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Cationic Ring-Opening Polymerization of Cyclic Carbonates with Alkyl Halides To Yield Polycarbonate without the Ether Unit by Suppression of Elimination of Carbon Dioxide[1]

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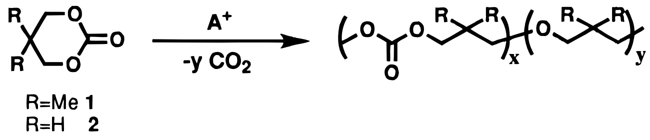
ABSTRACT: Cationic ring-opening polymerization of cyclic carbonates with alkyl halide as initiator during which no decarboxylation takes place is described in detail, using 5,5-dimethyl-1,3-dioxan-2-one (**1**), 1,3-dioxan-2-one (**2**), 5-*n*-butyl-1,3-dioxan-2-one (**5**), and 1,3-dioxaspiro[5.5]undecan-2-one (**6**) as monomers. Cationic polymerizations of **2**, **5**, and **6** with cationic initiators such as methyl triflate and boron trifluoride etherate were carried out under various conditions. In the polymerizations decarboxylation (elimination of carbon dioxide) during the polymerization occurred to yield the corresponding polycarbonate with ether units (5−10%) in the main chain. **6** only gave a small amount of polymer. Prolonged reaction time and enhanced temperature accelerated the decarboxylation. Reactions of the polycarbonate of **2** with several cationic initiators including methyl iodide were monitored by ^{1}H NMR and gel permeation chromatography. Both a decrease in the polymer molecular weight and an increase in the ratio of ether unit, which strongly depended upon the kind of initiator, were observed. The occurrence of the decarboxylation in the propagation step was suggested by PM3 molecular orbital calculations using model compounds. Direct reaction of **2** with an excess of alkyl halide such as methyl iodide and benzyl bromide at 120 °C afforded the corresponding 1:1 adducts **7**. Yield of **7a** from methyl iodide was only 10%, while yield of **7b** from benzyl bromide was 78%. Cationic polymerizations of **1**, **5**, and **6** with a few alkyl halides such as methyl iodide, benzyl bromide, and allyl iodide were studied under various conditions, and corresponding polycarbonates without any ether unit were obtained ($\bar{M}_n$ 1000−3700), while **6** gave no polymer. A terminal structure of the polymers obtained was determined by ^{1}H NMR, and the polymerization with ethyl 3-iodopropyl carbonate as its model compound was examined to prove the propagation structure of the active site. The mechanism of the decarboxylation was discussed from the viewpoint of degree of interaction between HOMOs and LUMOs of cyclic carbonate and initiator and on the basis of the experimental results obtained in this work.

Introduction

Five-membered cyclic carbonates, which are readily available, sluggishly polymerize to polycarbonates containing a considerable amount of ether units in the main chain through competitive elimination of carbon dioxide independent of the polymerization mode.[2] In contrast to it, six-membered cyclic carbonates undergo efficiently ring-opening polymerization to yield the corresponding linear polycarbonates, especially under anionic conditions.[3] Under cationic conditions, however, the polymerization is always accompanied with partial elimination of carbon dioxide to afford linear polycarbonates having an ether unit. Kricheldorf et al. reported that dimethyl-substituted (**1**) and unsubstituted (**2**) six-membered cyclic carbonates smoothly polymerized with cationic catalysts such as methyl triflate, but partial elimination of carbon dioxide occurred to yield polycarbonates containing ether units[4] (Scheme 1).

Scheme 1



It was reported by Albertsson et al. that high molecular weight polycarbonate containing 3−5% of ether unit was obtained by cationic polymerizations of **2** in bulk and in solution with nonpolar solvents.[3a] Thus complete polymerization without decarboxylation has not been achieved so far. Very recently, Kricheldorf et al. have reported the synthesis of high molecular weight and ether unit-free polycarbonate by ring-opening polymerizations of **1** with butyltin chlorides, although the detailed mechanism is not clear.[5] In our continuing study on ring-opening polymerization of cyclic carbonate,[1,6] we reported that cationic polymerization of a norbornene-containing cyclic carbonate (**3**) affords a polycarbonate having a complex structure probably due to participation of the olefinic group in the polymerization. Therefore, the structure of the polycarbonate has not been determined. Meanwhile, we have noticed that anionic ring-opening polymerization of cyclic carbonates shows expansion in volume during polymerization.[6,7] Since ring-opening polymerization with anionic initiator efficiently proceeds without decarboxylation as mentioned above, it is important to develop cationic polymerization systems in which no decarboxylation takes place, because occurrence of elimination of some small molecules during polymerization can spoil the characteristic nature of cyclic carbonates as novel expanding monomers.[7] Recently, we found that ring-opening polymerization of cyclic carbonates with alkyl halides used as cationic initiators proceeds without decarboxylation to give the corresponding linear carbonates.[1] In this paper mechanistic aspects of the polymerization as well as polymerization conditions suppressing decarboxylation are discussed in detail.

Experimental Section

^{1}H NMR spectra were recorded on JEOL PMX 60SI and EX-90 spectrometers, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C. FT IR spectra were

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obtained with a JASCO FT/IR-3 at 25 °C. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Toyo Soda HPLC CCP & 8000 system with a data processor, equipped with polystyrene gel columns (TSK gels 1000−3000), using tetrahydrofuran (THF) as solvent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. A Japan Analytical Industry recycling preparative HPLC LC 908, equipped with polystyrene gel columns (JAI gels H1 and H2), using chloroform or THF as products, was used for isolation of products. Density of solid monomers and polymers was measured by the density gradient tube method using a Shibayama density measurement apparatus type-A. Density of liquid monomers was measured by means of the glass tube method from the height and weight of the sample.

Solvents were purified by distillation according to the conventional methods. Commercially available BF_3OEt_2, MeOTf, benzyl bromide, methyl iodide, and allyl chloride were distilled over P_2O_5. Allyl iodide was prepared from allyl chloride and NaI.

Molecular Orbital Calculations. All computations were done on an Apple Macintosh IIvx computer with MOPAC version 6.00 (QCPE No. 455) revised as version 6.02 for Macintosh. The calculations were carried out by the PM3 program. Geometries were optimized in internal coordinates, and the calculations were terminated when the change in energy on successive iterations was less than 0.000 01 kcal/mol. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

Synthesis of Cyclic Carbonate Monomer: A Typical Procedure: Triethylamine (84.0 g, 0.825 mol) was added dropwise to a solution of 1,3-propanediol (29.9 g, 0.393 mmol) and ethyl chloroformate (85.4 g, 0.786 mol) in 2 L of THF (0.4 M) at 0 °C over a period 30 min. The reaction mixture was stirred for 2 h at room temperature. Precipitated triethylamine hydrochloride salt was filtered off, and the filtrate was concentrated under vacuum. The residue was recrystallized three times from THF−ether. A white crystal of 1,3-dioxan-2-one (**2**) was obtained in 62% yield (25.4 g): mp 45 °C, (lit.[8] mp 45 °C); d_{60} 1.250; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.52 (t, J = 6.0 Hz, 4H), 2.15 (q, J = 6.0 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 147.1 (s), 67.5 (t), 20.8 (t); IR (KBr) 2986, 2926, 1747, 1477, 1420, 1251, 1186, 1147, 1120, 981 cm^{-1}.

5,5-Dimethyl-1,3-dioxan-2-one (1): isolated yield was 87%; mp 109 °C (benzene, lit.[8] mp 109−110 °C); d_{25} 1.238; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.05 (brs, 4H), 1.10 (brs, 6 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 147.7 (s), 76.9 (t), 27.8 (s), 20.4 (q); IR (KBr) 2969, 1745, 1475, 1410, 1223, 1194, 1121, 768 cm^{-1}.

5-*n*-Butyl-1,3-dioxan-2-one (5): isolated yield was 72%; bp 103 °C/0.09 mmHg; d_{25} 1.100; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.42 (dd, J = 4.4, 8.3 Hz, 2H), 2.36−2.20 (m, 2H), 1.62−1.10 (brs, 6H), 1.10−0.71 (brs, 3H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 148.9 (s), 72.3 (t), 31.3 (d), 28.8 (t), 27.0 (d), 22.7 (d), 13.9 (q); IR (neat) 2958, 2927, 2860, 1751 1473, 1457, 1409, 1180, 1159, 1132, 800 cm^{-1}. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.54; H, 8.59.

1,3-Dioxaspiro[5.5]undecan-2-one (6): isolated yield was 80%; mp 98−99 °C (benzene, lit.[9] mp 92−93 °C); d_{25} 1.211; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.03 (s, 4H), 1.46 (s, 6H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 148.7 (s), 75.8 (t), 31.1 (s), 29.9 (t), 25.8 (t), 21.2 (t); IR (KBr) 2934, 2862, 1724, 1470, 1406, 1244, 1192, 1157, 1146, 1105, 1074, 791, 772 cm^{-1}.

Synthesis of 8-Iodo-3,5-dioxaoctan-4-one (7c): A Typical Procedure. Pyridine (0.87 g, 11 mmol) was added to a solution of 3-bromo-1-propanol (1.39 g, 10 mmol) and ethyl chloroformate (1.19 g, 11 mol) in 30 mL of THF (0.33 M) at 0 °C over a period of 30 min. The reaction mixture was stirred for 2 h at room temperature. To the resulting mixture was added excess ether, precipitated pyridine hydrochloride salt was filtered off, and the filtrate was concentrated under vacuum; 0.35 g of the residue was dissolved in 3.5 mL of acetonitrile containing 75 mg of sodium iodide as a suspension. The resulting mixture was poured into ether, precipitated sodium bromide was filtered off, and the filtrate was concentrated under vacuum. Vacuum distillation yielded a colorless liquid of **7c**: isolated yield was 92%; bp 105 °C/4 mmHg; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.27 (t, J = 3.1 Hz, 2H), 4.19 (q, J = 7.3 Hz, 2H), 3.24 (t, J = 8.1 Hz, 2H), 2.05 (q, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 153.9 (s), 66.5 (t), 64.1 (t), 31.4 (t), 27.0 (t), 14.3 (q); IR (neat) 2962, 1749, 1473, 1457, 1400, 1250, 1052, 847 cm^{-1}. Anal. Calcd for $C_6H_{11}O_3I$: C, 27.93; H, 4.93; I, 48.54. Found: C, 27.95; H, 4.92; I, 48.90.

Model compounds used for the assignment of the terminal group of the polymer (summarized in Table 4) were synthesized according to the same procedure.

7-Iodo-2,4-dioxaheptan-3-one (7a): isolated yield was 10%; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.28 (t, J = 3.1 Hz, 2H), 3.91 (s, 3H), 3.24 (q, J = 6.4 Hz, 2H), 2.05 (q, J = 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 153.9, 64.1 (t), 53.1 (q), 31.7 (t), 27.0 (t); IR (neat) 2962, 1749, 1473, 1457, 1400, 1250, 1052, 847 cm^{-1}. Anal. Calcd for $C_5H_9O_3I$: C, 24.61; H, 3.72; I, 52.00. Found: C, 24.69; H, 3.88; I, 52.33.

7-Bromo-1-phenyl-2,4-dioxaheptan-3-one (7b): isolated yield was 78%; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.36−7.24 (arom, 5H), 5.15 (s, 2H), 4.28 (t, J = 5.9 Hz, 2H), 3.45 (q, J = 6.4 Hz, 2H), 2.19 (q, J = 6.3 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 154.9 (s), 135.1 (d), 128.6 (d), 128.4 (d), 69.7 (t), 65.7 (t), 31.7 (t), 29.0 (t); IR (neat) 2972, 2851, 1750, 1500, 1457, 1400, 1248, 1047, 870 cm^{-1}. Anal. Calcd for $C_{11}H_{13}O_3Br$: C, 48.37; H, 4.80; Br, 29.26. Found: C, 48.77; H, 4.49; Br, 29.82.

Reaction of 2 with Excess Alkyl Halides: A Typical Procedure. To 131 mg of **2** (1.28 mmol) placed in an argon-purged glass tube was introduced, 0.575 g (3 equiv) of methyl iodide by a syringe. The tube was evacuated, sealed off, and heated at 120 °C for 96 h. The reaction mixture was evaporated under vacuum. The residue was separated by preparative HPLC. The corresponding ring-opening adduct and oligomer were obtained. The reaction of **2** with benzyl bromide was similarly carried out.

Cationic Polymerization: A Typical Procedure. Procedures of cationic polymerization except for workup were operated under argon atmosphere. To 131 mg of **2** (1.28 mmol) placed in an argon-purged glass tube were added 16 mL (20 mol %) of methyl iodide and 0.32 mL of benzonitrile by a syringe in a drybox. The tube was evacuated, sealed off, and heated at 120 °C for 48 h in the dark. The polymerization mixture was evaporated under vacuum and diluted with a small amount of methylene dichloride. The mixture was washed with Na_2SO_3 solution and water and poured into ether (50 mL) to precipitate the polymer of **2**. A colorless gummy solid was collected by a centrifugal separation. Yield of poly-**2** was 99 mg (76%). The spectral data of the polymer are summarized in Table 3.

In the polymerization with allyl iodide and benzyl iodide (Table 2, runs 12 and 13), allyl chloride or benzyl bromide was introduced in a glass tube together with an equimolar amount of sodium iodide. The workup was similarly carried out.

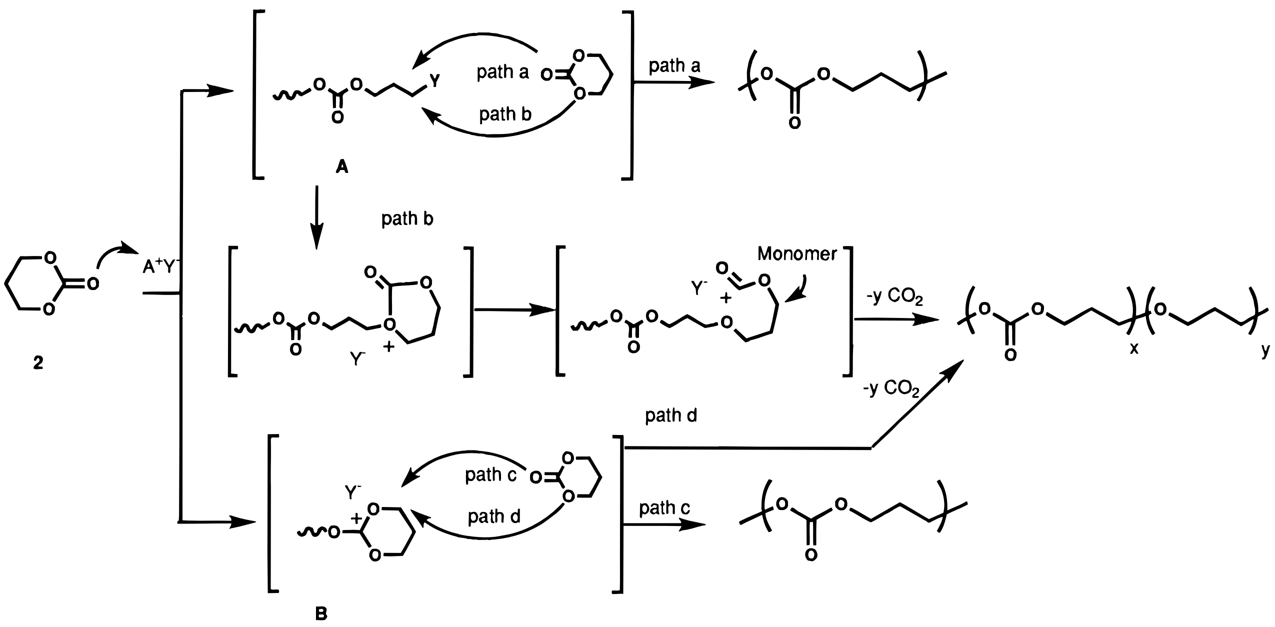
Polymer of 2 (Table 2, run 2): yield 76%; d_{25} 1.200; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.24 (t, J = 6.2 Hz, 4H), 2.05 (q, J = 6.2 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 155.1 (s), 64.2 (t), 28.0 (t); IR (neat) 2971, 2910, 1751, 1473, 1458, 1361, 1330, 1243, 1093, 1033, 933, 790 cm^{-1}.

Polymer of 5 (Table 3, run 3): yield 62%; d_{25} 1.105; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.15 (d, J = 5.7 Hz, 4H), 1.82−2.16 (m, 1H), 1.10−1.62 (br 6H), 1.10−0.71 (br, 3H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 155.0 (s), 67.3 (t), 37.7 (d), 29.0 (t), 27.2 (t), 22.5 (t), 13.7 (q); IR (neat) 2959, 2930, 2862, 1750, 1458, 1404, 1241, 934, 790 cm^{-1}.

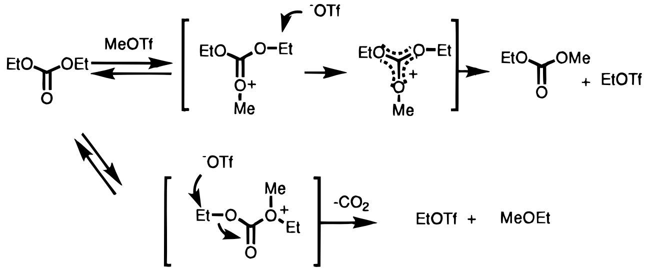
Polymer of 6 (Table 1, run 15): yield 42%; d_{25} 1.130; ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.10 (brs), 3.55 (brs), 1.48 (brs); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 155.7 (s), 70.1 (t), 37.4 (s), 29.7 (t), 25.9 (t), 21.2 (t); IR (neat) 2928, 2858, 1751, 1473, 1454, 1398, 1238, 1157, 1047, 964, 638 cm^{-1}.

Reaction of Polycarbonate with Cationic Initiators: A Typical Procedure. Poly-**2** ($\bar{M}_n$ 13 000), containing 4% of ether unit obtained by the cationic polymerization with methyl triflate, was used. A solution of poly-**2** (102 mg, 1 mmol) and methyl triflate (2.8 mL, 2.5 mol %) in 300 mL of $CDCl_3$ was introduced into an NMR sample tube under an argon atmosphere. The tube was sealed off and heated at 80 °C for 96 h in an oil bath. During the reaction the ^{1}H NMR spectrum of

Scheme 2



Scheme 3



the mixture was measured at appropriate intervals. From the ^{1}H NMR spectrum, the unit ratio of the polymer obtained (polycarbonate:polyether) was 23:77. The reaction mixture was washed with water and concentrated under reduced pressure. Molecular weight of the resulting polymer measured by GPC was $\bar{M}_n$ 2300.

Results and Discussion

Kricheldorf et al. proposed a mechanism of cationic polymerization of **2** with methyl triflate (A^+Y^-).[4b] From their detailed NMR study, they found that the propagating species consists of a mixture of two species, alkyl triflate ester (A, Y = OSO_2CF_3) and trialkylcarbenium triflate (B, Y = OSO_2CF_3), which are in equilibrium with each other. Further, they concluded that decarboxylation was caused by competitive attack of the ether oxygen of **2** and/or of the polymer formed at these propagating cationic species (Scheme 1, paths b and d). This attack yields an intermediate oxycarbonyl cation of which the β-carbon is attacked by **2** to lead to the formation of a trimethylene oxide unit along with elimination of carbon dioxide (Scheme 2). Of course, ordinary attack of the carbonyl oxygen of **2** gives the corresponding polycarbonate via paths a and b.

The decarboxylation by the attack of the polymer main chain at the propagating end is suggested by the experiment using diethyl carbonate as a polymer model compound in which ethyl methyl ether and ethyl triflate are produced in addition to carbon dioxide.[4a] This can be schematically shown as follows (Scheme 3). Namely, this result indicates that the decarboxylation like path b or d (Scheme 2), can similarly proceed between the propagating end and polymer main chain during the polymerization, although there is no direct evidence.

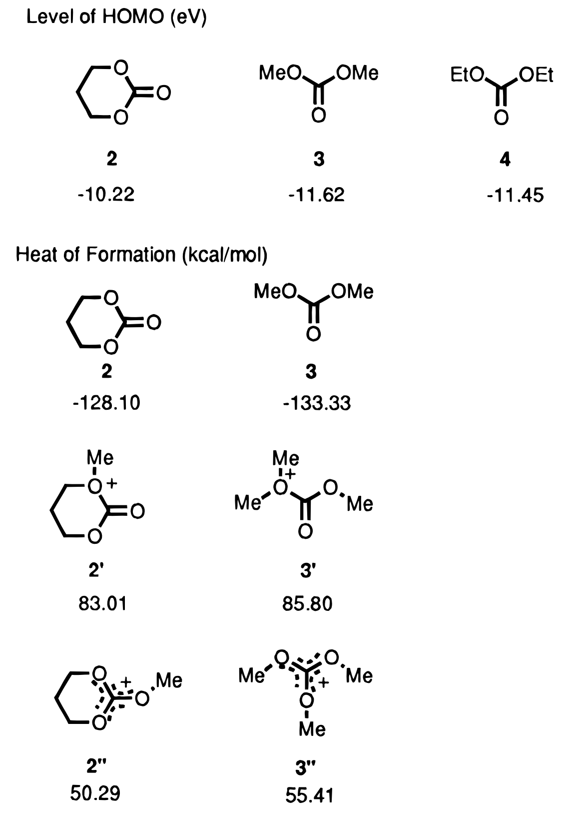


Figure 1. HOMO level and heat of formation of cyclic and acyclic carbonates and methylated cations, calculated by MOPAC Ver. 6.02/PM3.

The decarboxylation seems to occur by attack of the monomer at the propagation end more preferably than attack of the polymer at the propagation end. This is probably because the monomer is more nucleophilic than the polymer, as being judged from the results of the PM3 molecular orbital calculation by MOPAC Ver. 6.02 (Figure 1). As shown in Figure 1, comparison of the HOMO level of **2** and dialkyl carbonate (**3** and **4**) suggests that **2** is more nucleophilic than linear dialkyl carbonates.

On the other hand, the heat of formation (HF) of two cationic intermediates of the reaction of **2** and dimethyl carbonate **3** as the polymer model with methyl cation

Table 1. Cationic Polymerizations of 2 and 5

run	monomer	initiator (mol %)	solv (M)[c]	temp	time (h)	conv[a] (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	unit ratio X (%)[a]	unit ratio Y (%)[a]
1	**2**	MeOTf (1)	PhCl (2)	60	12	100	2200	3.05	91	9
2		MeOTf (1)	PhCl (5)	60	6	100	2000	1.37	93	7
3		MeOTf (1)	none	60	0.5	92	13000	1.87	94	6
4		MeOTf (1)	none	60	3	100	9000	2.05	93	7
5		MeOTf (1)	none	60	12	100	5700	2.14	71	29
6		MeOTf (1)	none	100	0.17	100	4600	2.67	90	10
7		BF_3OEt_2 (1)	PhCl (2)	60	12	54	2000	2.65	91	9
8		BF_3OEt_2 (1)	none	60	12	92	5200	2.05	93	7
9		BF_3OEt_2 (1)	none	100	0.17	89	4200	2.77	91	9
10		I_2 (5)	none	120	0.33	100	25000	3.48	93	7
11	**5**	MeOTf (1)	none	60	1	95	5000	1.67	96	4
12		MeOTf (1)	none	60	6	100	3900	2.01	93	7
13		MeOTf (1)	none	100	1	100	3500	1.87	93	7
14		MeOTf (5)	none	60	0.67	100	3900	2.58	92	8
15	**6**	MeOTf (5)	PhCl (2)	80	24	58	1500	1.53	81	19

[a] Determined by ^{1}H NMR. [b] Estimated by GPC (polystyrene standards). [c] Concentration of monomer.

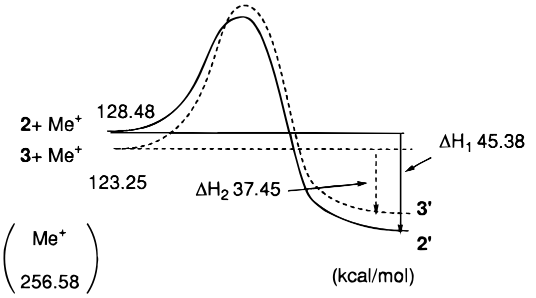


Figure 2. Energy diagrams of reactions of **2** and **3** with methyl cation, calculated by MOPAC Ver. 6.02/PM3.

as the propagation end model was calculated. The stabilization energy of the production of the oxonium type cation **2′** (ΔH_1 in Figure 2) is 7.93 kcal/mol larger than that of the oxonium type cation **3′** (ΔH_2). Therefore, decarboxylation from the monomer should be thermodynamically and kinetically predominated over that from the linear carbonate or polymer, that is, the decarboxylation would take place mostly in the propagation step of the polymerization.

Since the decarboxylation seems to be a competitive process with the normal propagation, one of the methods for suppression of the decarboxylation is to lower the reactivity of the propagating species, according to the selectivity–reactivity rule in organic chemistry. Therefore, if the reactivity of the propagating species is lowered by choosing the counteranion (Y^-), e.g., halide anion instead of triflate anion, the decarboxylation can be reduced or completely suppressed. As is discussed later, the polymerization of cyclic carbonates with alkyl halides is compared with that of ordinary cationic initiators to evaluate upon which factors the decarboxylation depends.

Cationic Polymerization with Common Initiators. Cationic polymerization of **2** with 1 mol % of methyl triflate and BF_3OEt_2 was carried out under various conditions. The degree of decarboxylation was determined by the integration ratio of the two triplet signals at 4.2 and 3.5 ppm assignable as main chain methylene protons adjacent to carbonate and ether groups, respectively, as shown in Figure 3A. Results are summarized in Table 1.

In accordance with Albertson's report,[3a] the degree of decarboxylation was 5–10% in the polymerizations with methyl triflate at 60 °C (runs 1–4). The polymerization was fast under the conditions, and the conversion of **2** reached 92% in 0.5 h. Prolonged reaction time (run 5) resulted in vigorous decarboxylation (29% Y unit). This means the occurrence of the decarboxylation between the propagation end and the polymer formed. This is consistent with the formation of higher molecular weight polymer in the polymerization in a shorter time (run 3). At higher temperature (100 °C, run 6) the decarboxylation is accelerated. Since the polymerization with BF_3OEt_2 gave 7–9% decarboxylation independent of the conversion of **2** (runs 7–9), it is clear that the decarboxylation takes place competitively with the normal propagation as mentioned above. These results suggest that the decarboxylation by the polymerization is not slow as compared with the normal propagation.

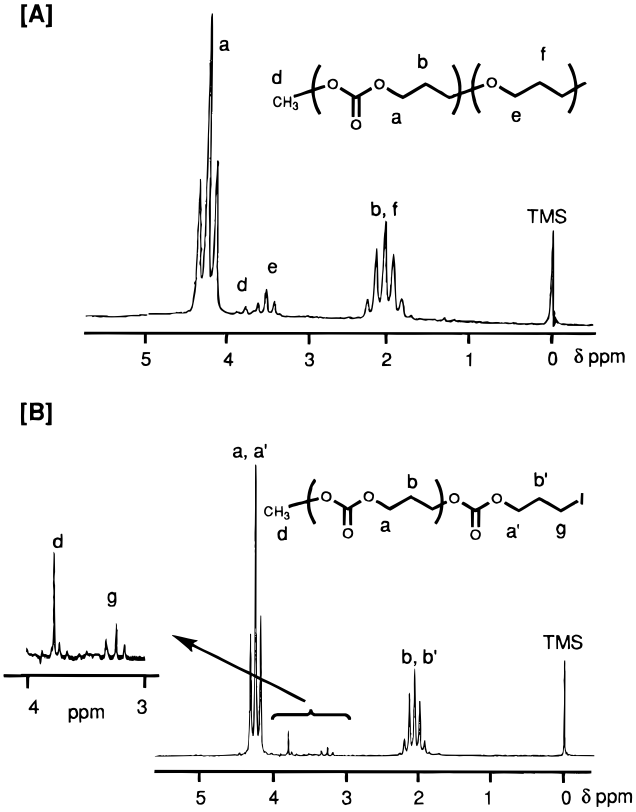
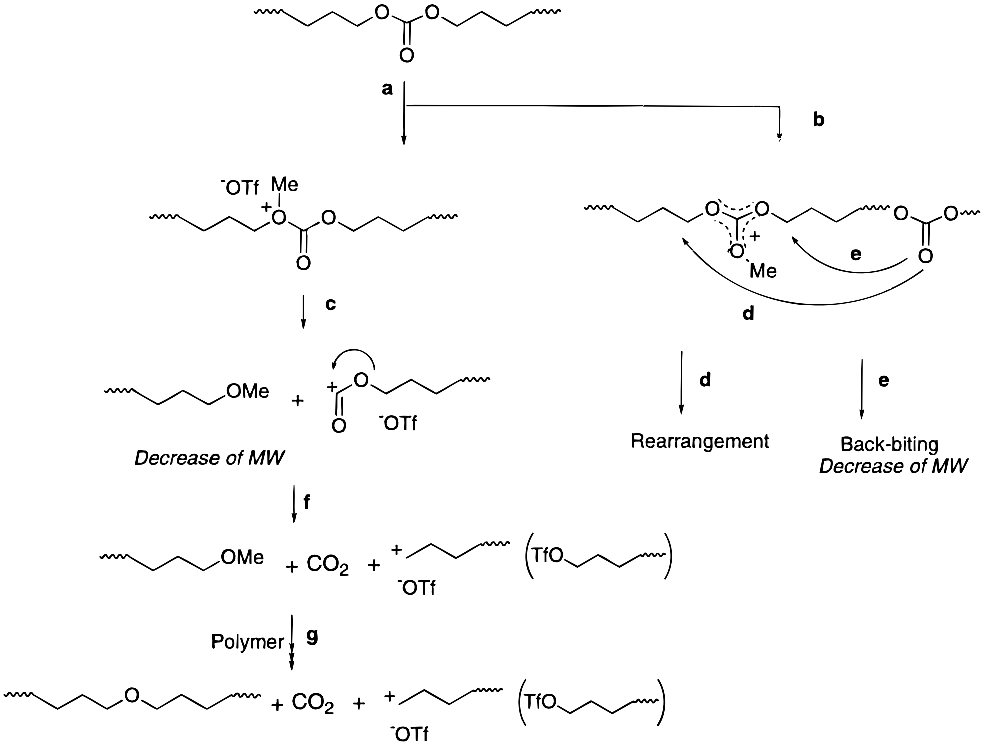


Figure 3. ^{1}H NMR spectra of poly-**2** obtained by polymerizations (A) with methyl triflate (Table 1, run 6) and (B) with methyl iodide (Table 2, run 2).

Cationic polymerizations of substituted cyclic carbonates such as 5-*n*-butyl- (**5**) and 5,5-cyclohexenyl- (**6**) substituted ones were carried out under similar conditions (Table 1, runs 11–15). Whereas **5** polymerized with MeOTf at 60 °C in a few hours, the polymerization

Scheme 4



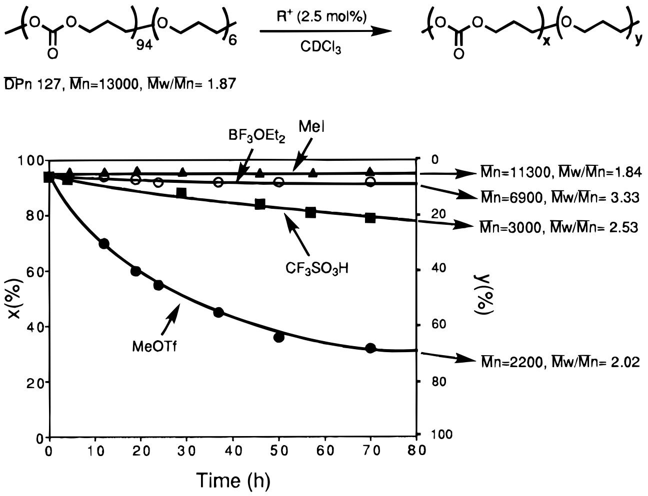


Figure 4. Time-dependent composition change by reactions of poly-**2** with cationic initiators (2.5 mol %) in $CDCl_3$ at 80 °C (120 °C in the case of methyl iodide).

always was accompanied by 4–8% decarboxylation, like in the case of **2**. The polymerization of **5** and **6** was slower than that of **2**. Especially, it took 24 h to reach 58% conversion of **6** even at 80 °C (run 15), so that the decarboxylation ratio of the Y unit becomes high (19%) and the molecular weight decreases. Iodine afforded high molecular weight polymer ($\bar{M}_n$ 25 000), but 7% of ether units in the main chain were observed (run 10).

Reaction of Polycarbonate with Cationic Initiators. Reaction of one of the obtained polycarbonates with a few cationic initiators was carried out to evaluate the reactivities of the initiators and the produced propagating species toward the polycarbonate main chain. Poly-**2** containing 4% of ether unit ($\bar{M}_n$ 13 000) was treated with a few cationic initiators such as methyl triflate in $CDCl_3$ at 80 °C (120 °C, in the case of methyl iodide). Figure 4 shows the relationship between unit ratio and reaction time. Although methyl triflate and methanesulfonic acid caused a sharp increase of the Y unit (ca. 70% and 20%, respectively), there was little increase of the Y unit in the cases of methyl iodide and BF_3OEt_2. These results indicate that decarboxylation by reaction of cationic species with polycarbonate formed can be suppressed, if methyl iodide can be used as the cationic initiator. In the case of BF_3OEt_2, the molecular weight of the polymer slightly decreased from 13 000 to 2000–7000 in accordance with the occurrence of a small degree of decarboxylation, indicating that BF_3OEt_2 is not a good initiator. The mechanism of this decarboxylation with methyl triflate is shown in Scheme 4.

The polycarbonate first reacts with methyl triflate to afford either oxonium (route a) and/or carbenium (route b) intermediates. The carbenium one can be intramolecularly attacked by the oxygen nucleophile of the main chain through routes d and e to lead to structural rearrangement and back-biting, respectively. Meanwhile, the oxonium one undergoes decarboxylation in a mode mentioned above via an oxycarbonyl intermediate to give the corresponding methyl ether and polymeric triflate (routes c and f). The polymeric triflate also serves as a cationic initiator to react with another polymer molecule and eventually results in the elimination of carbon dioxide along with formation of another polymeric triflate as byproduct. Both routes c and e should cause considerable decrease in polymer molecular weight.

Cationic Polymerization with Alkyl Halides. On the basis of the above results, cationic polymerizations of cyclic carbonates with alkyl halides were examined. Since organic reaction of cyclic carbonate with alkyl halide had never been reported, at first the reaction of **2** with 3 equiv of alkyl halides, such as methyl iodide and benzyl bromide, was carried out at 120 °C without solvent. As a result, the corresponding adducts **7a**,**b** were obtained (Scheme 5). The structures of the adducts **7** were determined by the spectral data as well as analytical data. Although the yield of **7a** was very low, a considerable amount of low molecular weight polymer ($\bar{D}_p$ = 3–4) (22 % yield) was formed. On the

Table 2. Cationic Polymerization of 2 with Alkyl Halides[a]

run	initiator (mol %)	solv	temp (°C)	time (h)	conv[a] (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	unit ratio[c] X (%)	unit ratio[c] Y (%)
1	MeI (20)	none	100	24	~0				
2	MeI (20)	none	120	18	100	3700	2.29	100	0
3	MeI (20)	1,1-DCE[d]	120	48	18	1000	1.69	100	0
4	MeI (10)	NB[e]	120	48	48	2200	1.45	96	4
5	MeI (20)	NB	120	48	59	1700	1.53	95	5
6	MeI (20)	PC[f]	120	48	67	2900	1.83	100	0
7	MeI (20)	BN[g]	120	48	87	3000	2.64	100	0
8	MeI (20)	BN	120	96	100	1600	2.82	100	0
9	BnBr (20)	none	120	48	88	3700	2.07	100	0
10	BnBr (20)	NB	120	48	7				
11	BnBr (20)	PC	120	48	12				
12	BnI (20)	BN	120	24	100	1100	1.87	100	0
13	allyl iodide (20)	BN	120	24	100	1400		100	0

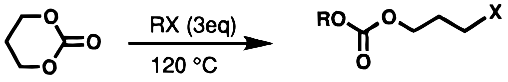
[a] Conversion of **2** determined by ^{1}H NMR. [b] Estimated by GPC (RI). [c] Determined by ^{1}H NMR. [d] 1,1-Dichloroethane. [e] Nitrobenzene. [f] Propylene carbonate. [g] Benzonitrile.

Table 3. Cationic Polymerization of Substituted Cyclic Carbonates with Methyl Iodide

run	monomer	initiator (mol %)	solv (M)[c]	temp (°C)	time (h)	conv[a] (%)	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	unit ratio[c] X (%)	unit ratio[c] Y (%)
1	**1**	MeI (20)	none	120	120	~0				
2		MeI (20)	NB[d] (4)	140	96	52	1100	1.52	80	20
3	**5**	MeI (20)	none	120	48	100	3200	1.05	100	0
4		MeI (20)	NB (4)	120	24	15				
5		MeI (20)	NB (4)	120	48	31	780	1.40	100	0
6		MeI (5)	PhCl (4)	120	24	10	600	1.47	100	0
7	**6**	MeI (20)	none	120	48	trace				

[a] Conversion of monomer determined by ^{1}H NMR. [b] Estimated by GPC (RI). [c] Concentration of monomer. [d] Nitrobenzene.

Scheme 5



2

7

7a, X=I
7b, X=Br

other hand, the yield of **7b** was 78%, and no polymer was detected.

This difference in yield of the adducts clearly suggests that these adducts can further react with **2**. Namely, **7a** reacts with **2** much faster than **7b** does, because the leaving ability of the iodide anion is higher than that of the bromide anion, leading to the formation of the polymer in the case of methyl iodide. That **7b** is fairly less electrophilic than benzyl bromide, whereas **7a** has a reactivity similar to that of methyl iodide, would also explain the formation of the polymer from methyl iodide and of the adduct from benzyl bromide as main products. Absence of an ether unit in these products was confirmed by the lack of a triplet ^{1}H NMR signal at 3.50 ppm assignable to methylene protons adjacent to the ether oxygen. Since the formation of these products strongly suggested that alkyl halide is capable of initiating the ring-opening polymerization of cyclic carbonate, cationic polymerizations of **2** with a few alkyl halides listed in Table 2 were carried out.

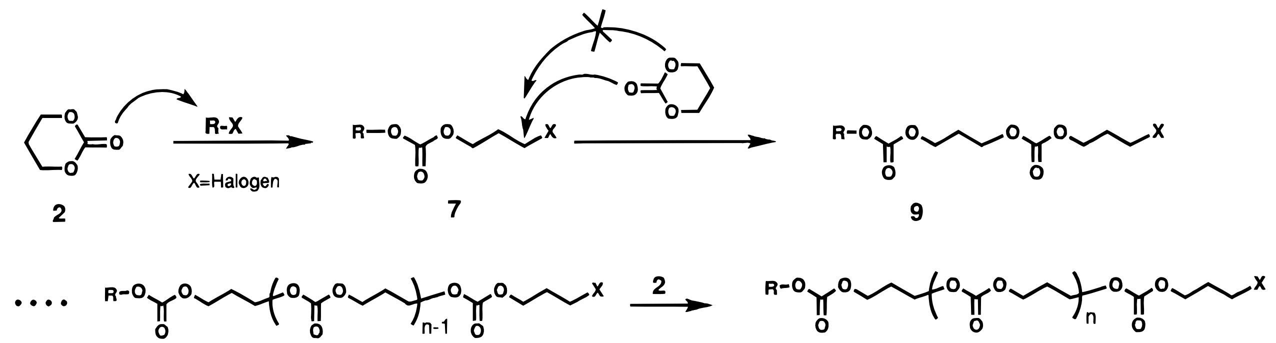
In the reaction of **2** with 20 mol % of alkyl halides (runs 2 and 9) at 120 °C without solvent, increase in viscosity of the reaction system was confirmed within 12−24 h. The final reaction mixture afforded highly viscous material with $\bar{M}_n$ 3000−5000, revealing the production of polymer. However at 100 °C, no polymer was obtained. In polar solvents such as nitrobenzene (NB) or benzonitrile (BN), fast and high conversion of monomer was observed and polymer was obtained, while in less polar solvent such as 1,1-dichloroethane (1,1-DCE), conversion of monomer was low (18%) (runs 3−8). Although there was no ether unit in most polymers, polymer obtained with NB contained 4−5% of ether unit. When benzyl bromide was employed as initiator, conversion of monomer was relatively low (runs 10 and 11, Table 2). Rate of polymerization initiated by benzyl and allyl iodides was higher than that by methyl iodide (runs 7, 12, and 13). This would be explained by highly efficient initiation in the case of benzyl iodide, as generally expected from the reactivity difference between methyl and benzyl groups. The high efficiency in the initiation may be supported by the polymer molecular weight being lower than that in the case of methyl iodide, since the structure of the propagation species is the same. Further, this result is consistent with those of reactions of **2** with excess alkyl halides as mentioned above.

Results of the cationic polymerizations of substituted cyclic carbonates with alkyl halides are shown in Table 3. Although corresponding polycarbonate having no ether unit was obtained from **5** by methyl iodide, no polymer was confirmed from **1** and **6** under similar conditions. Lack of polymerizability of **1** and **6** can be caused by extremely slow initiation and propagation reactions because of highly unfavorable nucleophilic substitution at the neopentyl position, i.e., sterically protected position.

Figure 5 shows typical examples of ^{1}H and ^{13}C NMR spectra of the polycarbonate derived from polymerization of **2** with benzyl bromide (Table 2, run 9) and can be compared with Figure 3. The assignment of the signals was performed using chemical shift data of a few model compounds for the expected terminal groups of the polymer, which are summarized in Table 4.

In the ^{1}H NMR, benzyl signals appeared as two singlets at 7.2 and 5.15 ppm which were based on the initiation terminal. Meanwhile, the end terminal group could be characterized by a triplet at 3.45 ppm which was assigned as the bromomethylene proton signal. The ^{13}C NMR data well supported the above assignments.

Scheme 6



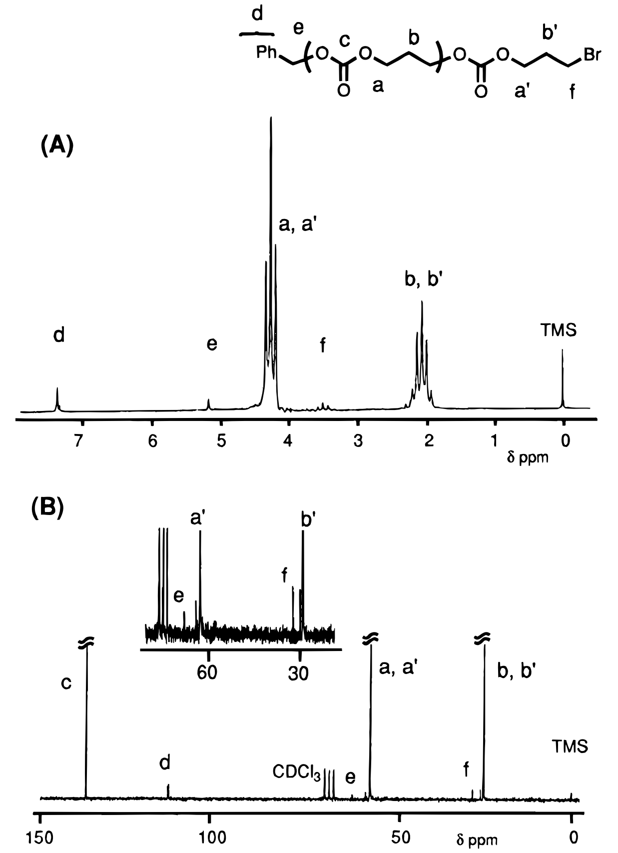
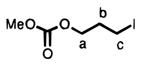
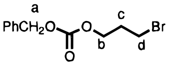
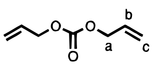


Figure 5. ^{1}H NMR (90 MHz) and ^{13}C NMR (22.5 MHz) spectra of poly **2** (Table 2, run 9, CDCl$_3$, 27 °C).

Table 4. NMR Chemical Shifts of Model Compounds of End Terminal Groups of Poly-2

	Proton signal (δ ppm)[a]				Carbon signal (δ ppm)[b)]			
	a	b	c	d	a	b	c	d
	4.24	2.10	3.21		66.5	27.1	31.4	
	5.20	4.28	2.19	3.45	69.4	65.6	29.0	31.7
	4.63	5.98	5.38 5.20		68.1	131.5	118.4	

[a] 90 MHz ^{1}H NMR, solvent: CDCl$_3$. [b] 22.5 MHz ^{13}C NMR, solvent: CDCl$_3$.

The terminal bromopropyl carbonate was confirmed in the ^{13}C NMR more cleanly than in the ^{1}H NMR, i.e., the signals a′ and b′ could be seen at 64 and 30 ppm, respectively. There was no signals around 67.0 ppm at which the carbon signal adjacent to ether oxygen appeared, but such signals could be observed in the case of polycarbonate obtained in the polymerization in nitrobenzene (Table 1, runs 4 and 5). In accordance with the clean NMR spectra, IR absorption at ca. 3500 cm^{-1} assignable to the OH group of the polycarbonate was much less than that of polycarbonate obtained by the methyl triflate-initiated polymerization (Table 1, run 1). Namely, an unstable terminal group (probably triflate ester) would be promptly changed to a hydroxy group through the workup process, whereas no such transformation took place in the case of the haloalkyl terminal group. Meanwhile, GPC analysis indicated incorporation of some UV-sensitive groups such as benzyl group in polymers in the case of allyl and benzyl halide-initiated polymerizations. This result also supports the polymer structure as assigned above.

As described above, the terminal structure of the polycarbonates obtained is considered as haloalkyl carbonate. Therefore, it is expected that the propagation end has the same structure. Haloalkyl carbonate structure can be formed firstly by the initial ring-opening reaction of the monomer with alkyl halide. To examine the structure of the propagating species, the polymerization of **2** with ethyl 3-iodopropyl carbonate (**7c**) was carried out in benzonitrile at 120 °C for 48 h. **7c** was prepared by the reaction of ethyl chloroformate with 3-bromo-1-propanol followed by halogen exchange reaction with sodium iodide. Polymer obtained in 63% yield by preparative HPLC separation showed both ethyl and iodopropyl groups in its ^{1}H NMR spectrum, indicating the proposed polymerization scheme (Scheme 6). Namely, **7c** is attacked by the monomer **2** at the iodomethylene carbon to afford biscarbonate (**9**) via the ring-opening of **2**, eventually yielding the corresponding polycarbonate which has both ethyl and iodopropyl groups (R = Et, X = I).

The fact that the polymerization with **7c** was faster than that with methyl iodide suggests that **7c** is more reactive than methyl iodide. If it is operative, the propagation reaction should be faster than the initiation reaction in the polymerization of **2** with methyl iodide. This is easily proved by the above-mentioned results of the reaction of **2** with excess methyl iodide where yield of the adduct is sufficiently low. Thus, from these results, halopropyl carbonate is suggested as the actual propagating species in the polymerization of **2** with alkyl halide.

It is known that generally alkyl halide, especially alkyl iodide, gradually decomposes to yield a halogen molecule such as iodine even at room temperature. Iodine is also able to initiate cationic polymerization of some cationically polymerizable monomers. When the polymerization of **2** was carried out with a catalytic amount of iodine (I$_2$), poly-**2** with a molecular weight much higher than that with alkyl halides was obtained in a short time (Table 1, run 10). The polymer contained 7% of ether unit but no iodomethylene group. Conse-

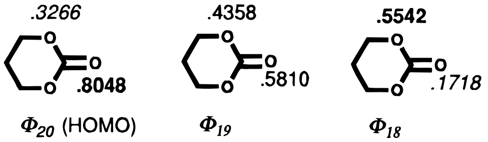


Figure 6. Coefficients of occupied MOs of **2**, calculated by MOPAC Ver. 6.02/PM3.

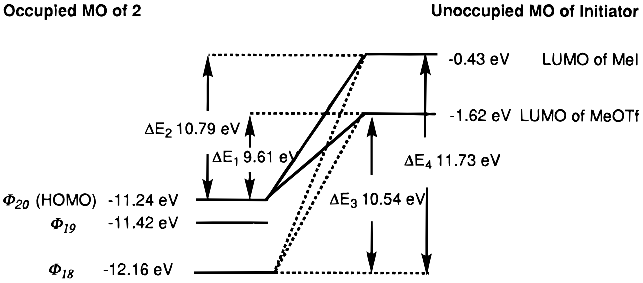


Figure 7. Levels of occupied MOs of **2** and LUMO of initiators, calculated by MOPAC Ver. 6.02/PM3.

quently, some influence of impurity such as iodine can be ruled out in the polymerization of alkyl iodide. Side reactions such as a back-biting reaction must occur in this polymerization, because molecular weight distribution is fairly large, especially in the case of polymerization in benzonitrile for a long time (96 h; Table 2, run 8), where 2.84 ($\bar{M}_w/\bar{M}_n$) and 1600 ($\bar{M}_n$) are compared with those of run 7 (48 h; $\bar{M}_w/\bar{M}_n$ 2.64, $\bar{M}_n$ 3000).

Consequently, if Scheme 2 is also operative in the present system, the polymerization of cyclic carbonate with alkyl halide should proceed through path a. Among the two possible propagation ends, covalent macrohalide (A) is favored more than carbenium species (B) owing to the high nucleophilicity of the halide anion. A similar propagation mechanism is reported in the ring-opening polymerization of oxazoline.[10]

In the polymerization with alkyl halide, path a completely predominates over path b according to the reactivity−selectivity rule, since the reactivity of the haloalkyl group is much less than that of alkyl triflate. This reactivity−selectivity could be explained by the results of the molecular orbital calculation. The levels of HOMO, second highest occupied MO (Φ_{19}), and third highest occupied MO (Φ_{18}) were calculated to be −11.24, −11.42, and −12.16 eV, respectively. The coefficients of HOMO of oxygen atoms of these orbitals are demonstrated in Figure 6. The largest coefficient in HOMO is localized in the carbonyl oxygen atom, while that of Φ_{18} is localized in the ether oxygen atom. Namely, LUMO of electrophiles such as methyl triflate interacts with HOMO of cyclic carbonate in the normal propagation reaction, whereas Φ_{18} should participate in the reaction containing decarboxylation. The differences in the energy level between HOMO including Φ_{18} and Φ_{19} and LUMO of the monomer and the initiators are shown in Figure 7. The band gap between F18 and LUMO of methyl iodide (ΔE_4) is 1.19 eV larger than that between Φ_{18} and LUMO of methyl triflate (ΔE_3). The calculated and experimental results suggested that ΔE_4 is too large to allow reaction between Φ_{18} and LUMO of methyl iodide, and therefore reaction of Φ_{20} with LUMO of methyl iodide selectively proceeds.

Thus, nucleophilic attack of monomer at the halomethyl carbon of the propagating species and/or initiator alkyl halide takes place by the carbonyl oxygen rather than ether oxygen, eventually yielding polycarbonate without the ether unit. Meanwhile, occurrence of partial decarboxylation in the polymerization of **2** in nitrobenzene might be explained by assuming that high solvent polarity assists the formation of the carbenium ion species (B) which can undergo partial nucleophilic attack along path d (Scheme 1) causing decarboxylation, but the degree of such attacking should be lower than that in the case of methyl triflate.

Volume Change on Polymerization. Since cationic polymerization of cyclic carbonates by alkyl halide cleanly afforded the corresponding polycarbonates, volume expansion on polymerization is expected like in the case of anionic polymerization.[7] The density of **2**, **5**, and their corresponding polymers obtained in Tables 2 (run 2) and 3 (run 3) was measured. By the calculation from the density data as shown in the Experimental Section, 3.5% volume expansion was observed in the cationic polymerization of **2**. Further, in the case of **5**, 1.8% volume expansion was also observed. We have reported 3.4% volume expansion on anionic polymerization of **1**;[7] it can be suggested that ring-opening polymerization of cyclic carbonate is accompanied by volume expansion independent of the polymerization mode.

Conclusion

Alkyl halide was demonstrated to be an effective initiator for cyclic carbonate polymerization which would control the decarboxylation observed usually in the cationic ring-opening polymerization of cyclic carbonate with common acid catalysts. Further, cyclic carbonates were found as novel expandable monomers upon not only anionic but also cationic polymerization. Cationic ring-opening polymerization of cyclic carbonate without decarboxylation achieved by this study will be extensively investigated, in comparison with Kricheldorf's results.[5]

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