Cationic Polymerization of Seven-Membered Cyclic Sulfites. Substituent Effect on the Polymerization Behavior

Natsuhiro Azuma, Fumio Sanda, Toshikazu Takata,† and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Received July 18, 1997; Revised Manuscript Received January 12, 1998

ABSTRACT: The syntheses and cationic polymerizations of seven-membered cyclic sulfites having phenyl (7PhCS), benzo (7BnCS), and cyclohexane (7CyCS) groups were examined. 7PhCS and 7CyCS underwent complete elimination of SO_2 to afford the corresponding tetrahydrofuran derivatives under the cationic conditions. On the other hand, 7BnCS underwent cationic polymerization in the presence of cationic initiators such as TfOH, TfOMe, $SnCl_4$, TsOMe, and MeI in bulk or chlorobenzene to afford the corresponding polymer with $\bar{M}_n$ 950−8700 without desulfoxylation. The benzo group was operative for polymerization and suppression of desulfoxylation. The polymerization of 7BnCS did not show equilibrium character. The steric hindrance of the benzene ring might be effective to suppress a back-biting reaction. The volume expansion during the polymerization of 7BnCS was 8.57%. This might be caused by the larger dipole−dipole interactions between the monomers and smaller ones between the polymers.

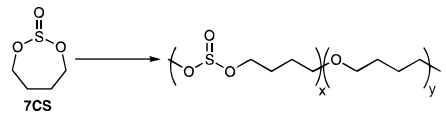
Introduction

Cyclic sulfites have been recently found to undergo cationic ring-opening polymerization. Their polymerization behavior depended on the ring size, initiator, and temperature.[1] Cationic polymerization of a seven-membered cyclic sulfite (7CS) with trifluoromethanesulfonate (TfOMe) at 60 °C affords a poly(sulfite) containing an ether unit, which is derived from desulfoxylation.[1a,b] On the other hand, the corresponding poly(sulfite) can be obtained by the cationic polymerization of 7CS with MeI at 60 °C without accompanying the desulfoxylation (Scheme 1).[1a,b]

The desulfoxylation during the polymerization may be explained by the stability of the propagating polymer end, in which there is an equilibrium between a sulfonium cation and a covalent species. The ratio of the sulfonium cation to the covalent species is larger in the case of TfOMe, while the ratio of the covalent species to the sulfonium cation is larger in the case of MeI.[1] It may be suggested that the desulfoxylation is difficult to proceed from the less reactive propagating polymer end generated by MeI. Thus, if some substituents were introduced into a cyclic sulfite to stabilize the propagating end, desulfoxylation would be suppressed during the polymerization.

As we have previously reported, cyclic carbonates undergo volume expansion during the polymerization and its mechanism may be explained by the difference between the large intermolecular interactions of the monomers and the small intermolecular interactions of the polymers.[2] Namely, the monomer molecules pack closely because of the larger dipole−dipole interaction, while the polymer molecules pack loosely because of the small interaction. The dipole moment of the monomer can be an important parameter to estimate the degree of the intermolecular interaction. It is expected that cyclic sulfites having an equatorial S═O group show larger dipole moments to show volume expansions during the polymerization by the PM3 molecular orbital calculation.[1] Although the conformation of the S═O group of a six-membered cyclic sulfite (6CS**)** is axial, there are some six-membered cyclic sulfites having an equatorial S═O group with bulky substituents.[3] Actually, substituted six-membered cyclic sulfites having an equatorial S═O group show larger dipole moments than those having an axial S═O group.[3b,c] Therefore, a pseudoequatorial S═O group is expected in seven-membered cyclic sulfites having bulky substituents, which may show volume expansion during the polymerization. In this paper, we report the substituent effect and the volume change in the cationic polymerization of seven-membered cyclic sulfites.

Scheme 1



Results and Discussion

Synthesis and Cationic Polymerization of a Seven-Membered Cyclic Sulfite Having a Phenyl Group. There are some reports of substituted of six-membered cyclic sulfites having axial and equatorial S═O groups.[3] Buchanan et al. have reported that six-membered cyclic sulfites having axial and equatorial S═O groups can be easily isolated by the introduction of a phenyl group at the 4-position (Chart 1).[3d] In this work, we deal with the synthesis and cationic polymerization of a seven-membered cyclic sulfite having a phenyl group at the 4-position (7PhCS).

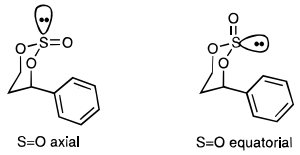
7PhCS was synthesized by the reaction of thionyl chloride and 1-phenyl-1,4-butanediol,[4] which was obtained by the reduction of benzoylpropionic acid with lithium aluminum hydride (Scheme 2). In the IR spectrum of 7PhCS, a peak assignable to a pseudoaxial S═O group was observed at 1203 cm^{-1}, but its equatorial S═O group could not be detected.

Cationic polymerization of 7PhCS was carried out with TfOMe or $BF_3{\cdot}OEt_2$ at 25 °C for 3 days to confirm

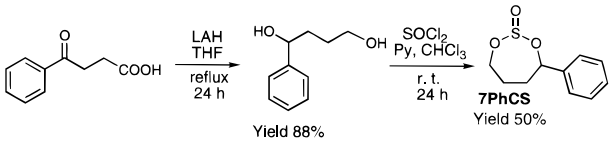
* Author to whom all correspondence should be addressed.
† Present address: Department of Applied Chemistry, Faculty of Engineering, University of Osaka Prefecture, Gakuen-cho, Sakai, Osaka 599-8531, Japan.

S0024-9297(97)01082-6 CCC: $15.00
Published on Web 03/05/1998

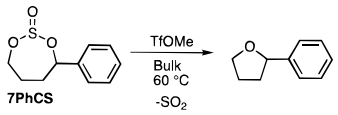
Chart 1



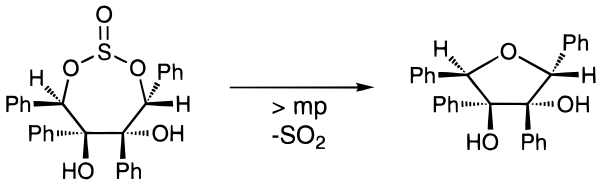
Scheme 2



Scheme 3



Scheme 4



Scheme 5

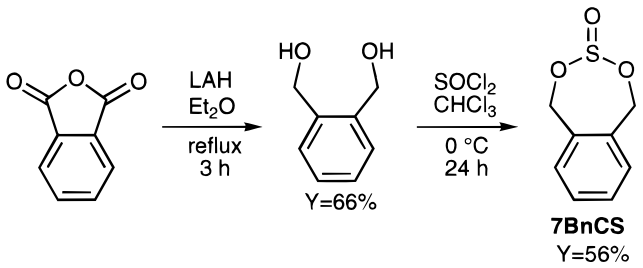


Table 1. $\nu_{S=O}$ Streching Frequencies Observed in the IR Spectra of 7BnCS

solvent	bulk	CCl_4	CH_3CN
$\nu_{S=O}$	1215 (s)	1220 (s) 1184 (w)	1210 (s) 1179 (s)

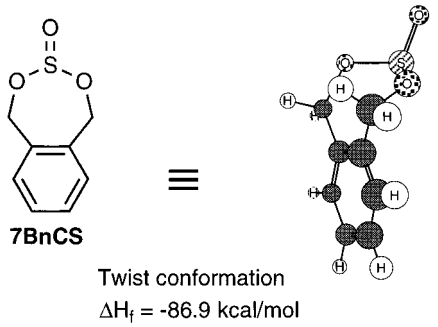


Figure 1. Stable conformation of 7BnCS obtained by the PM3 MO method.

no conversion of 7PhCS. The polymerization of 7PhCS afforded 2-phenyltetrahydrofuran quantitatively with TfOMe at 60 °C, which was produced by the desulfoxylation of 7PhCS (Scheme 3). The large thermal stability of 2-phenyltetrahydrofuran and steric hindrance by the phenyl group might suppress the polymerization of 7PhCS.

Waters et al. have reported that 4,5,6,7-tetraphenyl-1,3-dioxathiepan 2-oxide undergoes desulfoxylation to afford a tetrahydrofuran derivative by simply heating above the melting point (Scheme 4).[5] Substituents on the 4- and 7-positions of the seven-membered cyclic sulfites seem to be unfavorable to polymerization.

Synthesis and Cationic Polymerization of a Seven-Membered Cyclic Sulfite Having a Benzo Group in the 5,6-Position. The synthesis and the cationic polymerization of a seven-membered cyclic sulfite (7BnCS) having a benzo group in the 5,6-position were carried out. If the cationic polymerization of 7BnCS proceeded via an S_N1 mechanism, a stable benzyl cation should be formed as an intermediate. Consequently, 7BnCS may be expected to show large polymerizability. If the polymerization of 7BnCS proceeded via an S_N2 mechanism, steric hindrance by the benzo group should be operative to decrease the polymerizability, even though the electronic effect by the benzo group favored the reaction. 7BnCS was synthesized by the reaction of thionyl chloride and 1,2-benzenedimethanol[6] in 56% yield, which was obtained by the reduction of phthalic anhydride with lithium aluminum hydride (Scheme 5).

IR spectra of 7BnCS were measured in bulk, CCl_4, and CH_3CN to obtain some information on the conformation of 7BnCS (Table 1). The IR absorption peak of the S=O stretching vibration was observed at 1215 cm^{-1} in bulk, which is between the values of the axial and equatorial S=O groups of the six-membered cyclic sulfites.[7] Moreover, the IR absorption peaks of the S=O group of 7BnCS measured in CCl_4 (1220 cm^{-1}) and CH_3CN (1210 cm^{-1}) well agreed with those of a six-membered cyclic sulfite having a twisted conformation.[7] The conformation of 7BnCS was analyzed by the PM3 MO method to check the stability of the twisted S=O conformation (Figure 1).

Cationic polymerization of 7BnCS was carried out at 0 °C in the presence of trifluoromethanesulfonic acid (TfOH) or TfOMe in bulk to recover 7BnCS (runs 1 and 6 in Table 2), while the polymerization at 60 °C afforded a cross-linked polymer (runs 5 and 10 in Table 2), because the Friedel–Crafts reaction as well as polymerization might proceed. Next, the cationic polymerization of 7BnCS with TfOH or TfOMe was carried out at 25–40 °C to obtain the corresponding soluble polymer without gelation (Scheme 6, runs 2–4 and 7–9 in Table 2). The polymerization of 7BnCS afforded poly(7BnCS) (M_n = 8700) in 100% conversion with TfOMe in chlorobenzene (5 M) for 17 days (run 15 in Table 2). The polymerization of 7BnCS did not show an equilibrium character different from that of 7CS.[8] The polymerization of 7BnCS with $BF_3{\cdot}OEt_2$ did not afford a cross-linked polymer but rather poly(7BnCS) without gelation even at 60 °C (run 22 in Table 2). The cationic polymerization proceeded to afford poly(7BnCS) with less active initiator such as MeI and methyl *p*-toluenesulfonate (TsOMe) at 60 °C (runs 25 and 26 in Table 2).

The structure of poly(7BnCS) was determined by ^1H and ^{13}C NMR and IR spectroscopy, which are shown in Figures 2, 3, and 4, respectively. In the ^1H NMR spectrum of poly(7BnCS) (Figure 2), signals assignable to the benzo protons and the methylene protons α to the sulfite moiety were observed at 7.64–6.63 and 4.79–4.20 ppm, respectively. In the ^{13}C NMR spectrum

Table 2. Cationic Polymerization of 7BnCS

run	init.	solvent	temp, °C	time, day	covn,[a] %	yield,[b] %	$\bar{M}_n(\bar{M}_w/\bar{M}_n)^{b,c}$
1	TfOH (1)	none	0	5	0		
2	TfOH (1)	none	25	5	22	18	1800 (1.14)
3	TfOH (1)	none	25	12	49	43	4100 (1.43)
4	TfOH (1)	none	40	5	76	66	8500 (1.51)
5	TfOH (1)	none	60				gel
6	TfOMe (1)	none	0	5	0		
7	TfOMe (1)	none	25	5	18	15	1500 (1.12)
8	TfOMe (1)	none	25	12	40	35	3600 (1.41)
9	TfOMe (1)	none	40	5	75	67	8400 (1.60)
10	TfOMe (1)	none	60	1			gel
11	TfOMe (1)	PhCl (5 M)	25	5	27	21	2400 (1.24)
12	TfOMe (1)	PhCl (5 M)	40	1	38	33	3900 (1.40)
13	TfOMe (1)	PhCl (5 M)	40	5	60	53	5500 (1.51)
14	TfOMe (1)	PhCl (5 M)	40	12	62	54	6100 (1.61)
15	TfOMe (1)	PhCl (5 M)	40	17	100	91	8700 (1.71)
16	TfOMe (1)	PhCl (5 M)	60	1			gel
18	BF_3OEt_2 (1)	none	0	5	0		
19	BF_3OEt_2 (1)	none	40	5	10	7	950 (1.05)
20	BF_3OEt_2 (1)	none	40	12	16	11	1500 (1.29)
21	BF_3OEt_2 (1)	none	60	1	40	35	3700 (1.35)
22	BF_3OEt_2 (1)	PhCl (5 M)	60	1	19	10	1700 (1.22)
23	MeI (20)	none	60	5	0		
24	MeI (20)	none	100	5			gel
25	MeI (1)	none	100	5	12	8	1000 (1.05)
26	TsOMe (1)	none	100	5	15	19	1200 (1.12)

[a] Determined by ^{1}H NMR (solvent $CDCl_3$, 400 MHz). [b] Diethyl ether insoluble part. [c] Estimated by GPC (polystyrene standards, eluent THF).

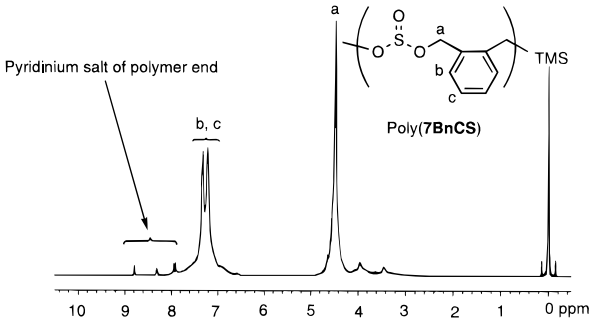
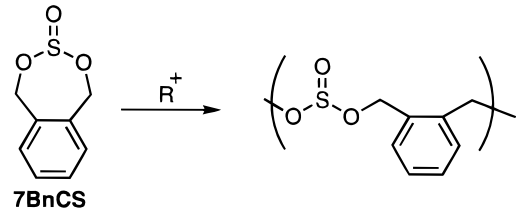


Figure 2. ^{1}H NMR spectrum of poly(7BnCS) (solvent $CDCl_3$, 400 MHz, run15 in Table 2).

Scheme 6



(Figure 3), three signals assignable to the benzo carbons and a signal assignable to the methylene carbon α to the sulfite moiety were observed at 136.3, 128.8, 127.8, and 69.8 ppm, respectively. In the IR spectrum (Figure 4), absorption peaks derived from υ_{C-H} of the benzo group and $\upsilon_{S=O}$ of the sulfite moiety were observed at 3067, 3029, and 1217 cm^{-1}, respectively.

Frontier electron densities of the oxygens of 7BnCS and 7CS for an electrophilic reaction were estimated by PM3 MO calculation to clear up the polymerization mechanism. The calculation result is shown in Figure 5. The frontier electron density of the S=O oxygen of 7BnCS was larger than those of the ether oxygens, similar to 7CS. Therefore, the cationic species should predominantly attack the S=O oxygen. Cationic polymerization of 7BnCS was carried out at 40 °C with TfOMe (10 mol %) in $CDCl_3$ (4 M) to observe a signal of

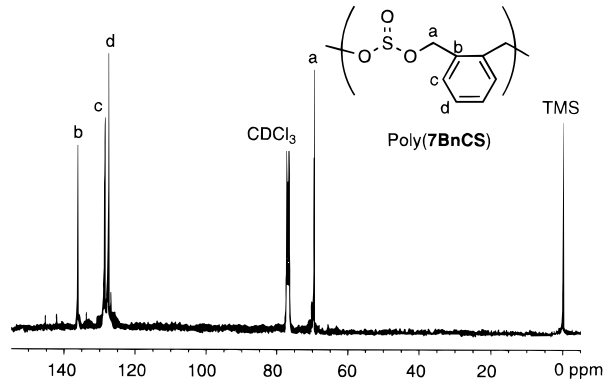


Figure 3. ^{13}C NMR spectrum of poly(7BnCS) (solvent $CDCl_3$, 100 MHz, run 15 in Table 2).

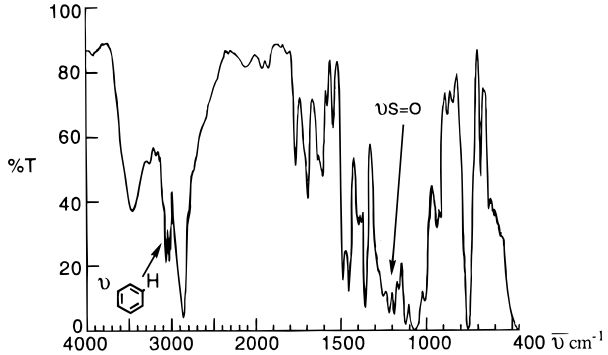


Figure 4. IR spectrum of poly(7BnCS) (neat on NaCl disk, run 15 in Table 2).

TfO^- at −78.8 ppm in the ^{19}F NMR spectrum of the polymerization mixture. Scheme 7 illustrates a plausible mechanism of the polymerization of 7BnCS with TfOMe. First, a methyl cation formed from TfOMe attacks the S=O oxygen of 7BnCS to form a trioxosulfonium cation. Subsequently, alkylation of the exocyclic oxygen of 7BnCS proceeds by the cleavage of the carbon−oxygen bond to form poly(7BnCS) by the successive reactions.

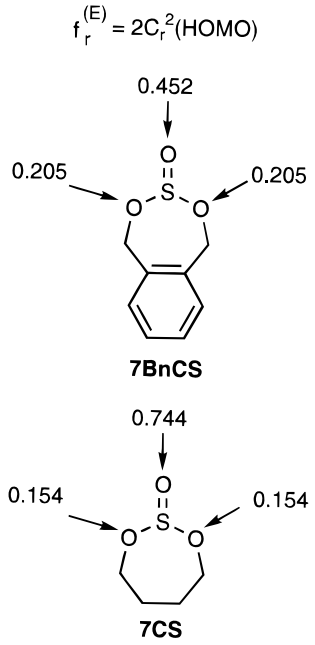
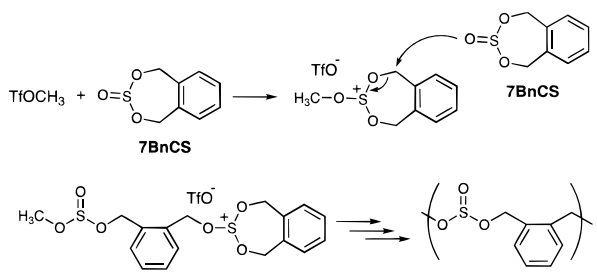
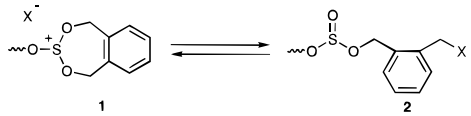


Figure 5. Frontier electron densities ($f_r^{(E)}$) of oxygen of 7BnCS (S═O twist conformation) and 7CS (S═O pseudoaxial conformation) for an electrophilic reaction.

Scheme 7



Scheme 8



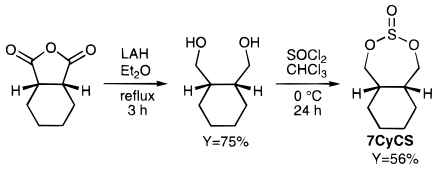
In the cationic polymerization of 7BnCS, the propagating end of the polymer might be in equilibrium between the ionic structure **1** and the covalent bond structure **2** (Scheme 8). The equilibrium lies toward **2** with MeI and TsOMe, which release a counteranion with large nucelophilicity.

The observed rate of polymerization can be calculated by eq 1, assuming the concentration of the active species is constant.[9] The rate constant (k_{obsd}) was estimated

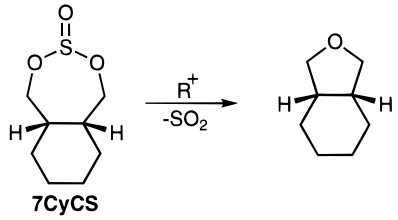
$$-d[M]/dt = k_p[P^*][M] = k_{obsd}[M] \qquad (1)$$

as 2.63×10^3 h^{-1} from the time−conversion relationship in the cationic polymerization of 7BnCS with TfOMe (1 mol %) at 25 °C in chlorobenzene (5 M), which was $^1/_{25}$-th smaller than that of 7CS.[1b] The steric hindrance by the benzo group seems to be the reason for the smaller k_{obsd} of 7BnCS. The benzo group also suppresses the back-biting reaction, since 7BnCS was quantitatively converted and 7CS was not. In eq 1, [M], [P*], k_P, and k_{obsd} represent the concentration of the monomer, the concentration of the propagating end, the rate of polymerization, and the observed rate of polymerization, respectively.

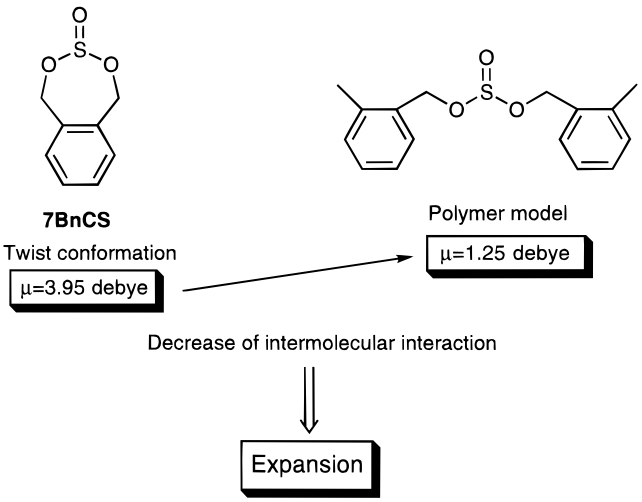
Scheme 9



Scheme 10



Scheme 11



Synthesis and Cationic Polymerization of Seven-Membered Cyclic Sulfite Having a Cyclohexane Ring. The synthesis and the cationic polymerization of a seven-membered cyclic sulfite (7CyCS) having cyclohexane were carried out. 7CyCS was synthesized by the reaction of thionyl chloride and *cis*-1,2-cyclohexanedimethanol,[6] which was obtained by the reduction of *cis*-1,2-cyclohexanedicarboxylic anhydride with lithium aluminum hydride (Scheme 9).

7CyCS was confirmed to have a twisted conformation from the IR absorption peak derived from $\nu_{S=O}$ of the sulfite moiety at 1210 cm^{-1}.[7] Surprisingly, no cationic polymerization of 7CyCS took place at 25 and 60 °C with TfOH, TfOMe, and $BF_3{\cdot}OEt_2$ as the initiators, but a THF derivative was formed quantitatively accompanied by desulfoxylation (Scheme 10). No polymerizability of 7CyCS should be caused by the steric hindrance of the cyclohexane ring. Although 7BnCS has a benzo group, whose size is similar to the cyclohexane ring, the electron-donating character of the benzo group should be effective for polymerization. Unfavorable formation of dihydrobenzofuran from 7BnCS may also be the reason for the successful polymerization of 7BnCS due to its anti aromatic 4π system.[6]

Volume Change of Poly(7BnCS) during Polymerization. Dipole moments of 7BnCS having a twisted S═O group and the polymer model were calculated as 3.95 and 1.25 D, respectively, by PM3 MO (Scheme 11). Therefore, 7BnCS is expected to show volume expansion during the polymerization, since the dipole−dipole

intermolecular interactions between the monomers are larger than those of the polymers. The volume change during the polymerization of 7BnCS was evaluated from the densities of 7BnCS and poly(7BnCS) measured by the density gradient tube method (eq 2). The density

$$V_C = \left(\frac{1/d_P}{1/d_M} - 1\right)100 \qquad (2)$$

$$V_C = \{(1/1.225)/(1/1.330) - 1\}100 = +8.57$$

of 7BnCS was 1.330 and that of poly(7BnCS) obtained in run 15 in Table 2 was 1.225 at 25 °C. Consequently, 7BnCS showed 8.57% expansion during the polymerization. The benzo group of 7BnCS is effective to increase the dipole moment by changing the conformation of the S═O group, since 7CS shows a smaller dipole moment value due to the pseudoaxial S═O group to cause volume shrinkage. In eq 2, V_C is the volume change (%), d_P is the density of the polymer, and d_M is the density of the monomer.

Properties of Poly(7BnCS). The glass transition temperature (Tg) and the 5% weight loss temperature (T_{d_5}) under a nitrogen atmosphere of poly(7BnCS) (run 15 in Table 2) were 62 and 172 °C, respectively. No melting temperature was observed. The refractive index (n^{25}_D) of poly(7BnCS) (run 15 in Table 2) was 1.6842.

Summary

In this paper, the syntheses and cationic polymerizations of seven-membered cyclic sulfites having phenyl (7PhCS), benzo (7BnCS), and cyclohexane (7CyCS) groups were examined to demonstrate the following results. (1) 7PhCS and 7CyCS underwent complete elimination of SO_2 to afford the corresponding THF derivatives under the cationic conditions. (2) 7BnCS undertook the cationic polymerization in the presence of the cationic initiators such as TfOH, TfOMe, TsOMe, and MeI in bulk or chlorobenzene to afford the corresponding polymer with $\bar{M}_n$ 950−8700 without desulfoxylation. The benzo group was operative for polymerization and suppression of the desulfoxylation. (3) The cationic polymerization of 7BnCS did not show equilibrium character. The steric hindrance of the benzene ring might be effective to suppress the backbiting reaction. (4) The volume expansion during the polymerization of 7BnCS was 8.57%. This might be caused by the larger dipole−dipole interactions between the monomers and smaller ones between the polymers.

Experimental Section

Materials. Chloroform, dichloromethane, and chlorobenzene were refluxed over P_2O_5, and distilled. 3-Benzoylpropionic acid, phthalic anhydride, hexahydrophthalic anhydride, lithium aluminum hydride, and thionyl chloride were used as received. Pyridine was dried over KOH and distilled. Diethyl ether was purified by distillation over sodium under a nitrogen atmosphere. Trifluoromethanesulfonic acid (TfOH) were distilled under a reduced pressure before use. Methyl trifluoromethanesulfonate (TfOMe) was dried over P_2O_5 for several hours and distilled. $BF_3{\cdot}OEt_2$ was distilled under a reduced pressure. Methyl *p*-toluenesulfonate (TsOMe) was used after recrystallization from diethyl ether. MeI was dried over P_2O_5 for several hours and distilled.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) on a JEOL JNM-EX400 spectrometer, using tetramethylsilane (TMS) as an internal standard in dimethyl-d_6 sulfoxide (DMSO-d_6) or chloroform-d ($CDCl_3$) at 27 °C. IR spectra were obtained with a JASCO FT/IR-5300 spectrometer. Mass spectra were measured on a Hitachi M-80 spectrometer. Elemental analyses were measured on a Yanaco MT-5. Molecular weights ($\bar{M}_n$ and $\bar{M}_w$: number- and weight-average molecular weights) and the distributions ($\bar{M}_w/\bar{M}_n$) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC CCP & 8000 system with a data processor, equipped with a refractive index detector and a polystyrene gel column (Tosoh TSK gel G3000H) using tetrahydrofuran as an eluent, a flow rate of 1.0 mL/min by polystyrene calibration at 30 °C. T_{d_5} and T_g were measured on SEIKO TG/DTA 200 and DSC 220C under a nitrogen atmosphere at a heating rate of 10 °C/min, respectively. The densities of 7BnCS and the polymer were measured by the density gradient tube method at 25 °C using aqueous lithium bromide solution as a density gradient liquid with a Shibayama Scientific Co., Ltd., Model A. The refractive index was measured on an Atago Abbe refractometer.

Synthesis of 1-Phenyl-1,4-butanediol. A solution of 3-benzoylpropionic acid (8.0 g, 44.9 mmol) in THF (200 mL) was added dropwise into a stirred suspension of $LiAlH_4$ (5.12 g, 135 mmol) in THF (200 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and heated under reflux for 24 h. The reaction mixture was cooled at 0 °C, and excess $LiAlH_4$ was inactivated by dropwise addition of ethyl acetate (10 mL). H_2O (100 mL) and subsequent 2 M HCl_{aq} (10 mL) were added to the reaction mixture, and the mixture was filtered. The residue was washed with THF (100 mL) twice. The combined filtrate was evaporate and then coevaporated with CH_3CN (100 mL) and toluene (100 mL). The solid was recrystallized from diethyl ether to give 1-phenyl-1,4-butanediol in 88% yield. Mp: 66−67 °C (lit.[5] mp 65−66 °C). ^{1}H NMR (DMSO-d_6): δ 7.38−7.25 (m, 5H, C_6H_5), 5.17 (d, 1H, J = 4.2 Hz, HOCH-(C_6H_5)), 4.53 (unresolved q, 1H, OH), 4.42 (t, 1H, J = 5.0 Hz, OH), 3.39 (unresolved q, 12H, $HOCH_2CH_2$), 1.70−1.30 (m, 4H, $HOCH_2CH_2CH_2$). IR (KBr): 3330 (ν_{O-H}), 1035 (ν_{C-O}) cm^{-1}. MS (DI−EI): m/z 166 (M^+).

Synthesis of 4-Phenyl-1,3-dioxa-2-thiepane 2-Oxide (7PhCS). A solution of thionyl chloride (15.0 g, 126 mmol) in chloroform (370 mL) was added dropwise at 0 °C into a solution of 1-phenyl-1,4-butanediol (18.4 g, 111 mmol) and pyridine (20.0 g, 253 mmol) in chloroform (740 mL). The reaction mixture was stirred at room temperature for 24 h. The residue was purified by silica gel column chromatography using dichloromethane as an eluent and distilled under a reduced pressure to afford 7PhCS as a colorless liquid in 50% yield. ^{1}H NMR ($CDCl_3$): δ 7.41−7.19 (m, 5H, C_6H_5), 4.88−4.80 (m, 1H, OSO_2CHPh), 4.12−3.79 (m, 2H, OSO_2CH_2C), 2.36−1.63 (m, 4H, CCH_2CH_2C). ^{13}C NMR ($CDCl_3$): δ 143.6, 128.1, 127.0, 125.4, 80.0, 67.6, 34.2, 25.6. IR (neat on NaCl disk): 1203 (pseudoaxial $\nu_{S=O}$) cm^{-1}. MS (DI−EI): m/z 212 (M^+). Anal. Calcd for $C_{10}H_{12}SO_3$: C, 56.58; H, 5.70; S, 15.11. Found: C, 56.48; H, 5.59; S, 15.39.

Synthesis of 1,2-Benzenedimethanol. Solid phthalic anhydride (59.2 g, 440 mmol) was added gradually into a suspension of $LiAlH_4$ (18.0 g, 474 mmol) in THF (1 L) at room temperature, so as to keep refluxing. After the addition, the reaction mixture was stirred under refluxing for 24 h. Saturated aqueous sodium sulfate (100 mL) was carefully introduced into the reaction mixture at 0 °C until the white mixture was solidified. The resulting white mass was filtered off and washed with THF (100 mL) twice. The combined filtrate was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The residual solid was recrystallized from benzene−THF (1:1) to obtain 1,2-benzenedimethanol in 66% yield. Mp: 63−64 °C (lit.[6] mp 62−63 °C). ^{1}H NMR ($CDCl_3$): δ 7.41−7.19 (m, 4H, C_6H_4), 4.58 (d, 4H, J = 12.0 Hz, C_6H_4-CH_2OH), 3.82 (t, 2H, J = 5.0 Hz, OH). ^{13}C NMR ($CDCl_3$): δ 139.2, 129.5, 128.4, 63.6. IR (KBr): 3330 (ν_{O-H}), 3050 ($\nu_{aromatic}$), 1035 (ν_{C-O}) cm^{-1}.

5,6-Benzo-1,3-dioxa-2-thiepane 2-Oxide (7BnCS). A solution of thionyl chloride (15.0 g, 126 mmol) in diethyl ether (370 mL) was added dropwise at 0 °C into a solution of 1,2-benzenedimethanol (15.3 g, 111 mmol) and pyridine (20.0 g,

253 mmol) in diethyl ether (740 mL). The reaction mixture was stirred at room temperature for 24 h. The residue was purified by silica gel column chromatography using dichloromethane as an eluent and distilled under a reduced pressure to afford 7BnCS as a colorless liquid in 56% yield. Bp: 65−66 °C/0.9 mmHg. ^{1}H NMR ($CDCl_3$): δ 7.41−7.08 (m, 4H, C_6H_4), 5.89 (d, 2H, J = 14.0 Hz, OSO_2CH_2C, pseudoaxial), 4.67 (m, 2H, J = 14.0 Hz, OSO_2CH_2C, pseudoequatorial). ^{13}C NMR ($CDCl_3$): δ 136.0, 129.1, 128.3, 62.6. IR (neat on NaCl disk): 1215 ($\nu_{S=O}$) cm^{-1}. MS (DI−EI): m/z 184 (M^+).

Synthesis of *cis*-1,2-Cyclohexanedimethanol. The title compound was prepared from *cis*-1,2-cyclohexanedicarboxylic anhydride similarly to 1,2-benzenedimethanol. The product was obtained by distillation under a reduced pressure as a colorless liquid in 75% yield. Bp: 111−113 °C/0.7 mmHg (lit.[6] bp 108−115 °C/1.1 mmHg). ^{1}H NMR ($CDCl_3$): δ 4.81−4.64 (m, 2H, $(CH_2)CCHCH_2OH$), 3.78−3.41 (m, 4H, CH_2O), 1.89 (s, 2H, OH), 1.61−1.18 (m, 8H, $CH_2CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 63.7, 40.0, 27.1, 24.0. IR (neat on NaCl disk): 3322 (ν_{O-H}), 1032 (ν_{C-O}) cm^{-1}.

1′,2′,3′,4′,5′,6′-Hexahydro-5,6-benzo-1,3-dioxa-2-tiepane 2-Oxide (7CyCS). The title compound was prepared from 1,2-cyclohexanedimethanol and thionyl chloride similarly to 7PhCS. Yield: 56%. Bp: 83−84 °C/0.3 mmHg. ^{1}H NMR ($CDCl_3$): δ 4.60−4.24 (m, 2H, OCH_2C, pseudoaxial), 4.09−3.80 (m, 2H, OCH_2C, pseudoequatorial), 2.08−1.98 (m, 2H, OCCH), 2.11−1.38 (m, 8H, $CH_2CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 66.1, 38.3, 26.5, 23.8. IR (neat on NaCl disk): 1210 ($\nu_{S=O}$) cm^{-1}. MS (DI−EI): m/z 190 (M^+). Anal. Calcd for $C_8H_{14}SO_3$: C, 50.50; H, 7.42; S, 16.85. Found: C, 50.61; H, 7.32; S, 17.05.

Cationic Polymerization of 7PhCS (Typical Procedure). TfOMe (4.46 mg, 0.0272 mmol) was introduced into a glass tube containing 7PhCS (577 mg, 2.72 mmol) in bulk at 25 °C under a nitrogen atmosphere. The glass tube was stoppered by a three-way stopcock. After the reaction mixture was kept at 60 °C for 3 h under stirring, the reaction mixture was quenched by the addition of pyridine (10.0 mg, 0.147 mmol). The residue was distilled under a reduced pressure not to afford poly(7PhCS) but 2-phenyltetrahydrofuran as a colorless liquid in 90% yield. Bp: 83−86 °C/2 mmHg. ^{1}H NMR ($CDCl_3$): δ 7.41−7.19 (m, 5H, C_6H_5), 4.41−4.29 (m, 1H, OCHPh), 3.71 (m, 2H, J = 6.6 Hz, OCH_2C), 1.99−1.79 (m, 4H, CCH_2CH_2C). IR (neat on NaCl disk): 3031 ($\nu_{aromatic}$), 1036 (ν_{C-O}) cm^{-1}. MS (DI−EI): m/z 148 (M^+).

Cationic Polymerization of 7BnCS (Typical Procedure). TfOMe (4.46 mg, 0.0272 mmol) was introduced into a glass tube containing 7BnCS (500 mg, 2.72 mmol) in chlorobenzene (166 μL) at 40 °C under a nitrogen atmosphere. The glass tube was stoppered by a three-way stopcock. After the reaction mixture was kept at 40 °C for 17 days with stirring, the reaction mixture was quenched by the addition of pyridine (10.0 mg, 0.147 mmol) and diluted with dichloromethane (5 mL). The solution was poured into diethyl ether (150 mL) to precipitate a solvent-insoluble pale brown transparent viscous liquid polymer in 91% yield. $\bar{M}_n$ = 8700, $\bar{M}_w/\bar{M}_n$ = 1.71. ^{1}H NMR ($CDCl_3$): δ 7.64−6.63 (m, 4H, C_6H_4), 4.79−4.20 (m, 4H, CH_2O). ^{13}C NMR ($CDCl_3$): δ 136.3, 128.8, 127.8, 69.8. IR (neat on NaCl disk): 3067 ($\nu_{aromatic}$), 3029 ($\nu_{aromatic}$), 1217 ($\nu_{S=O}$) cm^{-1}.

Cationic Polymerization of 7CyCS (Typical Procedure). Cationic polymerization of 7CyCS was carried out similarly to 7PhCS not to afford poly(7CyCS) but 1′,2′,3′,4′,5′,6′-hexahydrobenzofuran as a colorless liquid in 90% yield. Bp: 85−86 °C/1 mmHg. ^{1}H NMR ($CDCl_3$): δ 3.79 (dd, 2H, J = 7.5, 7.0 Hz, OCH_2C, pseudoaxial), 3.63 (dd, 2H, J = 7.6, 5.8 Hz, OCH_2C, pseudoequatorial), 2.21−2.10 (m, 2H, OCCH), 1.62−1.20 (m, 8H, $CH_2CH_2CH_2CH_2$). IR (neat on NaCl disk): 1035 (ν_{C-O}) cm^{-1}. MS (DI−EI): m/z 126 (M^+).

Molecular Orbital Calculation. All computations were done on an Apple Power Macintosh 7100/AV (Power PC601, 80 MHz, 72 MB RAM) with use of SONY Tektonix CAChe system version 3.7. Geometries were optimized first with molecular mechanics using the CAChe MM2 version 3.7 program, second with molecular dynamics using CAChe dynamics version 3.7 program, and finally with MOPAC version 6.00 using PM3 Hamiltonian by the restricted Hartree−Fock method. All calculations were done with full optimization of all geometrical variables (bond length, bond angles, and dihedral angles).

References and Notes

(1) (a) Azuma, N.; Takata, T.; Sanda, F.; Endo. T. *Macromolecules* **1995**, *28*, 7331. (b) Azuma, N.; Sanda, F.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1007. (c) Azuma, N.; Takata, T.; Sanda, F.; Endo. T. *Macromolecules* **1995**, *28*, 5967.

(2) Takata, T.; Sanda, F.; Ariga, T.; Nemoto, H.; Endo, T. *Macromol. Rapid Commun.* **1997**, *18*, 461.

(3) (a) Pihlaja, K.; Rossi, K.; Nikander, H. *J. Org. Chem.* **1985**, *50*, 644. (b) van Woerden, H. F.; Havinga, E. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 341. (c) Wood, G.; Buchanan, G. W.; Miskow, M. H. *Can. J. Chem.* **1972**, *50*, 521. (d) Buchanan, G. B.; Cousineau, C. M. E.; Mundell, T. C. *Can. J. Chem.* **1978**, *56*, 2019. (e) Virtanen, T.; Pihlaja, K.; Niksander, H. *Acta Chem. Scand.* **1982**, *B36*, 117.

(4) Mullah, K. B.; Bentrude, W. G. *J. Org. Chem.* **1991**, *56*, 7218.

(5) Juday, R. E.; Waters, W. L. *Tetrahedron Lett.* **1975**, 4321.

(6) Takata, T.; Endo, T. *Macromolecules*, **1988**, *21*, 900.

(7) Faucher, H.; Guimaraes, A.; Robert, J. B. *Tetrahedron Lett.* **1977**, 1743.

(8) Azuma, N.; Sanda, F.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *35*, 3235.

(9) This assumption is based on the fact that the cyclic sulfites polymerize via a pseudo living mechanism.[1c,8]

MA971082N