. 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 CHO with PH3M as a catalyst in chlorobenzene (CB) at 100°C for 18 h gave the polymer in about 73 to 58% (run CHO 6 and 7) yield with a \bar{M}_n of 1700 to 2000. At 100°C, the yields in polymerizations with PH3M (half-life, 10 h at 100°C) were better than those with PH25B (half-life, over 100 h at 100°C). The yields with BPO at 80°C were better than those with other catalysts. Thus, yields may be related to the half-life of the catalyst. In addition, the polymerization required over 10 mol% catalyst to obtain the polymers in isolable yields. In the polymerization without initiators over 100°C, the yield of polymer was almost zero (trace), as shown in Table I (run CHO 14–16). The reason for this may be that the retro-Diels-Alder reaction took place. Thus CHO was converted into *N*-

cyclohexylmaleimide and furan. This behavior was confirmed by HPLC. TG-DSC curves for CHO monomer are shown in Figure 1. Three endothermic peaks were observed. The peak A was attributable to melting for CHO and the peak B may be based on degradation of CHO by the retro-Diels-Alder reaction. The peak C may be ascribed to sublimation of CHMI produced by the retro-Diels-Alder reaction. Figure 2 indicates ¹H NMR spectra for (1) CHO polymer insoluble in methanol and (2) the product soluble in methanol polymerized for 18 h at 100°C. In spectrum (2), some signals of the oligomer were also observed besides CHMI monomer. That is, the smaller oligomers were soluble in methanol. Figure 3 shows molecular weight distributions of (1) CHO polymer insoluble in methanol and (2) the product soluble in methanol. Thus the products soluble in methanol were oligomers having the molecular weight below about 1000 and unreacted CHMI monomer.

Bulk copolymerization of FN with CHMI

Table I. Radical homopolymerizations of CHO at high temperature

Run No.	CHO	Initiator	Solvent ^a	Temp	Time	Yield ^b	N ^c	\bar{M}_n^d	\bar{M}_w/\bar{M}_n
	mmol	mmol	ml	°C	h	wt%	%	× 10 ³	
CHO-1	2.09	PH25B (0.18)	—	100	18	7.8	6.34	—	—
CHO-2	2.06	PH25B (0.19)	CB (2)	100	18	8.4	5.97	—	—
CHO-3	2.06	PH25B (0.09)	CB (2)	100	18	Trace	—	—	—
CHO-4	2.03	PH25B (0.09)	CB (2)	80	18	Trace	—	—	—
CHO-5	2.03	PH25B (0.19)	CB (2)	80	18	Trace	—	—	—
CHO-6	2.06	PH3M (0.21)	CB (2)	100	18	72.9	5.78	2.0	2.2
CHO-7	2.05	PH3M (0.07)	CB (2)	100	18	57.9	6.30	1.7	1.9
CHO-8	2.03	PH3M (0.08)	CB (2)	80	18	4.0	6.25	—	—
CHO-9	2.07	PH3M (0.16)	CB (2)	80	18	8.3	6.14	—	—
CHO-10	2.06	BPO (0.09)	CB (2)	100	18	12.5	—	1.3	1.5
CHO-11	2.04	BPO (0.22)	CB (2)	100	18	9.9	—	1.4	1.7
CHO-12	2.05	BPO (0.11)	CB (2)	80	18	Trace	—	—	—
CHO-13	2.04	BPO (0.22)	CB (2)	80	18	16.8	5.90	1.1	1.5
CHO-14	2.06	—	—	100	18	Trace	—	—	—
CHO-15	2.03	—	—	120	18	Trace	—	—	—
CHO-16	2.01	—	—	150	18	2.3	—	—	—

^a CB = monochlorobenzene.

^b Yield of the polymer insoluble in methanol.

^c Elemental analysis of polymers.

^d By GPC.

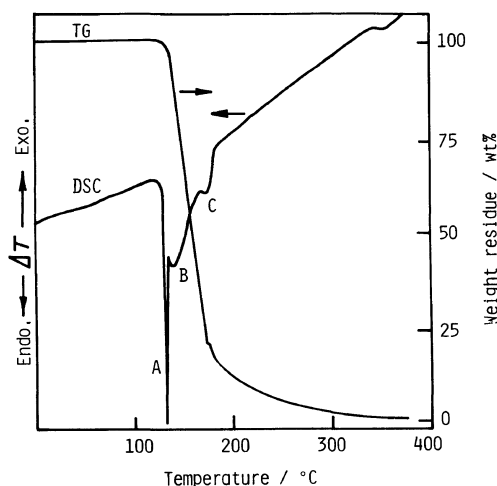


Figure 1. TG and DSC curves for the CHO monomer at a heating rate of $10^{\circ}\text{C min}^{-1}$ in nitrogen.

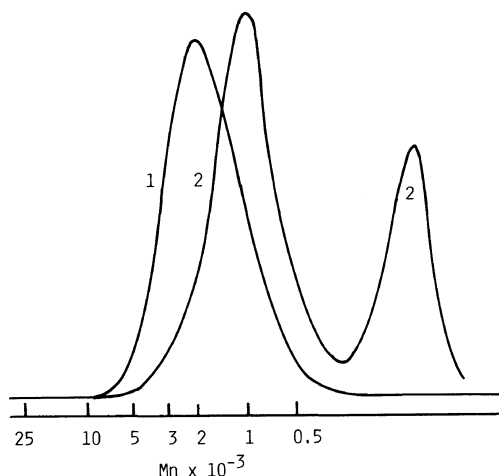


Figure 3. Molecular weight distributions of CHO polymer: (1) the product insoluble in methanol and (2) the product soluble in methanol obtained from the polymerization of CHO for 18 h at 100°C (run CHO-7).

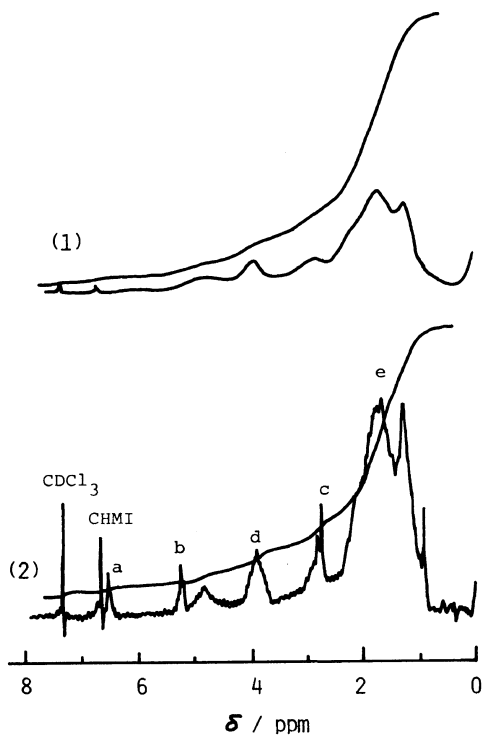
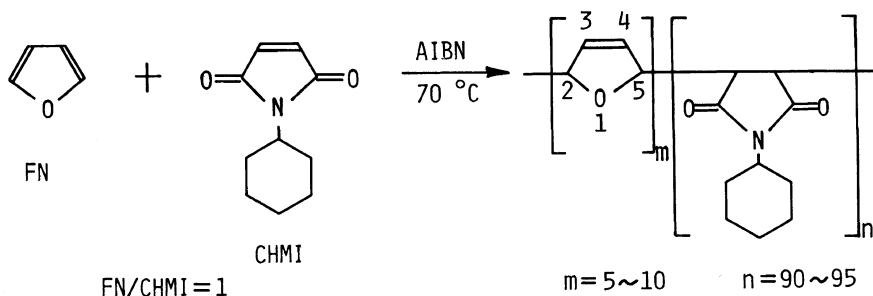


Figure 2. 100 MHz ^1H NMR spectra for (1) CHO polymer insoluble in methanol and (2) the products soluble in methanol polymerized for 18 h at 100°C (run CHO-7).

(FN/CHMI = 1.0) was performed with AIBN at 70°C to obtain the copolymer having the composition of FN/CHMI = (5—10)/(90—95), as shown in Scheme 2. Judging from ^{13}C NMR spectrum of the copolymer, the formation of Diels-Alder adducts, *i.e.*, CHO, could be ignored. ^1H NMR of the FN-CHMI copolymer is shown in Figure 4(1). The peaks at about 6.0 ppm were assigned to two methine protons of 3 and 4 position in the furan ring, and the peaks at around 5.2 ppm to two methine protons locating at 2 and 5 position in furan ring. On the other side, in the absence of radical initiators, CHO was almost decomposed at over 100°C to give CHMI and FN, as shown in Scheme 3. No poly(CHMI-*co*-FN) could be obtained, judging from Figure 4(2). In the case of CHN,⁶ as reported previously, the polymer obtained over 250°C consisted of a mixture among CHN, CHMI, and an adduct obtained CHN and CPD. In addition, CHN was also converted to *exo*-CHN. In CHO, however, no *endo*-*exo* rearrangement could be observed. It may be that CHO was almost decomposed by the retro-Diels-Alder reaction to give CHMI and FN in spite of relatively low temperature.



Scheme 2.

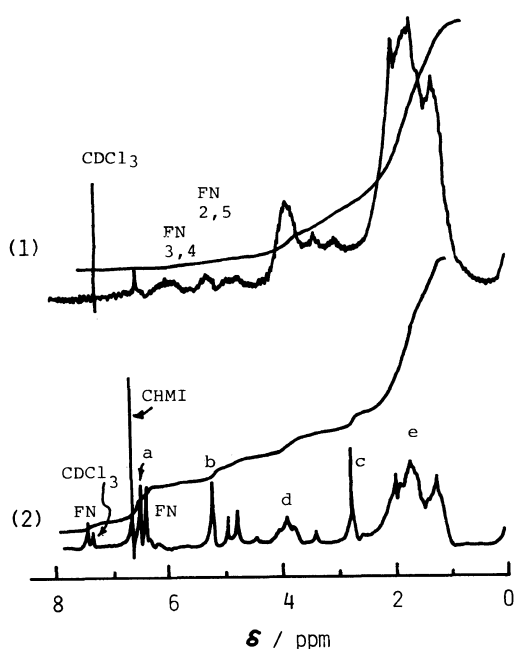
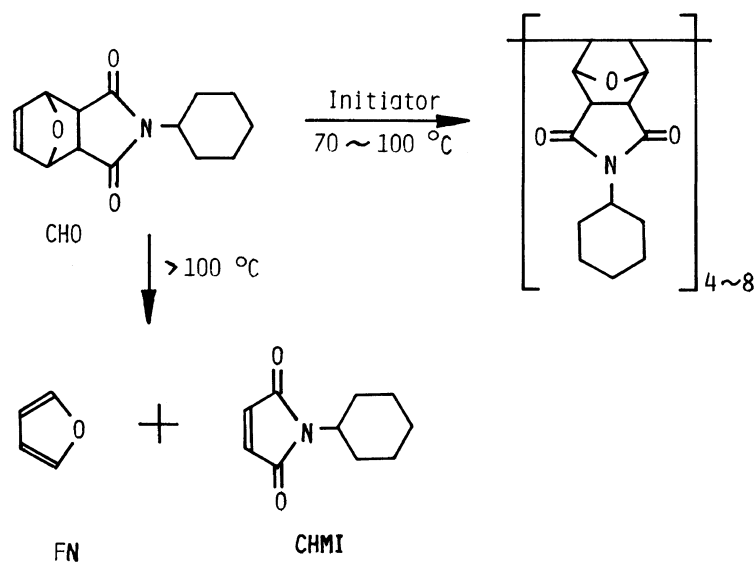


Figure 4. 100 MHz ^1H NMR spectra for (1) the product obtained from FN and CHMI (FN/CHMI=1.0) with AIBN at 70°C and (2) CHO polymerized for 18 h at 150°C (run CHO-16).

Radical Copolymerizations

Radical copolymerizations of CHO (0.51 to 1.24 mol l^{-1}) with ST (0.30 to 2.0 mol l^{-1}), MMA (0.31 to 2.1 mol l^{-1}), or VAC (0.31 to 2.3 mol l^{-1}) were performed in chlorobenzene (CB; 3 ml) [BPO ($2.21 \times 10^{-2} \text{ mol l}^{-1}$) at 70°C and in bulk using PH3M ($2.2 \times 10^{-2} \text{ mol l}^{-1}$) at 120°C]. All copolymerizations proceeded homogeneously throughout. The yields of copolymers in all systems decreased with

increase of CHO concentration in monomer feeds. The conversions in all systems were controlled to be less than 10% in order to calculate the monomer reactivity ratios, by changing the reaction time for 3 to 20 h. Copolymer-composition curves for CHO-ST, CHO-MMA, and CHO-VAC systems in CB at 70°C and in bulk at 120°C are shown in Figures 5 and 6. As compared with these composition curves, in the CHO and ST system, there was no difference between 120°C in bulk and at 70°C in CB. In the CHO-MMA system, the copolymers obtained at 120°C in bulk contained CHO units much more than those at 70°C in CB. But in the CHO-VAC system, the opposite tendency was observed. The monomer reactivity ratios (r_1, r_2) calculated according to the Integration method by Mayo and Lewis⁸ were obtained as follows: $r_1 = 0.84, r_2 = 1.01$ (120°C); $r_1 = 0.55, r_2 = 0.87$ (70°C) in the CHO(M_1)-ST(M_2); $r_1 = 0.44, r_2 = 0.76$ (120°C); $r_1 = 0.32, r_2 = 4.69$ (70°C) in the CHO(M_1)-MMA(M_2); $r_1 = 1.56, r_2 = 0.40$ (120°C), $r_1 = 8.12, r_2 = 0.026$ (70°C) in the CHO(M_1)-VAC(M_2) system. Since the CHO monomer has only 5.57% nitrogen, the composition of the copolymer contains considerable error. In CHO-ST system, the compositions of the polymers were calculated from carbon analysis, and the r_1 and r_2 were determined as follows: $r_1 = 1.40, r_2 = 1.33$ (120°C in bulk) and $r_1 = 1.44, r_2 = 1.38$ (70°C in CB). The Alfrey-Price⁹ Q and e values for CHO were 0.056 and 0.46, respectively,



Scheme 3.

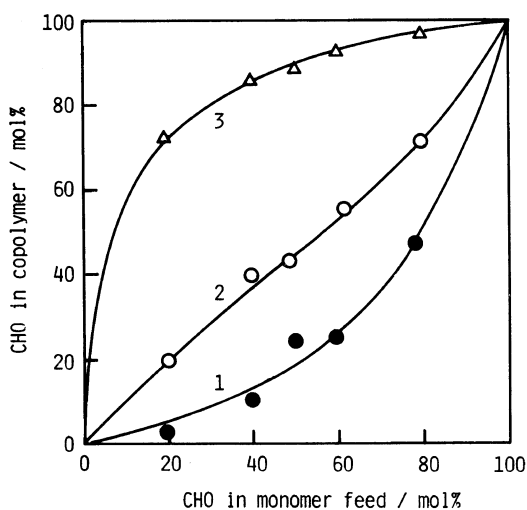


Figure 5. Copolymer-composition curves for (1) CHO-ST, (2) CHO-MMA, and (3) CHO-VAC systems in chlorobenzene at 70°C.

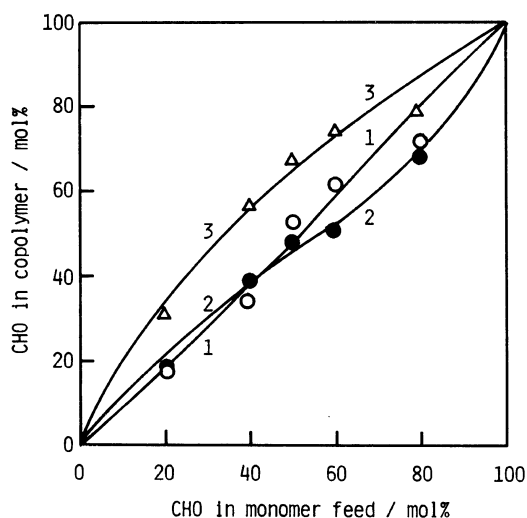


Figure 6. Copolymer-composition curves for (1) CHO-ST, (2) CHO-MMA, and (3) CHO-VAC in bulk at 120°C.

calculated from the CHO-VAC (120°C) system. These values indicate CHO to be consistent with the structure having a non-resonance character. Generally, as reported previously,^{6,10} the reactivity ratios (r_1) for norbornene derivatives: *i.e.*, CHN⁶ and endo-N-benzylbicyclo[2,2,1]hept-2-ene-5,6-dicar-

boximide (BZN)¹⁰ were very small, which suggests that CHN and BZN have very low homopolymerizability. These tendencies were recognized in other norbornene derivatives.¹¹⁻¹⁵ However the reactivity ratios for Diels-Alder adduct of furan (FN) and CHMI, *i.e.*, CHO, were considerably large. The reason

for this may be the decrease of steric hindrance around the reaction double by the five-membered cyclic ring containing an oxygen atom instead of a methylene. The Q value (0.056) for CHO was almost in agreement with the values reported in previous papers.^{11–15} The e value (0.46) was slightly larger than those for other norbornene derivatives.^{11–15} The molecular weight distributions of copolymers are shown in Figure 7. In all systems, \bar{M}_n decreased with increasing contents of CHO in copolymers. The order of the number-average molecular weight (\bar{M}_n) and polydispersity (\bar{M}_w/\bar{M}_n) for the copolymers were as follows: $\bar{M}_n = 2.3 \times 10^3$ – 6.3×10^3 , $\bar{M}_w/\bar{M}_n = 1.7$ – 2.1 (at 70°C in CB), $\bar{M}_n = 3.0 \times 10^3$ – 1.2×10^4 , $\bar{M}_w/\bar{M}_n = 1.1$ – 2.2 (at 120°C in bulk) for poly(CHO-*co*-ST)s; $\bar{M}_n = 2.9 \times 10^3$ – 7.6×10^3 , $\bar{M}_w/\bar{M}_n = 1.3$ – 2.1 (at 70°C in CB), $\bar{M}_n = 1.1 \times 10^4$ – 3.4×10^4 , $\bar{M}_w/\bar{M}_n = 1.1$ – 3.7 (at 120°C in bulk) for poly(CHO-*co*-MMA)s; and $\bar{M}_n = 2.5 \times 10^3$ – 4.9×10^3 , $\bar{M}_w/\bar{M}_n = 1.4$ – 4.5 (at 70°C in CB), $\bar{M}_n = 1.1 \times 10^4$ – 9.1×10^4 , $\bar{M}_w/\bar{M}_n = 1.1$ – 9.0 (at 120°C in bulk) for poly(CHO-*co*-VAC)s. \bar{M}_n of these copolymers were much larger than those for CHO homopolymers shown in Figure 3.

Ionic and Ziegler–Natta Polymerizations

Many patents have been reported for the polymerizations of norbornene derivatives with ionic and Ziegler–Natta catalysis.¹⁶ But no ionic polymerizations norbornene derivatives having *N*-substituted dicarboximide at 5,6-position in oxa-norbornene could be carried out in the presence of an ionic and Ziegler–Natta catalysts. Polymerizations of CHO were attempted with *n*-butyllithium, $\text{BF}_3\text{O}(\text{Et})_2$, FeCl_3 , AlCl_3 , or MoCl_5 or such Ziegler Natta catalysts as $\text{Al}(\text{Et})_3/\text{TiCl}_4$, $\text{Al}(\text{Et})_3/\text{MoCl}_5$, $(\text{Et})_2\text{AlCl}/\text{TiCl}_4$, $(\text{Et})_2\text{AlCl}/\text{WCl}_6$ under the same experimental conditions as reported previously.⁶ In all systems, however, the conversions were trace. This was also recognized in the polymerization of CHN⁶ and BZN,¹⁰ possibly due not only to

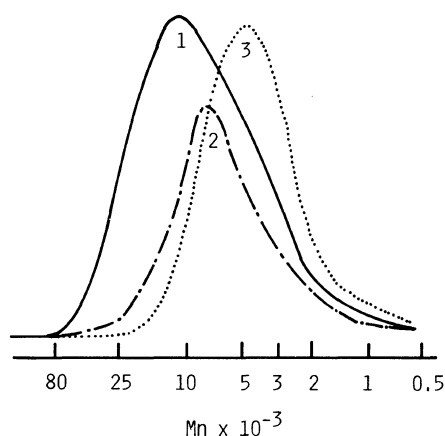


Figure 7. Molecular weight distributions of CHO Copolymers obtained from 50 mol% of CHO in monomer feeds at 70°C: (1) poly(CHO-*co*-ST), (2) poly(CHO-*co*-MMA), and (3) poly(CHO-*co*-VAC).

the activity of the catalyst but also to the steric hindrance of *N*-cyclohexyldicarboximide group at 5,6-position in oxa-norbornene.

Thermostabilities of the Polymers

Diagrams of a thermogravimetric (TG) and a differential scanning calorimetric (DSC) analysis for the polymers and copolymers obtained in bulk at 120°C are shown in Figures 8 and 9. Only the initial degradation temperatures (T_d) of the polymers could be observed as $T_d = 274$ to 308°C. There were no softening points (T_m) for the polymers. The thermostabilities of CHO polymers were much less than those of CHMI polymers.⁴ The thermostabilities of CHO-ST and CHO-MMA copolymers were less than those of the corresponding CHMI-ST and CHMI-MMA copolymers.⁴ The reason may be that five-membered ring containing an oxygen atom is easy to decompose. No glass transition temperature (T_g) could be observed for any polymer, as shown in Figures 8 and 9. T_m and T_d of the copolymers obtained in CB at 70°C were generally lower than those for the copolymers obtained in bulk at 120°C, and were as follows: $T_m = 183$ to 288°C, $T_d = 282$ to 322°C for poly(CHO-*co*-ST)s; $T_d = 206$ to

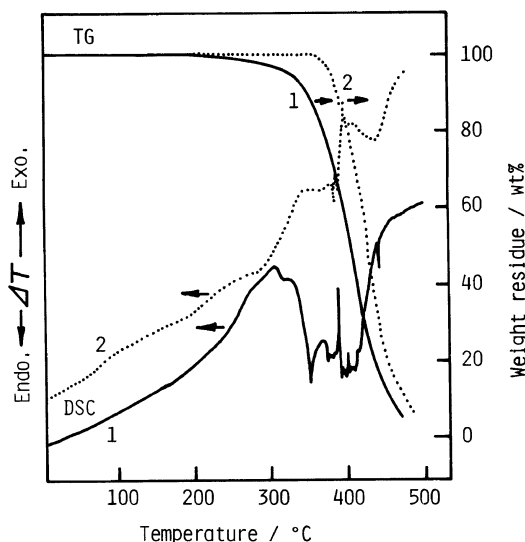


Figure 8. TG and DSC curves for (1) the CHO homopolymer (run CHO-7) and (2) poly(CHO-co-ST) [obtained from 50 mol% of CHO in monomer feeds at 120°C] at a heating rate of 10°C min⁻¹ in nitrogen.

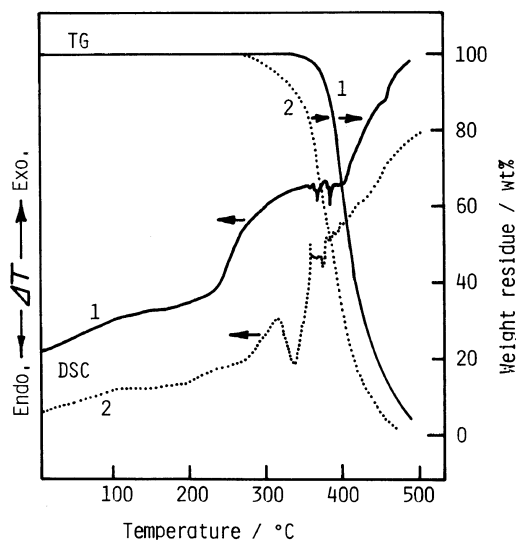


Figure 9. TG and DSC curves for copolymers obtained from 50 mol% in monomer feeds at 120°C: (1) poly(CHO-co-MMA) and (2) poly(CHO-co-VAC) at a heating rate of 10°C min⁻¹ in nitrogen.

260°C for poly(CHO-co-MMA)s; $T_d = 240$ to 260°C for poly(CHO-co-VAC)s. These T_m were reconfirmed by measurement with the ordinary capillary melting point methods.

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