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OLIGOMERIZATION AND COPOLYMERIZATION OF *endo-N*-BENZYLBICYCLO[2,2,1]HEPT-2- ENE-5,6-DICARBOXIMIDE

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ABSTRACT

endo-N-Benzylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (BZN or *endo*-BZN), one of the norbornene derivatives, was prepared from *N*-benzylmaleimide (BZMI) and cyclopentadiene (CPD) according to the Diels-Alder reaction. Yields of homopolymers, insoluble in methanol, were about 20 wt%. No BZN could be polymerized in bulk without radical catalysts under 220°C. At 220°C for 1 h, *endo*-BZN was converted to *exo*-BZN in a 50-mol% yield. The polymerization of BZN over 300°C for 1 h gave the polymer in about 100% yield. It was found that the polymer consisted of a mixture of BZN, BZMI, and an adduct obtained from BZN and CPD. BZN was copolymerized with styrene, methyl methacrylate, and vinyl acetate with radical initiators. The copolymerizabilities of BZN with VAc were better than those for other systems. The monomer reactivity ratios and Alfrey-Price *Q-e* values were determined.

INTRODUCTION

It is known that norbornene is polymerized by cationic and Ziegler-Natta catalysts to give a vinylene-type polymer and a 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 an oligomer of about molecular weight 800 [2]. A ^{13}C -NMR study was carried out on the polymers obtained from I 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 an improvement of the thermostabilities of the common vinyl polymers [4]. Polymerization and copolymerization of the CHMI-cyclopentadiene (CPD) Diels-Alder adduct, *endo*-*N*-cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHN), were investigated [5]. In this article, *endo*-*N*-benzylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (BZN or *endo*-BZN) containing a BZMI group at the 2,3-positions in norbornene, was polymerized with and without catalysts in bulk and in solvents at high temperatures. Copolymerizations of BZN with styrene (St), methyl methacrylate (MMA), or vinyl acetate (VAc) were performed with radical initiators at high temperatures. In addition, several ionic polymerizations of BZN were performed with cationic, anionic, and Ziegler-Natta catalysts.

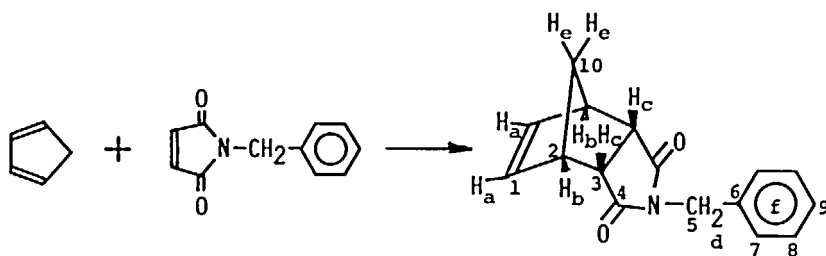
EXPERIMENTAL

Monomers

endo-BZN Monomer

BZN was prepared from BZMI and cyclopentadiene (CPD) by means of the Diels-Alder reaction. CPD (15.1 g, 0.23 mol) was added dropwise to a solution of BZMI [6], mp 69°C (50.1 g, 0.26 mol) in benzene (150 mL), and then the mixture was stirred for 2 h at room temperature. The precipitate was filtered and then recrystallized from cyclohexane to obtain a pure BZN in 61 % yield, mp 86°C.

^1H -NMR (δ , ppm in CDCl_3) (see hydrogen position a to f in Scheme 1): 7.31–7.24 (m, 5H, f), 5.91–5.88 (m, 2H, a), 4.50–4.48 (m, 2H, d), 3.37–3.35 (m, 2H, b), 3.25–3.24 (m, 2H, c), 1.72–1.42 (m, 2H, e). ^{13}C -NMR (δ , ppm in CDCl_3) (see carbon numbers 1 to 10 in Scheme 1): 177.67 (C4), 136.49 (C6), 134.72 (C1), 129.29 (C7), 128.75 (C8), 128.11 (C9), 52.51 (C5), 46.17 (C3), 45.44 (C2), 42.42 (C10).



SCHEME 1.

Elemental analysis (%). Calculated for $C_{16}H_{15}O_2N$: H 5.97, C 75.87, N 5.53. Found: H 5.87, C 75.91, N 5.58.

exo-BZN (Method A)

BZN 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 by using an activated alumina as the packing. *exo*-BZN was extracted from the reaction mixture with cyclohexane. The solvent was distilled thoroughly under reduced pressure and then the residue of the crude *exo*-BZN was recrystallized from methanol three times to obtain a pure *exo*-BZN in 42% yield, mp 103°C .

Method B

exo-5-Norbornene-2,3-dicarboxylic anhydride, mp $133\text{--}137^\circ\text{C}$ (lit. 141°C [2]) was prepared from the CPD-maleic anhydride (MAN) Diels-Alder adduct, *endo-cis*-5-norbornene-2,3-dicarboxylic anhydride [2]. *exo*-BZN was synthesized from the *exo*-anhydride and benzylamine according to the ordinary maleimide synthetic method [6] (yield: 78%), mp $101\text{--}102^\circ\text{C}$.

$^1\text{H-NMR}$ (δ , ppm in CDCl_3) (see hydrogen positions a' to f' in Scheme 2): 7.38–7.29 (m, 5H, f'), 6.28 (s, 2H, a'), 4.62 (s, 2H, d'), 3.26 (s, 2H, c'), 2.69 (s, 2H, b'), 1.43–1.05 (m, 2H, e'). $^{13}\text{C-NMR}$ (δ , ppm in CDCl_3) (see carbon numbers 1' to 10' in Scheme 2): 177.86 ($\text{C4}'$), 138.23 ($\text{C1}'$), 136.27 ($\text{C6}'$), 129.16 ($\text{C7}'$), 128.93 ($\text{C8}'$), 128.18 ($\text{C9}'$), 48.13 ($\text{C5}'$), 45.63 ($\text{C2}'$), 42.95 ($\text{C3}'$), 42.67 ($\text{C10}'$).

Elemental analysis (%). Calculated for $C_{16}H_{15}O_2N$: H 5.97, C 75.87, N 5.53. Found: H 6.01, C 75.73, N 5.62.

Comonomer and Materials

St, MMA, and VAc were purified by the usual methods. Benzoyl peroxide (BPO), aluminum trichloride, and the 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 BZN in bulk or in solvents were carried out in a sealed glass tube with or without the initiator at 100 to 330°C. After polymerization for a given time, the content of the tube was 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; 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 BZN with St, MMA, or VAc were achieved with the radical initiator in benzene or in bulk at 70 to 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 THF-methanol solution, and dried in vacuum. The composition of the copolymer was determined from nitrogen analysis.

Solution ionic polymerizations of BZN were performed with cationic, anionic, or Ziegler-Natta catalysts in some solvents at different temperatures. All polymerization procedures were performed under nitrogen atmosphere in a polyethylene bag.

Measurements

199.5 MHz 1H -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 a Shimadzu LC 3A equipped with a data processor with THF as the solvent and Shimadzu polystyrene gels HGS-20-15-10. TG and DSC data were obtained with a Rigaku Thermal analysis apparatus.

RESULTS AND DISCUSSION

Radical Polymerizations

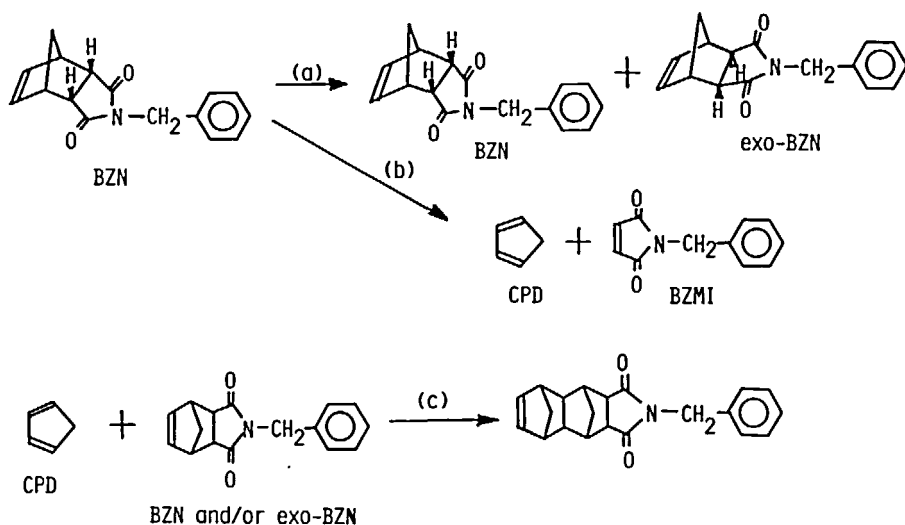
The results of radical homopolymerizations in bulk and in solvents are summarized in Table 1. Homopolymerization of BZN with PH3M as the catalyst in chlorobenzene (CB) at 120°C for 1 h gave the polymer in about 10% yield with an \bar{M}_n of 2100 to 2800, but under 80°C the yields were zero even if radical catalysts 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 150°C in bulk polymerizations with PH25B (half-life, 90 min at 150°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 isolable yields. No BZN could be polymerized in bulk without the radical initiators under 220°C. However, at 220°C for 1 h, BZN was converted to *exo*-BZN in about 50% yield, judging from the NMR spectra, as shown in Scheme 2(a). ¹H-NMR and ¹³C-NMR spectra of the reaction mixtures at 220 and 330°C are shown in Figs. 1 and 2. In the polymerization at 220°C for 1 h, the yield of polymer was zero, as shown in Table 1. Integration values of signals at 6.28 (a') and 4.62 (d') ppm in *exo*-BZN were almost equal to the corresponding two signals in BZN. Thus the reaction mixture obtained may have been a mixture of BZN/*exo*-BZN (1/1). This behavior was also confirmed by HPLC. In Figs. 1(a) and 2(a), the peaks of the double bond of BZMI and an adduct (II) obtained from BZN and CPD prepared by a retro-Diels-Alder reaction can be observed. This suggests that three reactions might occur, as shown in Scheme 2. In Figs. 1(b) and 2(b), no peaks of double bonds can be observed, which indicates that different kinds of monomers could not exist in the reaction mixture but that polymerization occurred. Figure 3 shows the relation between conversions of *exo*-BZN and reaction times at 220°C. Polymerization of BZN over 300°C for 1 h gave the polymers quantitatively. The \bar{M}_n of the polymers insoluble in methanol were about 1000, and the \bar{M}_n of the polymer soluble in methanol was about 600. It was found that the polymer obtained consists of a mixture of BZN, *N*-benzylmaleimide (BZMI), and an adduct (II) obtained from BZN and CPD prepared by a retro-Diels-Alder reaction because of high temperatures (Schemes 2 and 3, respectively). The relationship between the conversion of polymer insoluble in methanol and the reaction time is shown in Fig. 3. Molecular weight distributions of BZN homopolymers are

TABLE 1. Radical Homopolymerizations of BZN at High Temperatures

Run no.	BZN, mmol	Initiator, mmol	Solvent, mL	Temperature, °C	Time, h	Yield, ^b wt%	N, ^c %	$\bar{M}_n^d \times 10^{-3}$
1-1	3.96	BPO (0.08)	CB (4)	100	1.0	1.7	3.62	1.6
1-2	4.49	BPO (0.25)	CB (2)	100	1.0	1.6	4.51	1.7
1-3	5.04	BPO (0.25)	CB (2.5)	120	1.0	1.5	4.93	1.7
1-4	4.22	BPO (0.25)	—	120	1.0	1.8	4.94	1.5
2-1	4.28	PH3M (0.18)	CB (2)	120	1.0	12.0	5.13	2.1
2-2	4.08	PH3M (0.18)	CB (2)	120	1.0	6.0	5.18	2.1
2-3	4.05	PH3M (0.18)	—	120	1.0	5.9	5.01	2.8
2-4	4.57	PH3M (0.18)	DCB (2)	150	1.0	2.4	3.98	2.8
2-5	4.07	PH3M (0.18)	DCB (2)	150	1.0	2.3	5.07	2.1

2-6	4.09	PH3M (0.03)	CB (2)	100	14.5	2.9	5.42	—
2-7	2.02	PH3M (0.03)	—	100	24	1.6	4.28	—
3-1	4.11	PH25B (0.21)	DCB (2)	150	1.0	20.3	4.66	2.2
3-2	4.06	PH25B (0.21)	DCB (2)	150	1.0	7.8	4.83	—
4-1	1.97	—	—	220	4.0	—	—	—
4-2	1.97	—	—	250	3.5	67.9	5.33	0.8
4-3	2.04	—	—	270	3.0	54.0	5.69	1.0
4-4	1.98	—	—	280	2.0	72.8	5.56	0.9
4-5	1.99	—	—	300	1.0	43.0	5.82	0.8
4-6	1.57	—	—	330	1.0	71.6	5.61	0.8

^aCB = monochlorobenzene; DCB = dichlorobenzene.^bYield of the polymer insoluble in methanol.^cElemental analysis of polymers.^dBy GPC.



SCHEME 2.

shown in Fig. 4. The order of \bar{M}_n was: in bulk at 120°C (Run 2-3) > in CB at 100°C (run 1-2) > in bulk at 300°C (Run 4-5) > polymer soluble in methanol (Run 4-5).

Radical Copolymerizations

Radical copolymerizations of BZN (0.75 to 1.8 mol/L) with St (0.49 to 3.1 mol/L), MMA (0.42 to 3.2 mol/L), or VAc (0.44 to 3.3 mol/L) were performed in chlorobenzene (CB; 2 mL) [BPO (2.0×10^{-2} mol/L) at 70 and 90°C and PH3M (2.2×10^{-2} mol/L) at 120°C]. All copolymerizations proceeded homogeneously throughout. The yields of copolymers in all systems decreased with increasing BZN 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 from 6 to 24 h. Copolymer-composition curves are shown in Fig. 5. In solution polymerizations of BZN with St and MMA in benzene at 70 and 120°C, the contents of BZN in the polymers were very low. The copolymerizabilities of BZN with VAc were better than for the other systems. The monomer reactivity ratios (r_1 , r_2) calculated according to the integration method by Mayo and Lewis [7] and the Alfrey-Price [8] Q and

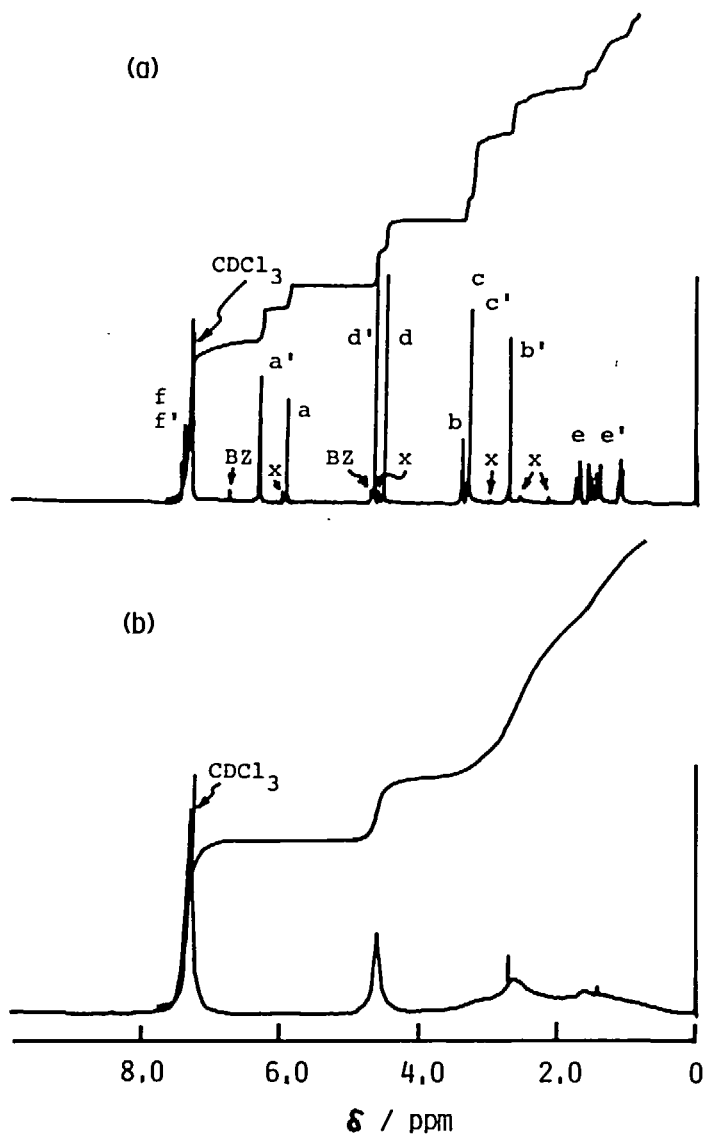


FIG. 1. 199.5 MHz ^1H -NMR spectra of BZN polymerized for 2 h at (a) 220 and (b) 330°C.

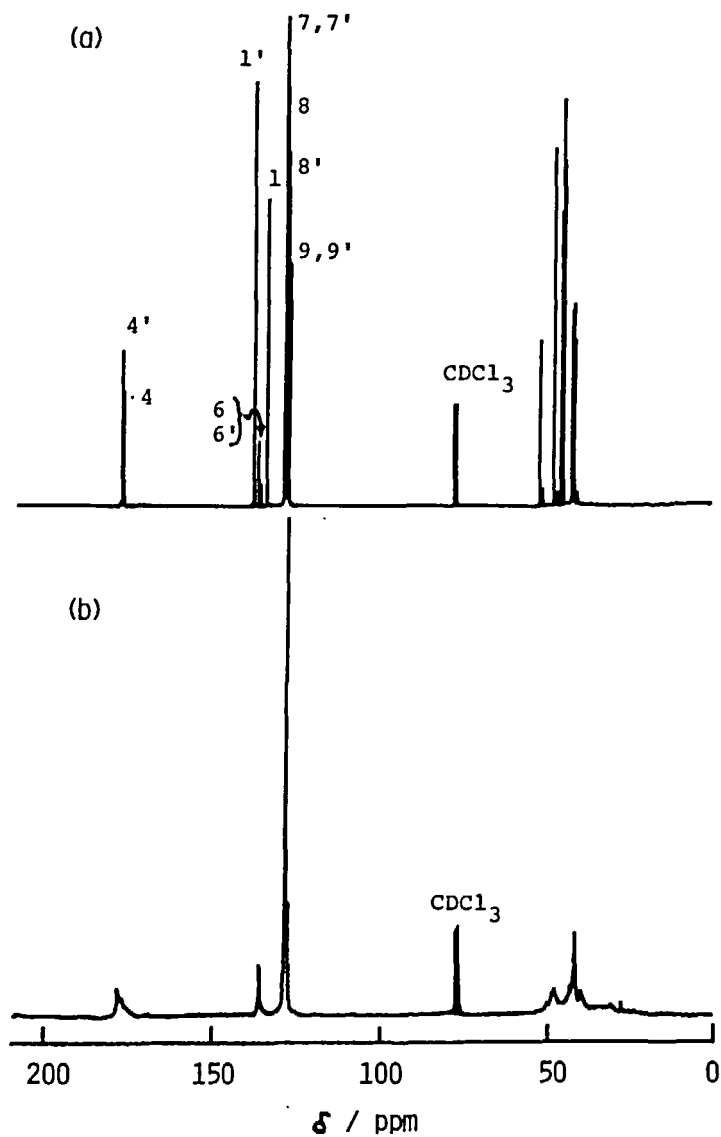


FIG. 2. 50.1 MHz ^{13}C -NMR spectra of BZN polymerized for 2 h at (a) 220 and (b) 330°C.

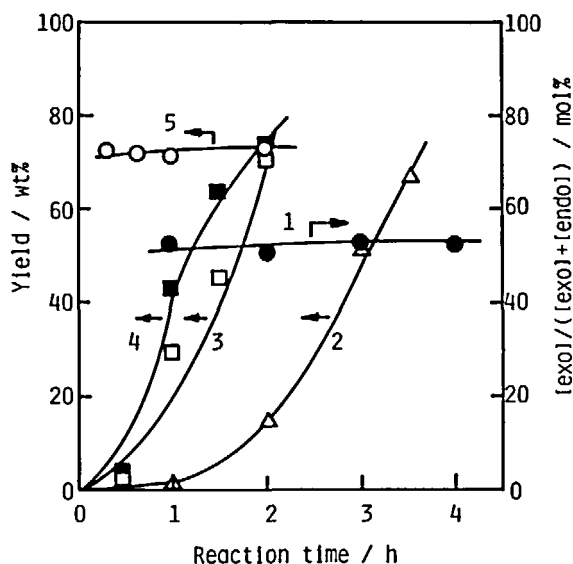
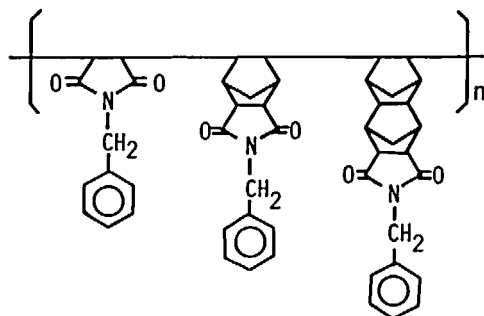


FIG. 3. Relationships between yields of polymer insoluble in methanol or mole fraction of *exo*-BZN and reaction time for polymerization of BZN in bulk at different temperatures: (1) 220, (2) 250, (3) 280, (4) 300, and (5) 330°C.



SCHEME 3.

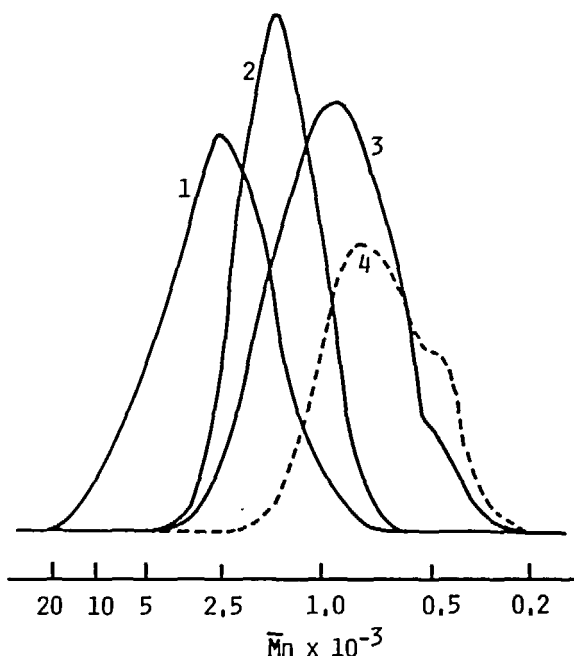


FIG. 4. Molecular weight distributions of BZN homopolymers obtained (1) in bulk at 120°C (Run 2-3), (2) in CB at 100°C (Run 1-2), (3) in bulk at 300°C (Run 4-5), and (4) the polymer soluble in methanol (Run 4-5).

e values were obtained for copolymerization as follows: $r_1 = 0.0$, $r_2 = 18.2$ (120°C); $r_1 = 0.0$, $r_2 = 89.2$ (70°C) in BZN (M_1)-St (M_2); $r_1 = 0.0$, $r_2 = 30.5$ (120°C); $r_1 = 0.0$, $r_2 = 108.3$ (70°C) in BZN (M_1)-MMA (M_2); $r_1 = 0.35$, $r_2 = 1.26$ (120°C), $r_1 = 0.15$, $r_2 = 1.46$ (90°C), $r_1 = 0.014$, $r_2 = 1.99$ (70°C) in BZN (M_1)-VAc (M_2). The values of Q and e were 0.017 and 0.68, respectively, calculated from the BZN-VAc (120°C) system, which indicates that BZN was consistent with a structure having a nonresonance character. Generally, the reactivity ratios (r_1 for BZN) were very small, which suggests that BZN has very low homopolymerizability. These tendencies are recognized in other norbornene derivatives [9-13]. The Q value (0.017) for BZN was very close to values reported in previous papers [9-11]. The e value (0.68) was slightly larger than those for other norbornene derivatives [9-11]. The reason for this may be the electron-attracting character of two carbonyl groups in the imide ring. The Q and

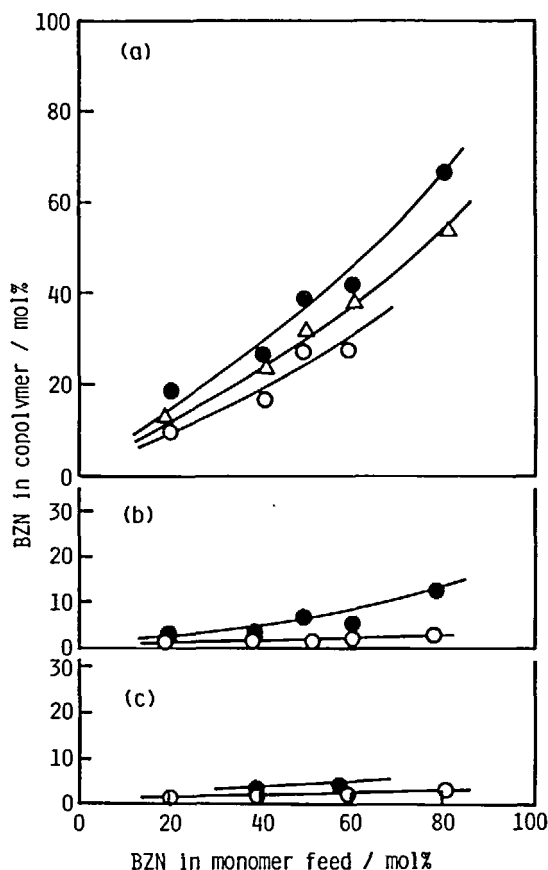


FIG. 5. Copolymer composition curves for (a) BZN-VAc, (b) BZN-St, and (c) BZN-MMA systems: (O) 70°C, (Δ) 90°C, and (\bullet) 120°C.

e values for BZN were considerably smaller than those ($Q = 0.79$), $e = 1.63$) for *N*-benzylmaleimide (BZMI) [6]. This may be understood from the fact that the reactive double bond of BZN is not conjugated with two carbonyl groups. The molecular weight distributions of the copolymers are shown in Fig. 6. The \bar{M}_n of BZN-St copolymers was generally larger than those for BZN homopolymers and copolymers in other systems. The \bar{M}_n of BZN-VAc copolymers were similar to those for BZN homopolymers.

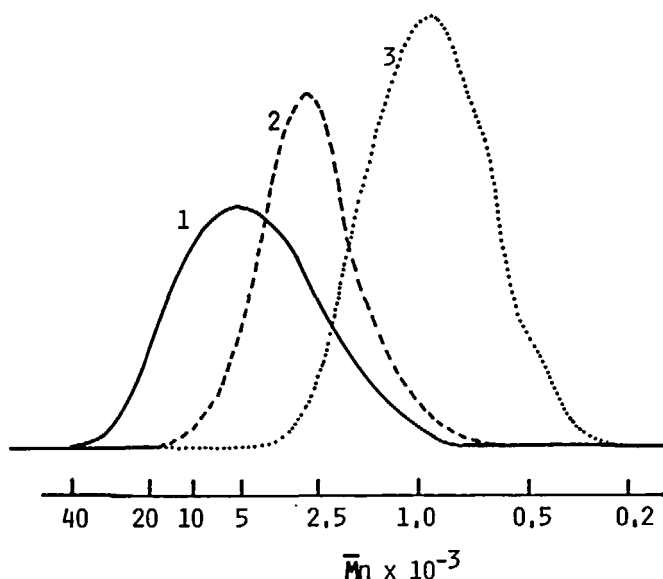


FIG. 6. Molecular weight distributions of BZN copolymers: (1) BZN-St (Run BS 1-3), (2) BZN-VAc (Run BV 1-3), and (3) BZN homopolymer obtained in bulk at 300°C (Run 4-5).

Ionic and Ziegler-Natta Polymerizations

There are many patents [14] for the polymerization of norbornene derivatives with ionic and Ziegler-Natta catalysts, but no ionic polymerization of norbornene derivatives having *N*-substituted dicarboximide at the 5,6-position in norbornene could be carried out in the presence of an ionic or a Ziegler-Natta catalyst. We attempted to polymerize BZN with *n*-butyllithium, $\text{BF}_3\text{O}(\text{Et})_2$, FeCl_3 , AlCl_3 , and MoCl_5 , and with such Ziegler-Natta catalysts as $\text{Al}(\text{Et})_3/\text{TiCl}_4$, $\text{Al}(\text{Et})_3/\text{MoCl}_5$, $(\text{Et})_2\text{AlCl}/\text{TiCl}_4$, and $(\text{Et})_2\text{AlCl}/\text{WCl}_6$ under the same experimental conditions as reported previously [5]. In all systems, however, the conversions were extremely small. This tendency was also recognized in the polymerization of *N*-cyclohexylbicyclo[2,2,1]hept-2-ene-5,6-dicarboximide (CHN) [5]. The reason for this may be attributable not only to the reactivity of the catalyst but also to the steric hindrance of the *N*-benzyldicarboximide

group at the 5,6-position in norbornene. Recently poly(*exo*-5-hydroxy-norbornene [15] and ω -norbornenyl polystyrene [16] were prepared by using metathesis polymerization with the $\text{WCl}_6/\text{Sn}(\text{CH}_3)_4$ system. Murdzek and Schrock reported low polydispersity in homopolymers and block copolymers by ring opening of 5,6-dicarbomethoxynorbornene with a special catalyst, i.e., $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{O-}i\text{-Bu})_2$ [Ar = 2,6-diisopropylphenyl] [17].

Thermostabilities of the Polymers

Diagrams of a thermogravimetric (TG) and a differential scanning calorimetric (DSC) analysis are shown in Figs. 7 and 8. Softening points (T_m) and initial degradation temperatures (T_d) of the polymers from the radical polymerizations were as follows: $T_m = 182$ to 240°C (A in Fig. 7) and $T_d = 260$ to 300°C (B in Fig. 7). The thermostabilities of BZN polymers were slightly worse than those of BZMI polymers from the viewpoint of softening points, but the weight loss of BZN polymers was

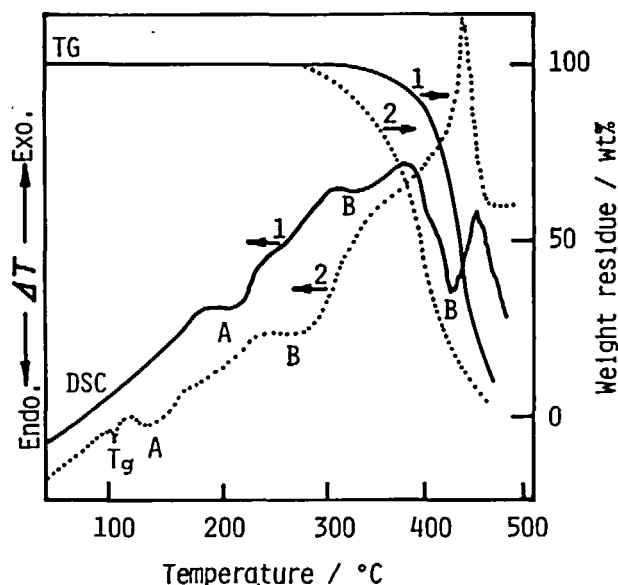


FIG. 7. TG and DSC curves for (1) BZN homopolymer (Run 4-2) and (2) BZN-St copolymer (Run BS 1-3) at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen.

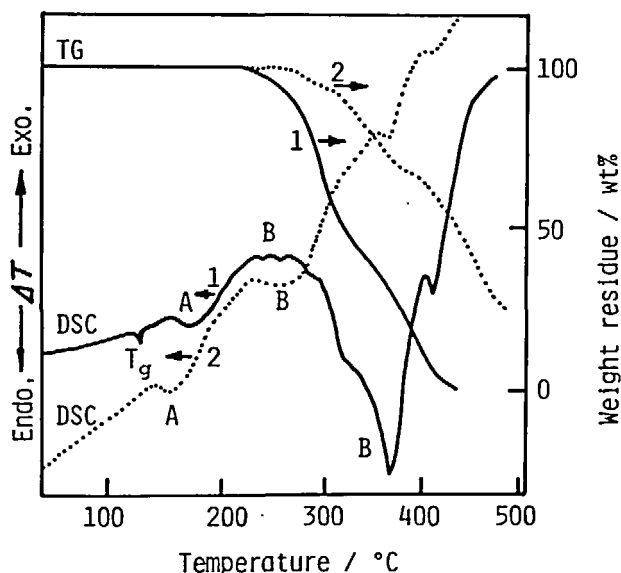


FIG. 8. TG and DSC curves for (1) BZN-MMA copolymer (Run BM 2-3) and (2) BZN-VAc copolymer (Run BV 1-3) at 170°C at a heating rate of 10°C/min in nitrogen.

almost equal to that of BZMI homopolymers. The thermostabilities of BZN-St and BZN-MMA copolymers were worse than those of the corresponding BZMI-St and BZMI-MMA copolymers [18]. The reason may be that BZN-St and BZN-MMA copolymers contain very small amounts of BZN units in the polymer side-chain. However, the thermostabilities of BZN-VAc copolymers were much better than those of BZMI-VAc copolymers because of better copolymerizability of BZN with VAc. T_m (A in Figs. 7 and 8) and T_d (B in Figs. 7 and 8) of the copolymers were as follows: $T_m = 111$ to 135°C , $T_d = 226$ to 274°C for poly(BZN-co-St)s; $T_m = 165$ to 191°C , $T_d = 208$ to 218°C for poly(BZN-co-MMA)s; $T_m = 170$ to 216°C , $T_d = 240$ to 283°C for poly(BZN-co-VAc)s. The glass transition temperatures (T_g) were observed at 100 to 104°C for BZN-St copolymers [obtained from BZN (20.0 to 50.0 mol% in monomer feeds) and St at 150°C] and at 130 to 135°C for BZN-MMA copolymers, as

shown in Figs. 7 and 8. These T_m values were reconfirmed by measurements with the ordinary capillary melting point methods.

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