Cationic Ring-Opening Polymerization of an Exomethylene Group Carrying Cyclic Carbonate. Pseudo-Living Polymerization of 5-Methylene-1,3-dioxan-2-one by the Assistance of the Exomethylene Group

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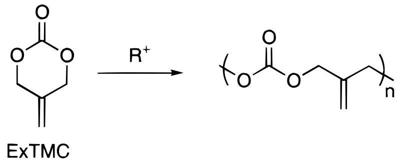
ABSTRACT: Cationic ring-opening polymerization of a cyclic carbonate carrying an exomethylene moiety, 5-methylene-1,3-dioxan-2-one (ExTMC), was carried out, and its behavior was compared with a cyclic carbonate having no exomethylene group, 1,3-dioxan-2-one (TMC). ExTMC afforded the polymers with larger molecular weights than TMC under any conditions. The observed molecular weights of the polymers agreed well with the calculated ones in the polymerization of ExTMC with TfOH at 0 °C. A linear relationship was observed between the conversion and number-average molecular weight of the polymer obtained in the polymerization of ExTMC, which could not be observed in the polymerization of TMC. After ExTMC was completely converted, the polymerization took place again when the same amount of ExTMC was introduced into the polymerization mixture. The effect of the exomethylene group on the polymerization behavior was analyzed by an ab initio molecular orbital calculation to determine the possibility of the presence of an allylic cationic intermediate. It was suggested that the stabilization of the propagating cation by the exomethylene group caused the living character of the cationic polymerization of ExTMC. Furthermore, a block copolymer of ExTMC with a vinyl ether was synthesized as an application of the pseudo-living polymerization of ExTMC.

Introduction

Ring-opening polymerization can introduce functional groups into the main chains of polymers that cannot be attained by vinyl polymerization. Ring-opening polymerization usually involves less shrinkage in volume than common vinyl polymerization, polyaddition, and polycondensation.[1] Cyclic carbonates undergo ring-opening polymerization, both with cationic and with anionic initiators, and show volume expansion during the polymerization. This volume expansion can be accounted for by the difference in strength of the intermolecular interaction between the monomers and polymers. That is, strong interaction in the monomers and weak interaction in the polymers eventually cause the volume expansion.[2] Six-membered cyclic carbonates efficiently undergo ring-opening polymerization to yield the corresponding linear polycarbonates, especially under anionic conditions.[3] Under cationic conditions, the polymerization commonly accompanies the partial elimination of carbon dioxide to afford linear polycarbonates containing an ether unit.[4] It is important to develop a cationic polymerization system without decarboxylation, because the elimination of some small molecules during the polymerization spoils the characteristic nature of cyclic carbonates as a novel expanding monomer. Kricheldorf et al. have recently reported that tin tetraiodide[5] and butyltin chlorides[6] polymerize a six-membered cyclic carbonate, 1,3-dioxan-2-one (TMC), to afford the high-molecular-weight polycarbonate without accompanying decarboxylation. We have recently reported the cationic ring-opening polymerization of cyclic carbonates with alkyl halide initiators to yield ether unit-free polycarbonates by suppression of decarboxylation.[7] We have also reported that a cyclic carbonate carrying an exomethylene group, 5-methylene-1,3-dioxan-2-one (ExTMC), can undergo cationic polymerization to afford the corresponding polycarbonate without decarboxylation (Scheme 1).[8] This may be explained by the stabilization of the propagating cationic end by the exomethylene group. If this assumption is operative, living cationic ring-opening polymerization of ExTMC may presumably proceed by controlling the propagating end with the exomethylene (allyl) group. This paper deals with the possibility of living cationic polymerization of ExTMC.

Scheme 1



Experimental Section

Measurements. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL EX-400 spectrometer using tetramethylsilane (TMS) or phosphoric acid as an internal or external standard in chloroform-*d* ($CDCl_3$). Number-average molecular weights (M_n) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system equipped with a polystyrene gel column (Tosoh TSK gel G3000H) and ultraviolet and refractive index detectors using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min observed by polystyrene calibration at 30 °C.

Materials. Boron trifluoride etherate ($BF_3 \cdot OEt_2$), methyl trifluoromethanesulfonate (TfOMe), methyl methanesulfonate, trifluoromethanesulfonic acid (TfOH), methyl iodide (MeI), trifluoroacetic acid (TFA), dichloromethane (CH_2Cl_2), and

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Table 1. Cationic Polymerization of ExTMC and TMC[a]

run	monomer	init	solv	temp (°C)	time (h)	conv[b] (%)	yield[c] (%)	M_n[d]	M_w/M_n[d]
1	ExTMC	TfOMe	CH_2Cl_2	20	48	99	94	3000	1.29
2	ExTMC	TfOH	CH_2Cl_2	20	48	99	93	21200	1.28
3	ExTMC	TfOH	CH_2Cl_2	0	48	99	94	11800	1.20
4	ExTMC	TfOH	CH_2Cl_2	−10	48	56	48	8800	1.13
5	ExTMC	TfOH	CH_2Cl_2	−10	168	98	96	9900	1.21
6	ExTMC	$BF_3{\cdot}OEt_2$	PhCl	60	48	97	81	3200	2.62
7	ExTMC	$BF_3{\cdot}OEt_2$	CH_2Cl_2	20	48	68	63	15900	1.58
8	ExTMC	$BF_3{\cdot}OEt_2$	CH_2Cl_2	0	48	3	5	7700	1.10
9	ExTMC	$BF_3{\cdot}OEt_2$	CH_2Cl_2	0	168	9	6	7800	1.11
10	ExTMC	MeI	PhCl	100	48	1	1	4300	1.14
11	ExTMC	MeI	CH_2Cl_2	20	48	8	7	4600	1.20
12	ExTMC	CH_3SO_3Me	PhCl	100	48	6	7	6700	1.15
13	ExTMC	CH_3SO_3Me	CH_2Cl_2	20	48	1	1	6300	1.12
14	ExTMC	TFA	CH_2Cl_2	20	48	1	3	4700	1.20
15	TMC	TfOMe	CH_2Cl_2	20	48	84	70	1100	1.52
16	TMC	TfOH	CH_2Cl_2	20	48	97	94	9600	1.24
17	TMC	TfOH	CH_2Cl_2	0	48	60	70	5400	1.10
18	TMC	$BF_3{\cdot}OEt_2$	CH_2Cl_2	20	48	47	46	8800	1.45
19	TMC	MeI	CH_2Cl_2	20	48	1	2	1300	1.04
20	TMC	CH_3SO_3Me	CH_2Cl_2	20	48	1	6	2200	1.16
21	TMC	TFA	CH_2Cl_2	20	48	2	1	1000	1.27

[a] Conditions: monomer concentration, 2 M; initiator, 1 mol %. [b] Determined by ^1H NMR. [c] Ether-insoluble part. [d] Estimated by GPC.

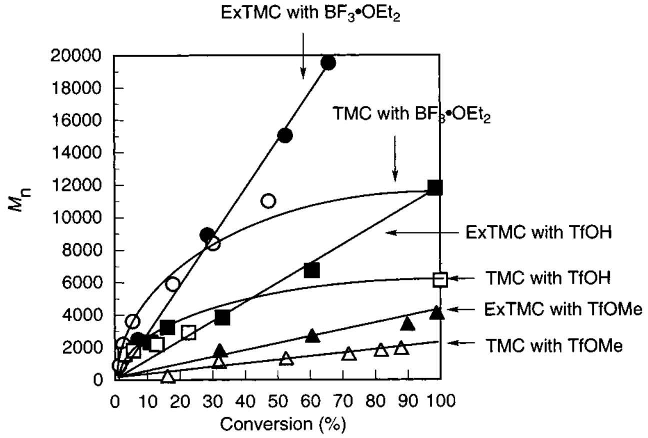


Figure 1. Relationships between the conversion and M_n in the cationic polymerization of ExTMC and TMC. Conditions: initiator, 1 mol %; initial monomer concentration, 2 mol/L in CH_2Cl_2; temperature, 20 °C with $BF_3{\cdot}OEt_2$ and TfOMe and 0 °C with TfOH.

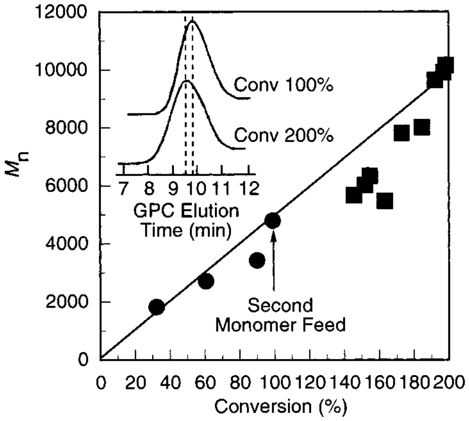


Figure 2. Relationship between the conversion and M_n in the cationic polymerization of ExTMC. After the quantitative consumption of ExTMC in the first stage, the same amount of ExTMC was added to the polymerization mixture. Conditions: TfOMe, 1 mol %; initial monomer concentration, 2 mol/L in CH_2Cl_2; temperature, 20 °C.

chlorobenzene (PhCl) were distilled over phosphorus pentoxide before use. ExTMC and 1,3-dioxan-2-one were synthesized according to the reported method.[8]

Cationic Polymerization: Typical Procedure. All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a stream of dry nitrogen. To a solution of 0.2 g (1.7 mmol) of ExTMC in 2 mL of CH_2Cl_2 was added 3.1 μL (1 mol %) of TfOH at 0 °C. After the reaction mixture was stirred at 0 °C for 48 h, a few drops of pyridine were added to the reaction mixture to quench the polymerization. The polymerization mixture was evaporated under vacuum and diluted with 4 mL of chloroform. The mixture was poured into 120 mL of ether to precipitate a polymer. A colorless gummy solid was collected by decantation quantitatively. ^1H NMR δ (400 MHz, $CDCl_3$): 5.37 (s, 2H), 4.68 (s, 4H). ^{13}C NMR δ (100 MHz, $CDCl_3$): 149.6, 135.7, 123.8, 67.6 ppm.

Molecular Orbital (MO) Calculation. The MO calculation was done on a Silicon Graphics Indigo2 IMPACT 10000 with the use of Gaussian 94. Geometries were fully optimized by the HF/STO-3G basis set, followed by a single-point calculation with the HF/3-21G** basis set.

Results and Discussion

As described in the Introduction, we have previously designed the cationic polymerization of ExTMC to obtain the polymer without the elimination of carbon dioxide.[8] In this work, we describe the possibility of living cationic polymerization of ExTMC. Table 1 summarizes the results and conditions of the cationic polymerization of ExTMC with several cationic initiators at −10 to +100 °C in CH_2Cl_2 and PhCl, along with the results of a six-membered nonsubstituted cyclic carbonate, TMC. The activity of the initiator decreased in the order TfOMe, TfOH > $BF_3{\cdot}OEt_2$ > MeI, CH_3SO_3Me, TFA, judged by the monomer conversion. ExTMC quantitatively converted at 20 °C both with TfOMe (run 1) and TfOH (run 2). In the former case, the M_n of the polymer was lower than that expected by the monomer–initiator ratio ($114 \times 100 = 11\,400$). Although the M_n of the polymer obtained with TfOH at 20 °C (run 2) was larger than that at 0 °C (run 3), the former polymer showed a bimodal GPC peak. In the polymerization with TfOH at −10 °C (run 4), ExTMC did not convert quantitatively. It seemed that the polymerization of ExTMC was the most satisfactory in the conditions in run 3 concerning the conversion, molecular weight, and polydispersity ratio. $BF_3{\cdot}OEt_2$ also achieved quantitative conversion of ExTMC at 60 °C in chlorobenzene (run

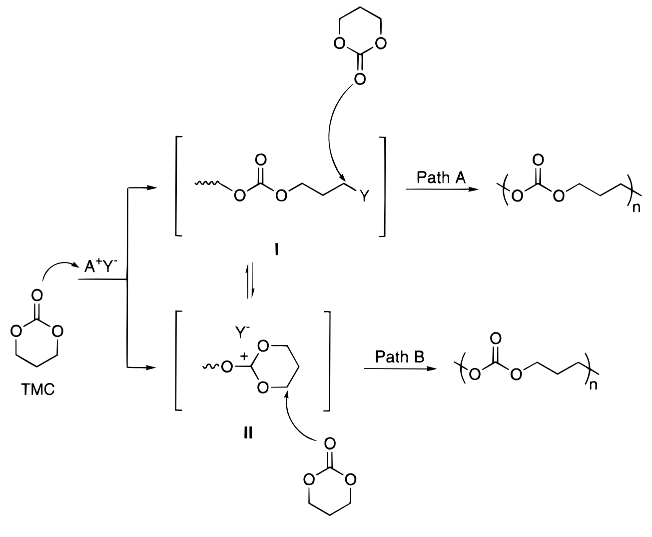
6) instead of a lower M_n (3200) and a larger polydispersity ratio (1.58). The initiator activities of MeI and CH_3SO_3Me were extremely low even at 100 °C (runs 10 and 12). Comparing the conversions and molecular weights in the polymerizations of ExTMC and TMC in the same conditions, it was concluded that the monomer reactivity of ExTMC was larger than that of TMC. These results could be supported by the relationships between the conversion and M_n in the polymerizations of the two monomers under a number of conditions as illustrated in Figure 1, which also suggested the living character of the polymerization of ExTMC. $BF_3{\cdot}OEt_2$ tended to afford the polymer with a larger M_n than TfOMe and TfOH did, which agreed with the result in the polymerization of 5,5-dimethyl-1,3-dioxan-2-one.[4a]

A second monomer feed experiment was carried out to elucidate the living character of the polymerization of ExTMC. Figure 2 depicts the relationship between the conversion and M_n in the polymerization of ExTMC at the first and second stages with 1 mol % of TfOMe in CH_2Cl_2 (monomer concentration 2 M) at 20 °C. After the complete consumption of ExTMC, the polymerization took place again when the same amount of ExTMC was introduced into the reaction mixture. The M_n of the obtained polymer increased in direct proportion to the monomer conversion even in the second stage of the polymerization.

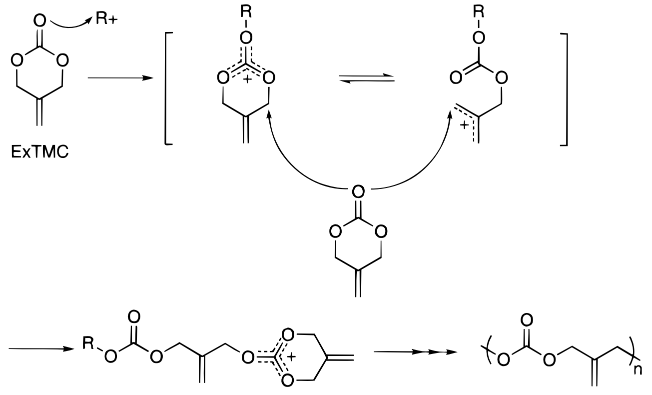
Furthermore, end-capping of the propagating polymer was carried out with triphenylphosphine. After the polymerization was carried out with TfOH for 48 h, 10 equiv of triphenylphosphine was added into the polymerization mixture. The polymer end structures were analyzed by ^1H and ^{31}P NMR spectroscopy. In the case of ExTMC, the monomer conversion was 97%, and the degree of polymerization was 93, which was calculated by the NMR integration ratio between the phenyl protons derived from triphenylphosphine capped at the polymer end and the protons of the polymer main chain. The degree of polymerization calculated by GPC was 77, which agreed with the value calculated by NMR spectroscopy. Meanwhile, TMC showed about half of the values compared with those of ExTMC concerning the conversion, degree of polymerization, and molecular weight of the polymer. Capping with triphenylphosphine at the polymer end was also confirmed by the presence of phosphonium signals at 21 and 24 ppm in the ^{31}P NMR spectra of the polymers obtained from ExTMC and TMC, respectively.

Comment on the Polymerization Mechanism. Kricheldorf et al. have proposed a mechanism of cationic polymerization of cyclic carbonates with TfOMe (A^+Y^-).[4b] On the basis of NMR spectroscopic analysis, they have reported that the propagating species consists of a mixture of two species, an alkyl triflate ester (**I**, Y = TfO) and a trialkyl carbenium triflate (**II**, Y = TfO), showing an equilibrium in the each other (Scheme 2). In the cationic polymerization of ExTMC, participation of an allyl cationic species is expected, which stabilizes the cationic charge by delocalizing the entire molecule as illustrated in Scheme 3. Consequently, stabilization of the propagating end by allyl cation would enable the living polymerization of ExTMC.

Scheme 2



Scheme 3



The possibility of the participation effect of the exomethylene group on the polymerization is examined by the molecular orbital calculation. Figure 3 illustrates the energy profile diagrams of the cationic ring-opening reaction of ExTMC and TMC with methyl cation calculated by the ab initio method. The formation of trialkyl carbenium ions was exothermic in 98.1 and 100.9 kcal/mol, and the energy differences between the initial states and the ring-opened cations were 66.1 and 36.5 kcal/mol in the cases of ExTMC and TMC, respectively. The generated cation by ring-opening of ExTMC should be much more stabilized than that from TMC due to the contribution of the conjugation effect by the allyl cationic structure.

When the leaving ability of the counteranion was larger, such as for the triflate anion, it is more plausible that the ring-opening process proceeds with attack by another monomer, because the ring-opened cation is less stable than the trialkylcarbenium ion.[4b,7b] However, participation of an allyl cationic species is somewhat expected, which stabilizes the cationic charge by delocalizing the entire molecule as illustrated in Scheme 3. Consequently, stabilization of the propagating end by the allyl cation might drive the living character. Figure 4 illustrates the highest occupied molecular orbitals (HOMOs) of ExTMC and TMC calculated by the ab initio method. The HOMO of ExTMC involves both the carbonate and exomethylene groups, which supports the possibility of delocalization of the cationic charge throughout the $R^+{-}$ExTMC molecule.

We have recently reported that the rate of cationic polymerization of a seven-membered cyclic carbonate, 1,3-dioxepan-2-one (7CC), was 100 times larger compared with that of TMC.[9] This would be explained by the smaller activation energy of the polymerization, which might be caused by the larger ring strain of the

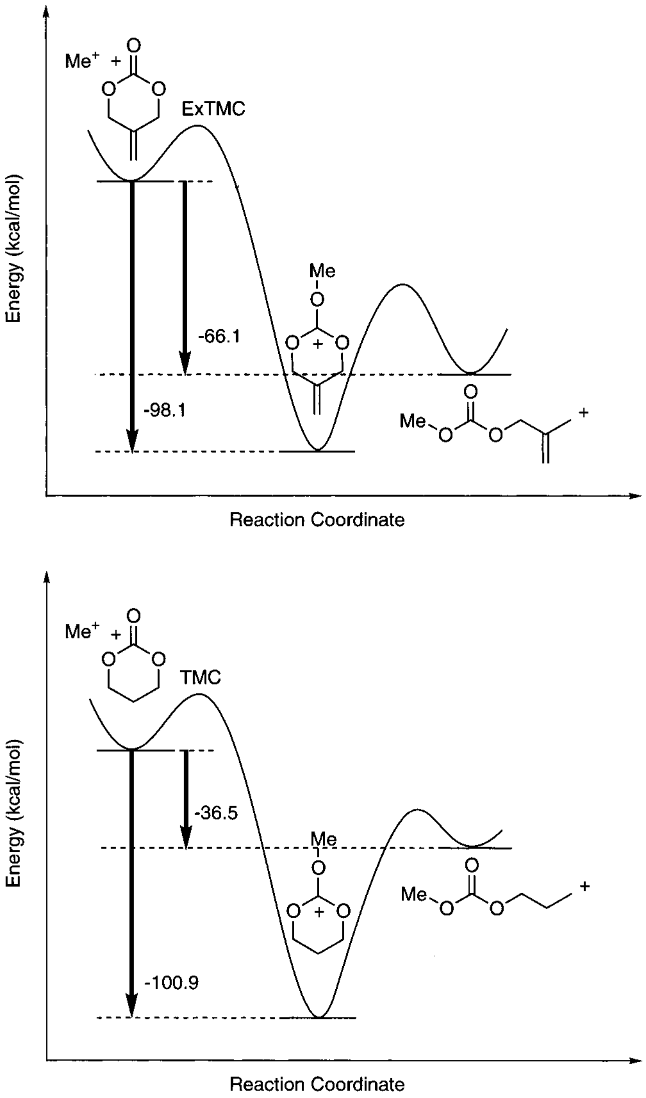
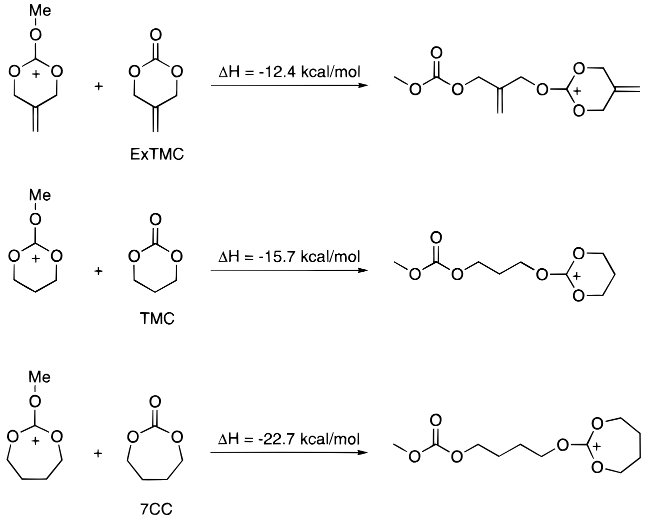


Figure 3. Energy profile diagrams of the cationic ring-opening reaction of ExTMC and TMC calculated by Gaussian 94, HF/3-21G** basis set.

Scheme 4



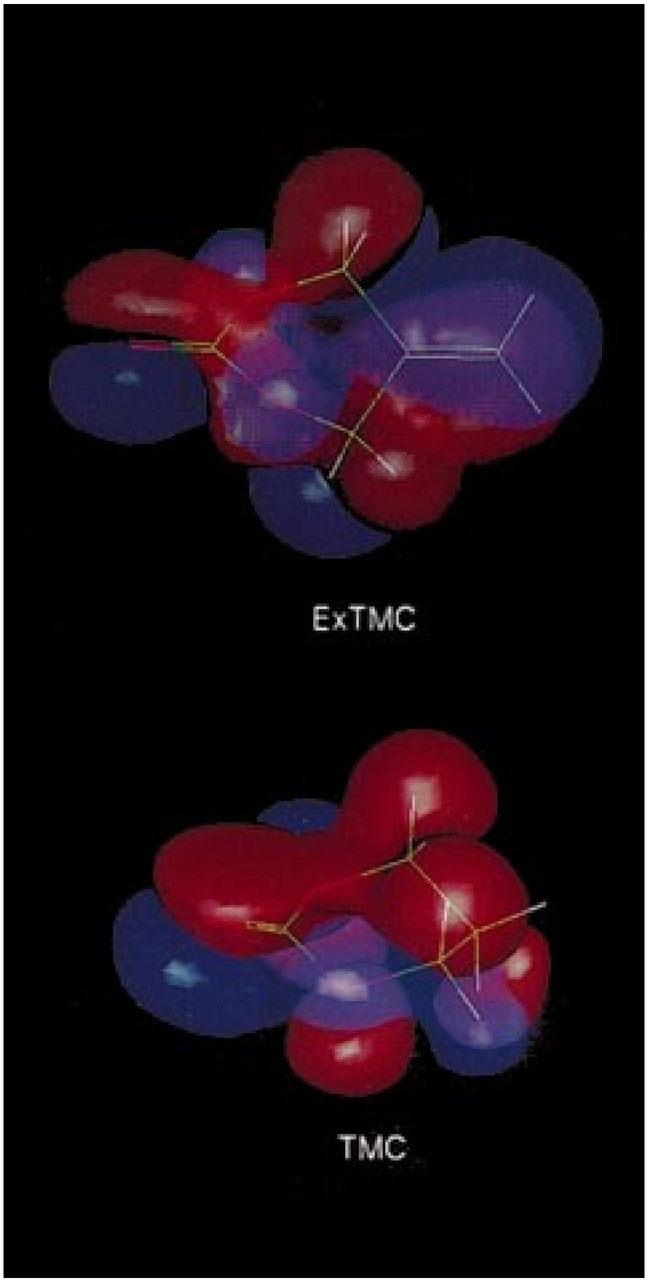


Figure 4. Highest occupied molecular orbitals (HOMOs) of ExTMC and TMC calculated by Gaussian 94, HF/3-21G** basis set.

seven-membered ring than that of the six-membered one. We have calculated the ring strain of ExTMC and TMC along with 7CC to examine the effect on the polymerization behavior. The ring strains of the monomers were estimated by the energy differences between the dimeric trialkyl carbenium ions, monomers, and monomeric trialkyl carbenium ions as shown in Scheme 4. The ΔHs of ExTMC, TMC, and 7CC were −12.4, −15.7, and −22.7 kcal/mol, respectively. The much smaller ΔH in the ring-opening reaction of 7CC than that of TMC agrees with the smaller activation energy of the cationic polymerization of the former than that of the latter, which confirms the large ring strain of the seven-membered ring. On the other hand, the ΔH for the ring-opening reaction of ExTMC was even smaller than that of TMC, suggesting that only the ring strain is not the main factor for the large polymerizability of ExTMC.

Block Copolymerization of ExTMC with a Vinyl Ether. Block copolymers have been paid much attention in the field of precisely controlled polymer synthesis. Higashimura and Sawamoto et al. have reported the

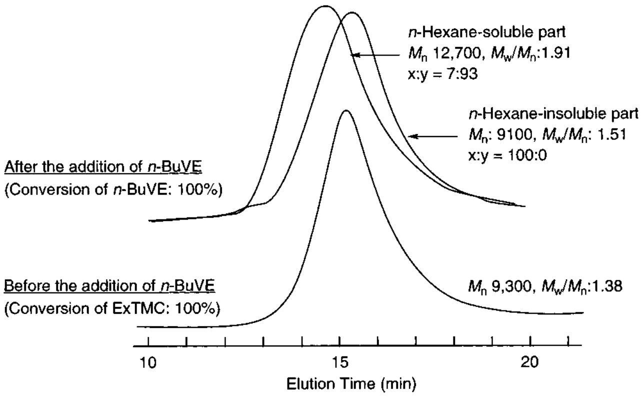
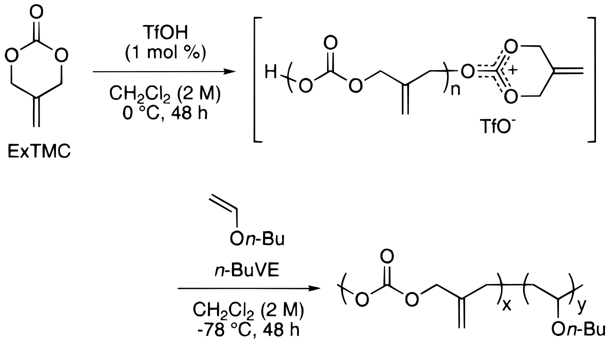


Figure 5. GPC profiles before and after the addition of *n*-butyl vinyl ether into the polymerization mixture of ExTMC. Conditions: TfOH, 1 mol %; initial monomer concentration, 2 mol/L in CH_2Cl_2; temperature, 0 °C. *n*-Butyl vinyl ether was added 48 h after the polymerization of ExTMC had been initiated, followed by stirring for 48 h at −78 °C.

Scheme 5



synthesis of block copolymers of vinyl ethers with styrene derivatives by sequential living cationic polymerizations with a hydrogen iodide−zinc halide initiating system.[10] We have reported the block copolymerization of a cyclic carbonate with oxetanes in one-shot feeding, where the oxetanes reacts much faster than the cyclic carbonate with the propagating species. The cyclic carbonate reacts slowly but sufficiently with the propagating species of the oxetane after most oxetane molecules are consumed to lead the block copolymer.[11] In this work, we have challenged the block copolymerization of ExTMC with a vinyl ether; a unique block copolymerization of a cyclic monomer with a vinyl monomer (Scheme 5). After the polymerization of ExTMC was carried out with TfOH at 0 °C for 48 h, *n*-butyl vinyl ether was added into the polymerization mixture at −78 °C to obtain a block copolymer of ExTMC with *n*-butyl vinyl ether. Figure 5 illustrates the GPC profiles before and after the addition of the vinyl ether. The M_n of the polymer was 9300 before the addition of the vinyl ether. After the addition of the vinyl ether, the corresponding block copolymer with an increased molecular weight (M_n 12 700) was obtained, which was soluble in *n*-hexane. The ratio between the carbonate unit and the vinyl ether unit was 7:93. Although the efficiency of block copolymerization was not so high, we could obtain a novel block copolymer consisting of polycarbonate and polyvinyl ether units.

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