Notes

Anionic Ring-Opening Polymerization of a Cyclic Carbonate Having a Norbornene Structure with Amine Initiators

Mitsumoto Murayama

Fundamental Research Laboratory, Sumitomo Bakelite Co., Ltd., Akiba-cho, Totsuka-ku, Yokohama 245, Japan

Fumio Sanda and Takeshi Endo*

Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta-cho,
Midori-ku, Yokohama 226, Japan

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Introduction

Common vinyl monomers such as styrene and methyl methacrylate undergo polymerization with volume shrinkage.[1] Thermosetting resins such as epoxides also show a 4−5% shrinkage in volume during the curing process. The occurrence of the volume shrinkage of the monomers and resins induces serious problems in their industrial applications for composites, adhesives, coatings, precision castings, and sealant materials. Therefore, development of monomers and materials that show volume expansion or zero-shrinkage is one of the most important and essential subjects in material science.[1,2] A few bicyclic and spirocyclic monomers such as spiro orthocarbonates have been proposed as exceptionally expandable monomers. Their syntheses, polymerizations, and applications have been extensively developed by Bailey et al.,[3,4] Endo et al.,[2,5,6] and other researchers.[7] Meanwhile, cyclic carbonates have been reported to undergo both cationic and anionic polymerizations to afford the corresponding polycarbonates in many papers, but none of them describes the volume change on the polymerization.[8−12] We have recently found that cyclic carbonates show volume expansion during the polymerization.[13,14] The volume expansion is explained by the large intermolecular interaction between the monomers and the small intermolecular interaction between the polymers. We have already reported the synthesis and anionic ring-opening polymerization of a cyclic carbonate having a norbornene structure, 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one (NBC).[13,15,16] NBC is expected to show high thermal stability because it has a rigid norbornene structure. Alkoxide initiators such as sodium methoxide, and alkyllithium initiators such as secondary butyllithium have been commonly used in the anionic ring-opening polymerizations of cyclic carbonates.[13,17] However, industrial use of these initiators may be difficult because of their instabilities and high reactivities. In this work, anionic ring-opening polymerization of NBC with several amine initiators is examined. Furthermore, copolymerization of NBC and glycidyl 1-naphthyl ether (GNE) by amine initiators and the possibility of controlling the volume shrinkage of epoxy resins during curing are also described.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra of the monomers and polymers were recorded on a JEOL JNM EX-400 spectrometer, using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) at 27 °C. Molecular weights and the distributions were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with a polystyrene gel column (TSK gel, G3000H), using tetrahydrofuran as an eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. FD-mass spectrum was recorded on a HITACHI M-80B. Melting points (mps), and glass transition temperatures (T_gs) were measured by a Seiko DSC 220C. Ten percent weight loss temperatures ($T_{d_{10}}$) of the polymers were measured under nitrogen by a Seiko TG-DTA 220. Densities of the monomers and polymers were measured by density gradient tubes at 25 °C with a Shibayama Kagaku Seisakusho Model A.

Molecular Orbital Calculations. All computations were done on an Apple Power Macintosh 7100/80AV with use of MOPAC version 3.7. The calculations were carried out by the PM3 Hamiltonian. The starting geometries were obtained by Cambridge Scientific Computing, Inc., Chem 3D Plus version 3.1. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

Materials. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine, aniline, and pyridine were distilled by the usual methods before use. Triethylenediamine (Dabco), quinuclidine, 4-(dimethylamino)pyridine (DMAP), and *N,N*-dimethylaniline were used as received. NBC was synthesized as follows according to the method reported with modification.[18,19] GNE was synthesized from epichlorohydrin and 1-naphthol with an aqueous solution of sodium hydroxide.

Synthesis of 5-Norbornene-2,2-dimethanol. To an aqueous KOH solution (45.3 wt %, 200 mL) was added dropwise norbornenecarboxaldehyde (153 g, 1.25 mol), formaldehyde (250 g, 3.08 mol), and methanol (500 mL). The reaction mixture was heated with refluxing for 5 h. After removal of the solvent, the mixture was washed with water. The residue was recrystallized from water to afford a white crystal (130.9 g): yield 68.0%; mp 113 °C (lit.[20] mp 110 °C). ^{1}H NMR ($CDCl_3$): δ 6.15 (s, CH=, 2H), 3.45−3.90 (s, CH_2O, 4H), 3.18 (s, OH, 2H), 2.96 (s, CH, 1H), 2.82 (s, CH, 1H), 1.26−1.56 (m, CH_2, 3H), 0.69−0.72 (m, CH_2, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 137.0 (CH=), 135.1 (CH=), 71.2 (CH_2O), 70.3 (CH_2O), 48.6 (CH_2), 46.9 (C), 44.5 (CH), 42.0 (CH), 32.8 (CH_2) ppm. IR (KBr): 3100−3600, 2967, 2945, 1633, 716 cm^{-1}.

Synthesis of NBC. Triethylamine (69.0 g, 0.68 mol) was added dropwise to a solution of ethyl chloroformate (69.7 g, 0.64 mol) and 5-norbornene-2,2-dimethanol (47.8 g, 0.31 mol) in toluene (680 mL) at 0 °C during 2 h. The suspension was washed with water and the solvent of the organic layer was removed by distillation. The residue was recrystallized from toluene to afford a white crystal (27.8 g): yield 49.4%, mp 89 °C (lit.[16] 92−94 °C). ^{1}H NMR ($CDCl_3$): δ 6.14−6.31 (m, CH=,

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* To whom all correspondence should be addressed.

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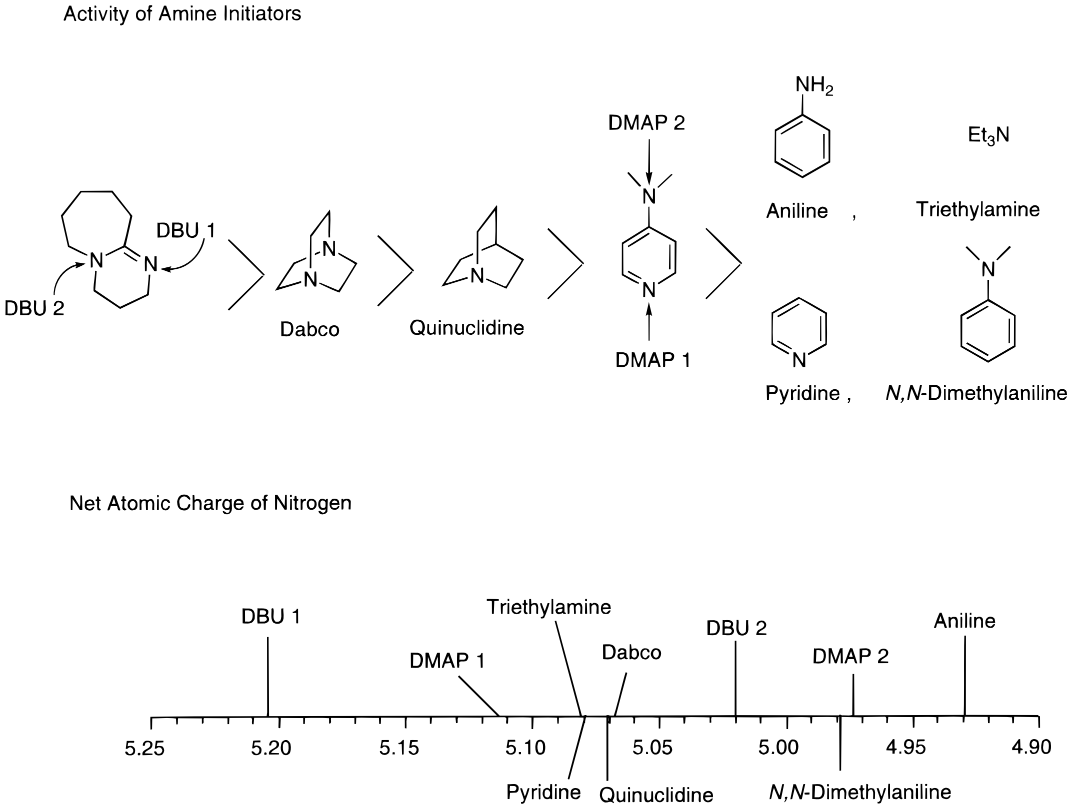


Figure 1. Activity of amine initiators and net atomic charges of nitrogens in the initiators calculated by PM3 MO method.

2H), 4.01–4.43 (m, CH_2O, 4H), 2.97 (s, CH, 1H), 2.89 (s, CH, 1H), 1.52–1.66 (m, CH_2, 3H), 1.02–1.05 (m, CH_2, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 147.9 (C=O), 137.8 (CH=), 132.6 (CH=), 75.7 (CH_2O), 74.2 (CH_2O), 46.5 (CH_2), 44.2 (C), 41.2 (CH), 39.4 (CH), 32.4 (CH_2) ppm. IR (KBr): 2968, 1736, 1476, 1400, 1182, 1092 cm^{-1}.

Anionic Homopolymerization of NBC. Typical Procedure. NBC (0.36 g, 2.0 mmol) and an amine initiator (4.0 mol %) were placed in a polymerization tube. The tube was cooled, evacuated, sealed off, and heated at 120 °C for 1 h. After the mixture was cooled, a solution of acetic acid in dichloromethane (1 vol %, 2.0 mL) was added to the mixture, and it was poured into 200 mL of methanol to isolate the polymer. ^1H NMR ($CDCl_3$): δ 6.07–6.21 (m, CH=CH, 2H), 3.89–4.32 (m, CH_2O, 4H), 2.88 (s, CH, 1H), 2.75 (s, CH, 1H), 1.48–1.64 (m, CH_2, 3H), 0.90 (m, CH_2, 1H) ppm. ^{13}C NMR ($CDCl_3$): δ 155.2 (C=O), 138.0 (CH=), 134.2 (CH=), 70.9 (CH_2O), 70.1 (CH_2O), 47.2 (CH_2), 46.4 (C), 45.9 (CH), 42.4 (CH), 32.7 (CH_2) ppm. IR (KBr): 2973, 1748, 1474, 1399, 1254, 974, 951, 789, 727 cm^{-1}.

Anionic Homopolymerization of GNE. Anionic polymerization of GNE was carried out similarly to the homopolymerization of GNE. ^1H NMR ($CDCl_3$): δ 6.51–8.16 (m, arom, 7H), 3.84–3.98 (m, 5H) ppm.

Anionic Copolymerization of NBC and GNE. Anionic copolymerization of the two monomers was carried out similarly to the homopolymerization of NBC. ^1H NMR of poly($NBC_{0.47}$-*co*-$GNE_{0.53}$) ($CDCl_3$): δ 7.41–8.22 (m, arom, 7H × 0.53), 6.07–6.21 (m, CH=CH, 2H × 0.47), 3.30–4.25 (m, CH_2O, 4H × 0.47, CH_2, CHO, CH_2, 5H × 0.53), 2.74–2.88 (m, CH, 2H × 0.47), 0.84–1.70 (m, CH_2, 4H × 0.47) ppm.

Scheme 1

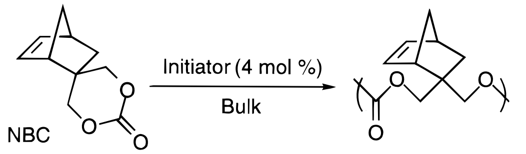


Table 1. Anionic Ring-Opening Polymerization of NBC by Amine Initiators

run	initiator	temp (°C)	time (h)	convn[a] (%)	yield (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[d]
1	triethylamine	120	20	0	0	
2	aniline	120	20	0	0	
3	*N*,*N*-dimethylaniline	120	20	0	0	
4	pyridine	120	20	0	0	
5	DMAP[e]	120	5	10	7[b]	500 (1.25)
6	DMAP	120	20	59	52[b]	3400 (1.45)
7	quinuclidine	120	1	9	6[b]	500 (1.34)
8	quinuclidine	120	5	56	55[b]	5400 (1.45)
9	quinuclidine	120	20	67	66[b]	6100 (1.42)
10	Dabco[f]	120	1	7	7[b]	800 (1.26)
11	Dabco	120	5	60	61[b]	6100 (1.43)
12	Dabco	120	20	70	70[b]	4800 (1.34)
13	DBU[g]	100	1	73	68[c]	6000 (1.49)
14	DBU	120	1	69	53[c]	6400 (1.48)
15	DBU	140	1	59	39[c]	5300 (1.43)

[a] Determined by ^1H NMR. [b] Isolated by preparative HPLC. [c] MeOH-insoluble part. [d] Estimated by GPC based on polystyrene standards. [e] DMAP: 4-(dimethylamino)pyridine. [f] Dabco: 1,4-diazabicyclo[2.2.2]octane. [g] DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene.

Results and Discussion

Anionic ring-opening polymerization of NBC was carried out with 4 mol % of several amine initiators at 100–140 °C in bulk (Scheme 1). Triethylamine, aniline, *N*,*N*-dimethylaniline, and pyridine could not afford the corresponding polymer at 120 °C for 20 h (runs 1–4 in Table 1). On the other hand, DMAP could initiate the polymerization even for 5 h (run 5 in Table 1), and the conversion reached 59% for 20 h to yield the polymer with $\bar{M}_n$ 3400 in 52% (run 6 in Table 1). Quinuclidine, Dabco, and DBU could also initiate the polymerization to afford the polymer. DBU afforded the polymer with the highest yield and $\bar{M}_n$ (runs 13–15 in Table 1). Both the conversion and yield decreased with increase of the

Table 2. Anionic Copolymerization of NBC and GNE[i]

run	monomer feed ratio NBC:GNE (mol %)	yield[b] (%)	unit ratio[c] in copolymer NBC:GNE (mol %)	$\bar{M}_n$ (M_w/M_n)[d]	vol change[e] (%)	T_g[f] (°C)	T_{d10}[g] (°C)
1	100:0	53	100:0	6400 (1.48)	+8.2	108	207
2	75:25	64	66:34	1200 (1.60)	+3.5	h	h
3	50:50	72	47:53	1300 (1.60)	+0.1	92	225
4	25:75	73	27:73	1300 (1.47)	−0.9	h	h
5	0:100[a]	31	0:100	940 (1.50)	−3.6	51	288

[a] Time: 46 h. [b] Isolated by preparative HPLC. [c] Determined by ^{1}H NMR. [d] Estimated by GPC based on polystyrene standards. [e] Calculated by the densities of the monomer and polymer. [f] Estimated by DSC. [g] 10% weight loss temperature measured by TGA under nitrogen. [h] Not determined. [i] Conditions: initiator, DBU (4 mol %), temperature, 120 °C; time, 1 h; bulk.

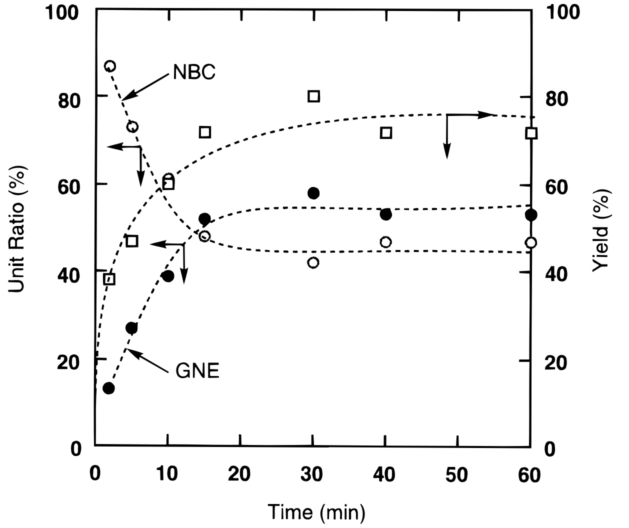
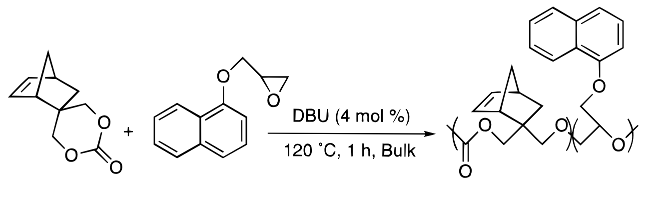


Figure 2. Time–unit and yield relationships of the copolymer of NBC and GNE. Conditions: monomer feed ratio NBC:GNE (mol %) = 50:50, initiator, DBU (4 mol %); temperature, 120 °C; bulk. The copolymer was isolated by preparative HPLC. The unit ratios in the copolymer of NBC and GNE were determined by ^{1}H NMR.

temperature. Occurrence of a considerable amount of back-biting reaction could be suggested from this result. The polymerizability of NBC depended on the amine initiators.

The net atomic charges on the nitrogens of the amines were determined by MO calculation to examine the reactivity. The order of the activity of the amine initiators was following; DBU > Dabco, quinuclidine > DMAP > aniline, triethylamine, *N*,*N*-dimethylaniline, pyridine, which could be explained by the order of the net atomic charges on the nitrogens (Figure 1). DMAP and pyridine showed activities smaller than those expected from the net atomic charges, probably due to the aromatic resonance effect to decrease the nucleophilicity. The much lower activity of triethylamine than those of Dabco and quinuclidine may be caused by the steric hindrance around the nitrogen atom.

Scheme 2



Anionic copolymerization of NBC and GNE was carried out in the monomer feed ratio of 100–0 mol % with 4 mol % of DBU in bulk at 120 °C for 1 h (Scheme 2). The results are summarized in Table 2. The yield of the polymer was 31% even for 46 h in the homopolymerization of GNE. Meanwhile, the copolymerization of NBC and GNE satisfactorily proceeded for 1 h. DBU seems to attack NBC predominantly and immediately to afford the polymer. The volume expansion during the polymerization increased with increase of the feed ratio of NBC. The volume shrinkage of epoxy resins can be controlled according to the feed ratio.

The time–unit ratio and the yield of the copolymer were monitored in the copolymerization of NBC and

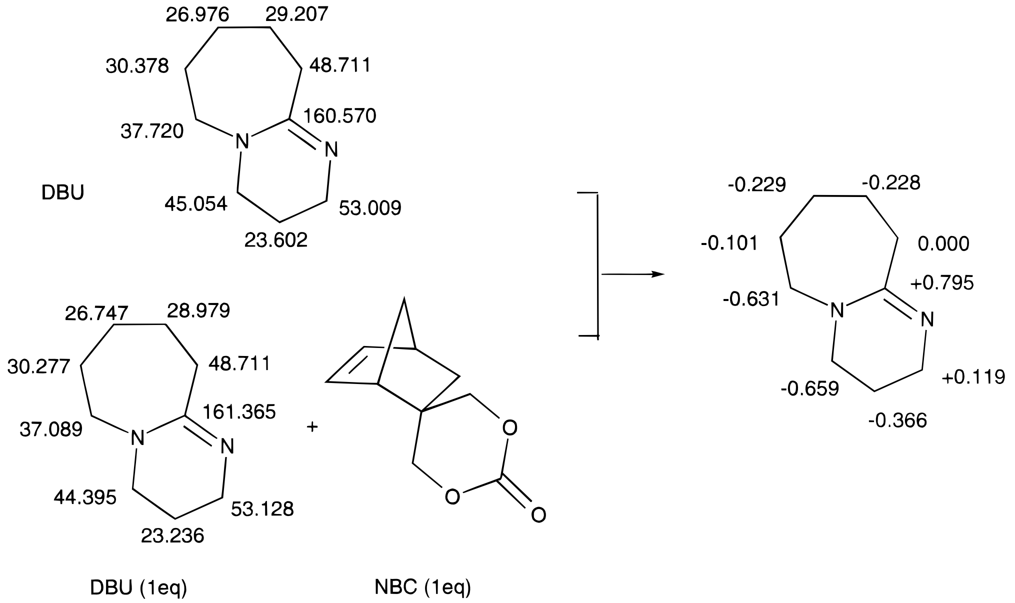


Figure 3. Change of the chemical shift of the ^{13}C NMR signals of DBU by the addition of NBC (solvent: nitrobenzene-d_5, 1.3 M).

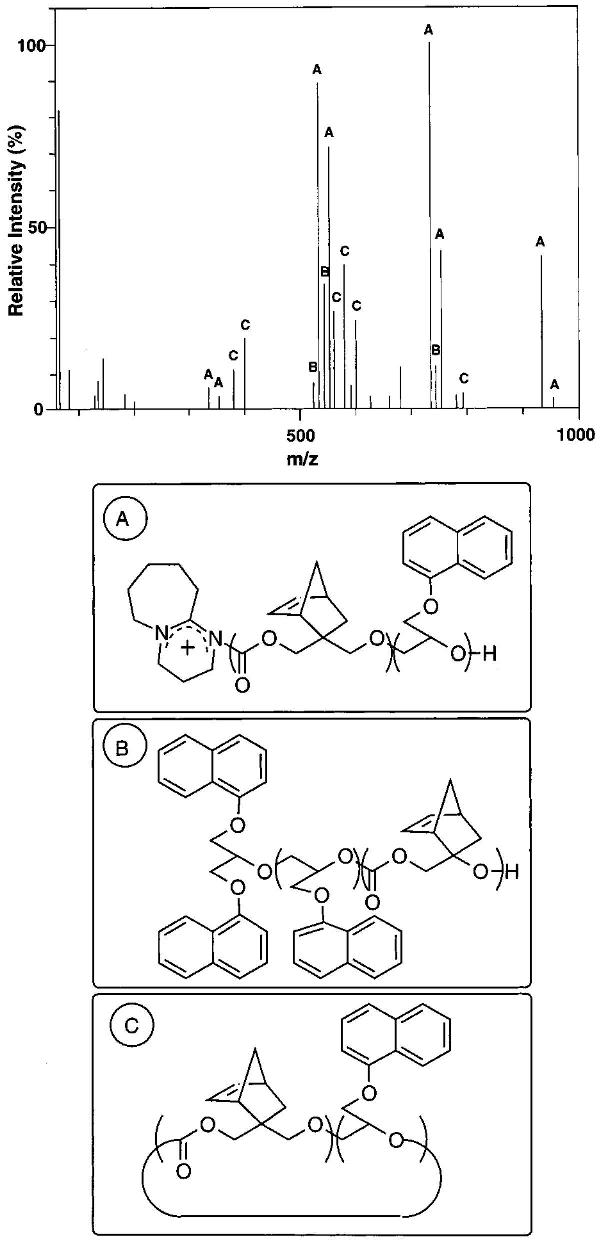


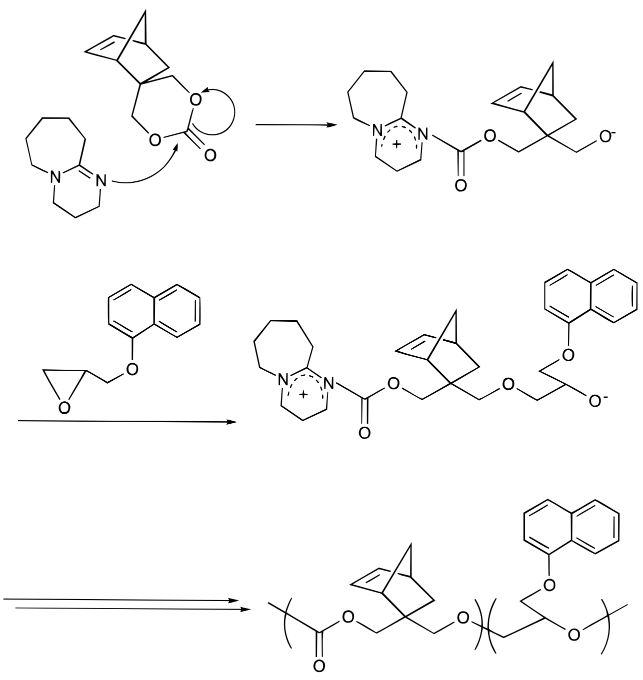
Figure 4. FD−MS spectrum of the copolymer obtained in the anionic copolymerization of NBC and GNE (run 3 in Table 2).

GNE to obtain more information about the mechanism of the copolymerization. The copolymerization of NBC and GNE yielded the copolymer in 38% only for 2 min (Figure 2). NBC predominantly polymerized in the first stage of the copolymerization, and the consumption of GNE gradually increased as the time progress. The unit ratio of GNE attained nearly 50% after 15 min.

The initiation mechanism with DBU was investigated in detail. The change of the chemical shift in the ^{13}C NMR signals of DBU was determined by the addition of NBC in nitrobenzene-d_5 in 1.3 mol/L concentration. The imino carbon of DBU showed a lower field shift in 0.795 ppm, while the two carbons next to the amine nitrogen showed higher field shifts at 0.631−0.659 ppm (Figure 3). The imino nitrogen of DBU might attack the carbonate carbonyl group of NBC to initiate the polymerization.

The FD−MS spectrum of the copolymer, obtained by the anionic copolymerization of NBC and GNE, was measured to examine the copolymerization (Figure 4). The three structures A, B, and C were confirmed as the main fractions. The peak A is due to a unit having DBU as an initiating polymer end. Peak B is due to a unit which was formed by the reaction of the polymer end with naphtholate. Peak C is due to a cyclic unit. All peaks confirmed the proceeding of the copolymerization of NBC and GNE.

Scheme 3



A plausible mechanism of the copolymerization can be illustrated as shown in Scheme 3. The initiation step of the polymerization is the reaction between DBU and NBC to form an alkoxide anion. The alkoxide anion attacks the carbonyl group of NBC predominantly to the epoxy ring of GNE.

The glass transition temperatures (T_gs) increased with increase of the unit ratio of NBC, and the 10% weight loss temperatures ($T_{d_{10}}$s) decreased.

Summary

In this work, the anionic ring-opening polymerization of NBC was carried out with several amine initiators. DBU, Dabco, and DMAP could initiate the polymerization to afford the corresponding polycarbonate. The copolymerization of NBC and GNE by DBU was also performed. The net atomic charges on the nitrogens of the amine were determined by MO calculation, which well explained the order of the activity of the amine. Polymerization of NBC predominantly proceeded in the first stage of the copolymerization of NBC and GNE, and the consumption of GNE gradually increased as the time progress. The FD−MS spectrum of the copolymer, obtained by the anionic copolymerization of NBC and GNE, confirmed the proceeding of the copolymerization of NBC and GNE. The control of volume shrinkage of epoxy resins by NBC could be demonstrated.

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