Communications to the Editor

Cationic Polymerization Behavior of 1,3,2-Dioxathiepane 2-Oxide: First Cationic Ring-Opening Polymerization of Cyclic Sulfite

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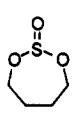
Cyclic monomers that undergo ring-opening polymerization are important in the field of precision materials, adhesives, and so on, since they show lower shrinkage or sometimes expansion in volume on polymerization. In these 20 years, we have proposed several oxabicyclic and oxaspirocyclic monomers such as spiroorthoesters,[1] bicycloorthoesters,[2] and spiroorthocarbonates[3] that can be expected to show no shrinkage or some expansion in volume on double ring-opening polymerization.[4] Recently, a new type of monomer that undergoes ring-opening polymerization to show volume expansion on polymerization has been developed. Cyclic carbonates can undergo single ring-opening polymerization to show as large as 10% volume expansion in both cationic and anionic polymerizations (Scheme 1).[5] The evaluation of dipole moments of the monomers and polymers calculated by the molecular orbital method suggested the mechanism of volume expansion of cyclic carbonates. Namely, this volume expansion would be caused by the difference of large intermolecular interaction of the monomer and small intermolecular interaction of the polymer.[6]

In the course of the study on the polymerization of cyclic carbonates, we have designed another new candidate of expandable monomer, cyclic sulfite. Cyclic sulfite might be expected to show volume expansion since the sulfite moiety has large polarity[7] similar to the carbonate moiety. Cyclic sulfite has been studied as an interesting compound to have axial–equatorial conformation isomers;[7,8] however, the polymerization behavior has not been reported so far. In this paper the first cationic polymerization of a seven-membered cyclic sulfite, 1,3,2-dioxathiepane 2-oxide (**1**), is disclosed.



1

The monomer **1** was prepared from thionyl chloride and 1,4-butanediol in 51% yield according to the reported method.[9] The cationic polymerization of **1** with methyl trifluoromethanesulfonate (TfOMe) as an initiator was carried out at 0, 25, or 60 °C in bulk under a nitrogen atmosphere. After quenching the polymerization by the addition of pyridine, the polymer was isolated as a pale brown viscous oil by reprecipitation with diethyl ether. The results and conditions of the polymerization of **1** are summarized in Table 1. The conversion monitored by ^{1}H NMR was nearly equal to the yield of the polymer. The conversion of **1** increased as the polymerization temperature and time increased. The molecular weight of the polymer obtained in the polymerization within 24 h was 8000–10 400 at any temperature (runs 1–3 and 5) with 42–66% conversion. Meanwhile, the polymerization at 60 °C for 72 h proceeded quantitatively to afford a polymer with lower molecular weight (run 4).

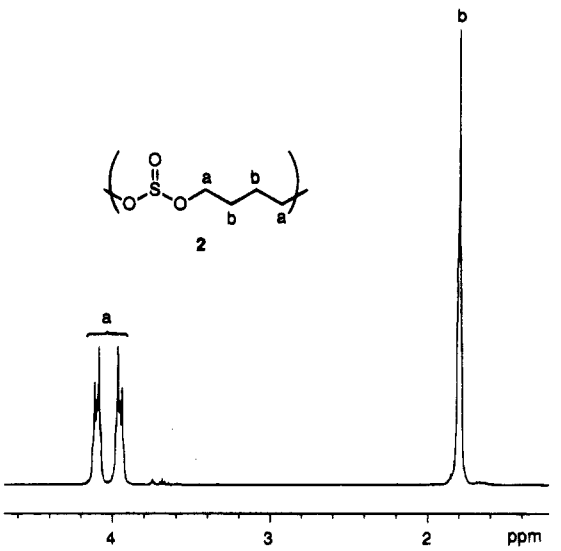
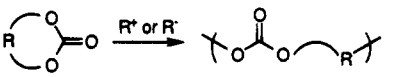


Figure 1. ^{1}H NMR spectrum of poly(sulfite) **2** (solvent, $CDCl_3$; 400 MHz, run 2 in Table 1).

Table 1. Cationic Polymerization of 1

run	TfOMe (mol %)	temp (°C)	time (h)	conv[a] (%)	yield[b] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	content of unit **3**[a] (%)
1	1	0	24	48	44	9300 (1.87)	0
2	1	25	3	52	49	10400 (1.84)	0
3	1	60	3	66	55	8600 (1.89)	5
4	1	60	72	100	8	1000 (1.21)	100
5	5	25	3	42	38	8000 (1.76)	0

Scheme 1



The structure of the polymer obtained in the polymerization at 25 °C (run 2 in Table 1) was examined by ^{1}H and ^{13}C NMR and IR spectra besides elemental analysis.[10] In the ^{1}H NMR spectrum (Figure 1), two signals around 4 ppm assignable to the methylene protons α to the sulfite moiety and a signal at 1.8 ppm assignable to the methylene protons β to the sulfite moiety were observed. The split of the signal around 4

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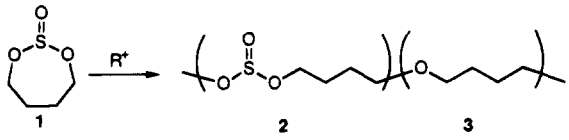
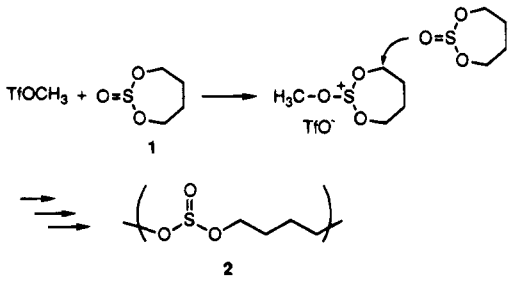
Scheme 2



Scheme 3



ppm should be caused by the "pseudoasymmetry" of the sulfur atom. In the ^{13}C NMR spectrum of the polymer, two signals at 61.6 and 26.0 ppm assignable to the methylene protons α and β to the sulfite moiety, respectively, were observed. The ^{1}H and ^{13}C NMR spectra of the polymer were nearly the same as those of **1**, although the polymer showed slightly broad signals. In the transformation from **1** to polymer, the signal of lower field methylene protons α to the sulfite moiety in the ^{1}H NMR spectrum of the polymer was shifted to the higher field by 0.35 ppm, and the signal of β-methylene protons was shifted to the higher field by 0.07 ppm than those of **1**, respectively. The signals of methylene carbons α and β to the sulfite moiety in the ^{13}C NMR spectrum of the polymer were similarly shifted to the higher field by 2.6 and 2.5 ppm than those of **1**, respectively. In the IR spectrum of the polymer, the absorption derived from $\nu_{S=O}$ was observed at 1200 cm^{-1}, which was slightly lower (2 cm^{-1}) than that of **1**. Therefore, the structure of the obtained polymer was determined as **2**, which was undoubtedly formed by ring-opening polymerization of **1** (Scheme 2). Meanwhile, the polymer obtained in the polymerization at 60 °C (run 3 in Table 1) was confirmed to have poly(ether) unit **3** as well as **2**, since a signal at 3.40–3.46 ppm in the ^{1}H NMR spectrum assignable to the methylene protons adjacent to the ether oxygen was observed. The content of unit **3** was determined to be 5% from the integration ratio.[11] Unit **3** should be formed by desulfoxylation of the polymer similar to the decarboxylation in the cationic polymerization of cyclic carbonates.[12] The content of unit **3** in the polymer obtained in the polymerization at 60 °C for 72 h was 100% (run 4), which should be related to the lower molecular weight of the polymer as described above.

The plausible mechanism of the polymerization of **1** is proposed as shown in Scheme 3. The trioxosulfonium cation formed by the addition of TfOMe to the monomer is attacked by another monomer, and subsequently by cleavage of the carbon–oxygen bond, and then alkylation of exocyclic oxygen of monomers will proceed. Consequently, poly(sulfite) **2** can be formed by the successive reactions. The formation of the trioxosulfonium cation was examined by the reaction of **1** with a 1.1 equimolar amount of TfOMe in deuteriochloroform at 25 °C for 24 h. In the ^{1}H NMR spectrum of the reaction mixture (Figure 2), signals assignable to the methylene protons α and β to the trioxosulfonium cation moiety were clearly observed at 4.92 and 2.50 ppm, respectively. The similar polymerization mechanism of

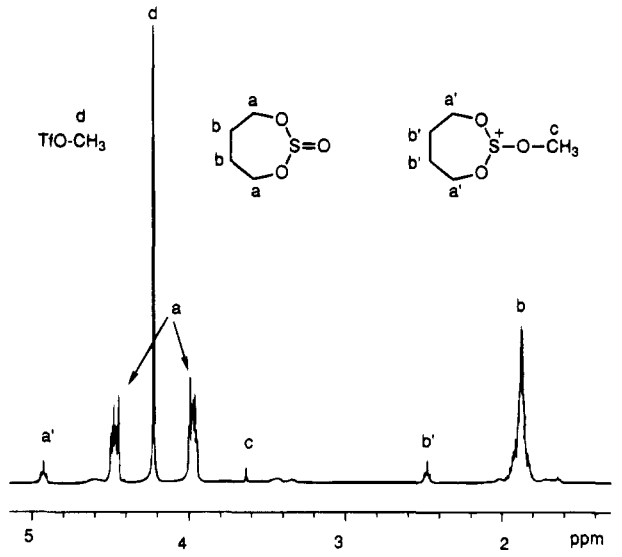


Figure 2. ^{1}H NMR spectrum of the reaction mixture prepared from **1** and TfOMe (molar amount of ratio 1:1.1) in $CDCl_3$ at 25 °C for 24 h (400 MHz).

cyclic carbonate through trioxocarbenium cation has been reported by Kricheldorf *et al.*[13]

The volume change during the polymerization of **1** was evaluated from the densities of **1** and the polymer measured by the density gradient tube method at 25 °C using a lithium bromide solution as a density gradient liquid. The density of **1** was 1.256, which was as large as those of cyclic carbonates as expected.[5b,d] The density of the polymer obtained in run 2 in Table 1 was 1.313. Consequently, **1** showed 4.54% shrinkage on polymerization differently from cyclic carbonates. Large intermolecular interaction between monomers as well as polymers should cause this unexpected result.

T_g and 5% weight loss temperature under a nitrogen atmosphere of the polymer (run 2 in Table 1) were −67 and +152 °C, respectively. Poly(sulfite) is amorphous since no T_m was observed.

In conclusion, the first cationic polymerization of the seven-membered cyclic sulfite 1,3,2-dioxathiepane 2-oxide (**1**) has been demonstrated. The cationic polymerization of **1** efficiently proceeded with complete ring opening to afford the corresponding linear poly(sulfite) (**2**) without any side reaction. The polymerization was suggested to proceed through trioxosulfonium cation. The desulfoxylation was confirmed in the polymerization at 60 °C, while the monomer conversion was higher than the polymerizations at 0 and 25 °C. The volume shrinkage during the polymerization of **1** was 4.54%. Further studies on the relationship between the ring number of cyclic sulfite and the polymerization behavior, mechanistic aspects on desulfoxylation, and so on are now under investigation.

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(10) Anal. Calcd for $C_4H_8SO_3$: C, 35.28; H, 5.92; S, 23.55. Found: C, 35.69; H, 6.13; S, 23.25 (run 2 in Table 1).

(11) The content of unit **3** was determined to be 6% from the elemental analysis of the polymer.

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