Sulfur Analog of Spirocyclic Orthocarbonate Capable of Undergoing Tandem Double Ring-Opening Polymerization: Synthesis, Structure, and Cationic Polymerization of Dibenzo[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]tridecane, Property of the Polymer, and Volume Change on Polymerization

Toshikazu Takata,† Masami Kanamaru,‡ and Takeshi Endo*,‡

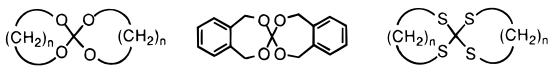
Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka 593, Japan, and Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 226, Japan

Received January 22, 1997; Revised Manuscript Received July 18, 1997[⊗]

ABSTRACT: The sulfur analog of spiroorthocarbonate (SOC) capable of undergoing tandem double ring-opening polymerization (dibenzo[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]tridecane, **4**) was synthesized, and its polymerization behavior was studied. Some properties of the polymers obtained and the volume change on polymerization of **4** were also examined. The synthesis of **4** was performed by the acid-catalyzed ester-exchange reaction of tetrakis(methylthio)methane with *o*-xylenedithiol and was obtained in 98% yield. The structure of **4** was determined by the spectral and elemental analysis data. Cationic polymerization of **4** with latent thermal initiator benzyl tetrahydrothiophenium hexafluoroantimonate in nitrobenzene proceeded efficiently at more than 150 °C to give the corresponding poly(thioether−trithiocarbonate) **5**. The polymer structure was determined by the spectral data and further confirmed by the structures of the decomposition products formed by the reductive cleavage of the trithiocarbonate bond of **5** with $LiAlH_4$. The mechanism of the polymerization was postulated from the results obtained. Thermal properties of **5** such as T_g and T_m were examined and compared with those of its oxygen analog (**13**). The volume change was studied in the polymerizations of **4** and its oxygen analog (**2**), during which 5.2 and 6.7% volume expansions were observed, respectively.

Introduction

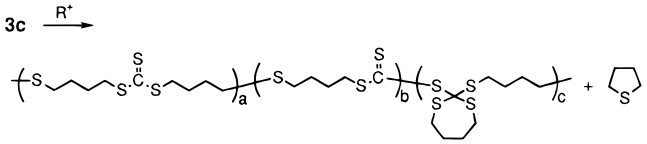
Volume shrinkage during polymerization or the curing process is a serious problem in the polymer materials field, while a few monomers and materials showing volume expansion on polymerization and curing are reported.[1−3] The authors have extensively studied the synthesis, polymerization, and volume change during polymerization of these expanding monomers and materials.[1,2] Spiroorthocarbonate (SOC, **1**) is an especially



1 **2** **3**

potent monomer among the expanding monomers, because of its clean polymerization and high degree of volume expansion. Especially, six-membered SOCs (**1b**, $n = 3$) efficiently yield poly(ether−carbonate)s via clean cationic tandem double ring-opening polymerization accompanied by volume expansion. However, there were no five- and seven-membered SOCs (**1a**, $n = 2$, and **1c**, $n = 4$) displaying volume expansion, because they did not polymerize without elimination of a considerable amount of small molecules during polymerization.[4] In our study on the development of five- and seven-membered SOCs capable of undergoing polymerization without elimination of a small molecule, a seven-membered SOC showing volume expansion could be synthesized by introducing benzo moieties onto its ring skeleton, *i.e.* dibenzo[3,4;10,11]-1,6,8,13-tetraoxaspiro-[6.6]tridecane (**2**), which polymerizes under mild conditions to give the corresponding poly(ether−carbonate) quantitatively, like **1b**.[5]

Scheme 1



Meanwhile, polymerization of sulfur analogs of **1** (spirotetrathioorthocarbonate: STOC, **3**, $n = 2−4$) as well as other possible expanding monomers has also been studied.[6] It has been found that only seven-membered STOC (**3c**, $n = 4$) polymerizes smoothly but yields a structure-complicated polymer having three components including both a single ring-opened unit and a small rate of trithiocarbonate unit formed by the elimination of tetrahydrothiophene (Scheme 1).[6]

Expanding monomers can display their characteristic properties only when they undertake tandem double ring-opening polymerization, during which no elimination of small molecule occurs.[1,2] The above mentioned results seem to suggest that the sulfur analog of **2** would undergo a selective tandem double ring-opening polymerization similarly to **2**, because the introduction of the two benzo groups dramatically changed the polymerizability.[5] The authors have recently succeeded in preparing the dibenzo derivative of **3c** or the sulfur analog of **2** (dibenzo[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]-tridecane, **4**) and examined the polymerization behavior of **4** from the viewpoint of accomplishing complete tandem double ring-opening polymerization, like in the oxygen systems of **1c** and **2**. This paper shows that **4** undergoes cationic tandem double ring-opening polymerization and can be regarded as the first sulfur-based expanding monomer.

* To whom all correspondence should be addressed.
† Osaka Prefecture University.
‡ Tokyo Institute of Technology.
⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S0024-9297(97)00078-8 CCC: $14.00

Experimental Section

Measurements. ^{1}H NMR spectra were obtained by JEOL PMX60si, EX-90, and FX100 NMR spectrometers, and ^{13}C NMR spectra were recorded on JEOL FX-100 and GX-500 spectrometers, using tetramethylsilane (TMS) as the internal standard in deuteriochloroform at 27 °C, unless otherwise stated. IR spectra were obtained with a JASCO FT/IR-3. Determination of number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) were carried out with a TOYO SODA CCP&8000 system equipped with three polystyrene gel columns (TSK gel 2000H, 2500H, and 3000H), using tetrahydrofuran (THF) as an eluent and ultraviolet and refractive index detectors. Preparative gel permeation chromatography (preparative GPC) was performed by a JAI LC908 (recycling preparative HPLC) with two polystyrene gel columns (JAIGEL 1H and 2H) using chloroform as an eluent. The gas chromatograph−mass spectrum was taken at 25 °C with a Hitachi M-80 spectrometer at an ionizing potential of 40 eV. Thermal analyses were carried out with a Seiko differential scanning calorimeter (DSC220C) at a heating rate of 10 °C/min and a Seiko thermogravimetric analyzer (TG/DTA220) operated at a heating rate of 10 °C/min under a nitrogen atmosphere. The densities of the monomer and polymer were obtained by the density gradient tube method at 25 °C using a Shibayama Kagaku Seisakusho Model A.

Materials. Solvents (carbon tetrachloride, benzene, and nitrobenzene) and *o*-xylene were distilled and stored over drying agents according to conventional methods. Anhydrous *p*-toluenesulfonic acid was obtained by azeotropic removal of water in refluxing benzene and subsequent vacuum drying. Commercially available extra pure grade reagents of *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), and thiourea were used without further purification. Benzyl tetramethylenesulfonium hexafluoroantimonate (BSH), a polymerization initiator, was synthesized according to the reported methods.[7] Polymerization of **2** was carried out according to the reported method of Takata *et al.* and the corresponding polymer was purified by repeated precipitation as reported.[5] A few STOCs (1,4,6,9-tetrathiaspiro[4.4]nonane, 1,5,7,11-tetrathiaspiro[5.5]undecane, and 1,5,7,13-tetrathiaspiro[6.6]-tridecane) were prepared according to the literature method.[6]

Preparation of Tetramethyl Tetrathioorthocarbonate. [Tetrakis(methylthio)methane]. Backer's procedure[8] was applied with some modification. A heterogeneous mixture of thiourea (45.6 g, 0.60 mol) and dimethyl sulfate (41.4 g, 0.33 mol) in water (21 mL) was heated carefully. In a short time, vigorous reaction took place and the mixture was cooled in an ice-water bath. The colorless clean solution was refluxed for 1 h and cooled. Crystallized product (*S*-methylisothiourea) was filtered off after addition of ethanol (60 mL), washed with ethanol (100 mL), and dried.

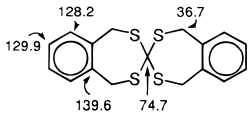
Twenty five grams of the white crystals obtained were dissolved in dilute hydrochloric acid (50 mL of 2 M HCl plus 25 mL of water), and the mixture was cooled with an ice-water bath. After addition of ether (15 mL), sodium nitrite (25 g, 0.36 mol) was added in one portion, violently evolving nitrogen dioxide. After the gas evolution ceased, water (75 mL) was added to yield a reddish yellow solution, to which the isothiourea prepared above (20 g) was further added at once. Then ammonia water (28%, 30 mL) was poured into the resulting homogeneous solution, and after a time exothermic evolution of gaseous nitrogen occurred. The mixture was kept at 50 °C, sometimes by heating until the gas evolution was ceased, causing separation of organic material. The mixture was extracted with ether three times, and the combined organic extract was dried over anhydrous magnesium sulfate, filtered, and evaporated. Residual reddish brown oil was distilled to yield a pale yellow oil, which was easily solidified to colorless crystals by allowing it to stand at room temperature. Yield: 36%. Bp: 129 °C/12 mmHg. Mp: 59−63 °C. (Lit.:[8] bp 126−129 °C/12 mmHg, mp 65 °C.) ^{1}H NMR ($CDCl_3$, δ): 2.18 (s, 12H). ^{13}C NMR ($CDCl_3$, δ): 79.2, 14.2.

Preparation of Xylenedithiol. A mixture of *o*-xylene (7.44 g, 0.07 mol), NBS (25 g, 0.14 mol), and BPO (0.2 g) in carbon tetrachloride (120 mL) was heated to *ca.* 70 °C. After cessation of the initial vigorous reaction, the mixture was refluxed for 1.5 h. The precipitates formed were filtered off, and the resulting filtrate was evaporated to give 18.9 g (100% yield) of α,α′-dibromo-*o*-xylene.

The crude dibromide prepared above (25 g, 0.095 mol) and 18 g of thiourea (0.24 mol) were dissolved in 95% ethanol (240 mL) by heating to reflux. The mixture was further refluxed for *ca.* 5 h. The solvent was removed by evaporation, giving a brown viscous oily material, to which sodium hydroxide solution (65.8 g of 90% NaOH plus 615 mL of water) was added. The resulting mixture was refluxed for 6.5 h. Then, the cooled mixture was acidified using 30% sulfuric acid (*ca.* 50 mL) and was extracted with benzene three times. The combined organic layer was washed with water and dried over anhydrous magnesium sulfate. Residual odor oil obtained by the solvent evaporation was distilled in vacuo to afford the dithiol as a colorless oil, which was solidified by allowing it to stand. Yield: 14.7 g (91%). Bp: 114 °C/2.5−3.0 mmHg. The purity by gas chromatography (GC) was 84%, while the ^{1}H NMR purity was more than 96%. The impurity was considered to be the corresponding cyclic disulfide probably formed by air oxidation during the GC measurement. ^{1}H NMR ($CDCl_3$, δ): 7.16 (s, 4H), 3.76 (d, 4H, J = 6.6 Hz), 1.18 (t, 2H, J = 6.6 Hz).

Preparation of Dibenzo[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]tridecane (4). A mixture of the distilled dithiol prepared above (1.7 g, 10 mmol), tetramethyl tetrathioorthocarbonate (1.0 g, 5.0 mmol), and 40 mg of anhydrous *p*-toluenesulfonic acid in dry benzene (30 mL) was refluxed for 4 h. White precipitates formed during the reaction were collected by filtration and washed with ethanol three times and then with benzene. Vacuum drying of the product yielded **4** as a white powder. Yield: 1.73 g (98%). Mp: 282.5−283.0 °C dec (sublimation was observed at a temperature higher than 210 °C). IR (KBr, cm^{-1}): 3030, 3000, 1594, 1482, 1423, 779, 759, 661. ^{1}H NMR ($C_6D_5NO_2$, δ): 7.17 (s, 8H), 4.22 (s, 8H). ^{1}H NMR (*p*-ClC_6H_4OH−$CDCl_3$ 1:1 mixture, δ): 7.17 (s, 8H), 4.10 (s, 8H). ^{13}C NMR ($C_6D_5NO_2$, δ): 139.6, 129.9, 128.2, 74.7, 36.7. Anal. Calcd for $C_{17}H_{16}S_4$: C, 58.57; H, 4.63. Found: C, 58.28; H, 4.47.

The ^{13}C NMR assignment is as follows:



Polymerization of 4. Typical Procedure. A heterogeneous mixture of **4** (318 mg, 1.0 mmol) and BSH (12.5 mg, 3.0 mol %) in nitrobenzene (0.5 mL) was heated in an evacuated sealed tube at 150 °C for 30 min. In a short time, the mixture turned homogeneous. To the obtained black mixture was added triethylamine (0.2 mL) in dichloromethane (4.0 mL), and the resulting mixture was precipitated with *n*-hexane (100 mL). Evaporation of the hexane-soluble fraction afforded 100 mg of a dark brown oil−solid mixture. The *n*-hexane-insoluble fraction (241 mg) was concentrated and divided into dichloromethane-soluble (170 mg) and -insoluble fractions (71 mg), which were a greenish black oil and black solid, respectively. These three fractions were evaluated by various analytical methods.

Data for *n*-hexane-insoluble and dichloromethane-soluble fraction: softening point, 60−70 °C; decomposition point, more than 200 °C; IR (KBr, cm^{-1}) 3059, 3018, 2918, 1599, 1489, 1450, 1427, 1060, 673; ^{1}H NMR ($CDCl_3$, δ) 7.18 (br, 8H), 4.64 (br, 4H), 3.67 (br, 4H). ^{13}C NMR ($CDCl_3$, δ) 221.8, 138.7, 136.4, 136.0, 135.8, 135.3, 133.6, 133.1, 131.9, 130.5, 129.6, 129.0, 128.5, 128.2, 127.4, 39.2. GPC (THF, polystyrene standards) $\bar{M}_n$ 2600, $\bar{M}_w/\bar{M}_n$ 1.79. Anal. Calcd for $C_{17}H_{16}S_4$: C, 58.57; H, 4.63; S, 36.80. Found: C, 58.24; H, 4.84; S, 36.62.

Polymer Reaction of 5. A dry THF solution (5 mL) of **5** (polymer soluble in chloroform and insoluble in *n*-hexane, 180 mg) obtained by the polymerization at 150 °C for 30 min was treated with lithium aluminum hydride (57 mg, 1.5 mmol) at room temperature for 3 h. To the mixture was added an excess

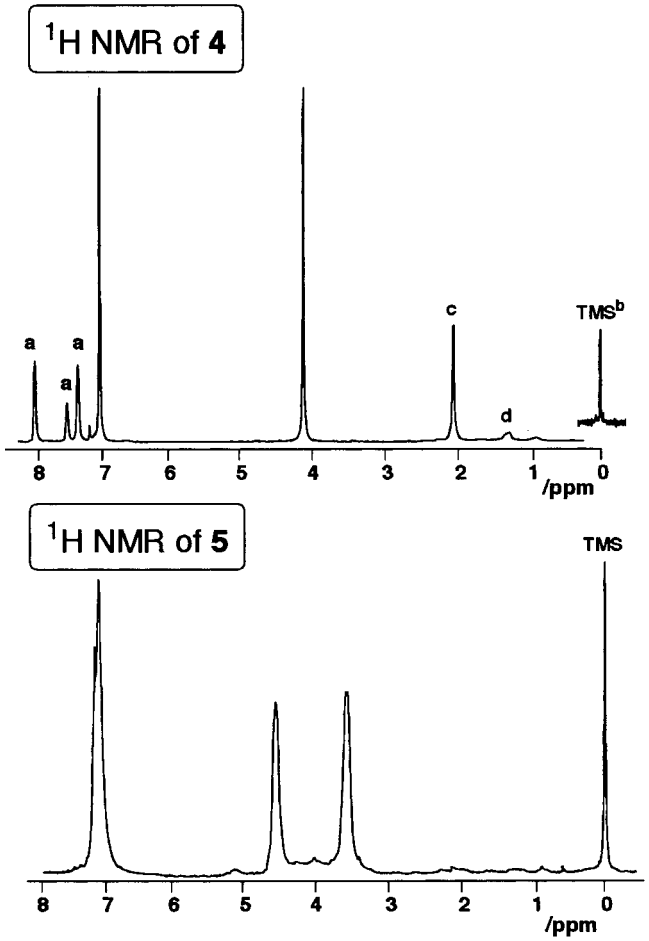
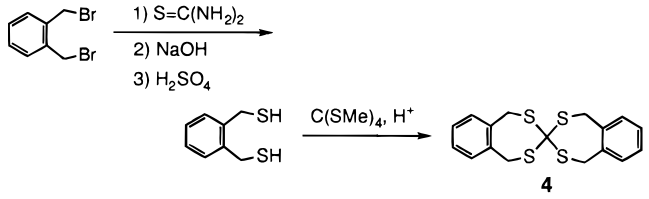


Figure 1. ^{1}H NMR spectra of monomer **4** (100 MHz, nitrobenzene-d_5, 90 °C) and polymer **5** (100 MHz, $CDCl_3$, 27 °C): (a) signals based on solvent nitrobenzene-d_5; (b) external TMS; (c) signal of H_2O; (d) unidentified signal.

Scheme 2



amount of methyl iodide (710 mg, 5.0 mmol), and the mixture was stirred at room temperature for 5 h. A saturated sodium sulfate solution was poured into the resulting mixture dropwise with cooling with an ice bath until excess lithium aluminum hydride was completely quenched. The resulting heterogeneous mixture was filtered, and the precipitate was washed with THF several times. The combined filtrate was washed with water and dried over anhydrous magnesium sulfate. Evaporation yielded an oily mixture (yield 135 mg). The mixture was subjected to the preparative HPLC to separate a low molecular weight polymer (**7**, 52%) and bis[(2-((methylthio)methyl)phenyl)methyl] sulfide (**6**, 25%).

Results and Discussion

Benzo-substituted seven-membered spirotetrathioorthocarbonate (STOC **4**) was prepared according to Scheme 2 in 89% overall yield (mp 282.5−283 °C) from *o*-xylene-α,α′-dibromide. Namely, treatment of the dibromide with thiourea yielded *o*-xylene-α,α′-dithiol, which was converted to **4** via an acid-catalyzed ester-exchange reaction using tetrakis(methylthio)methane as synthesized from thiourea and dimethyl sulfate by the

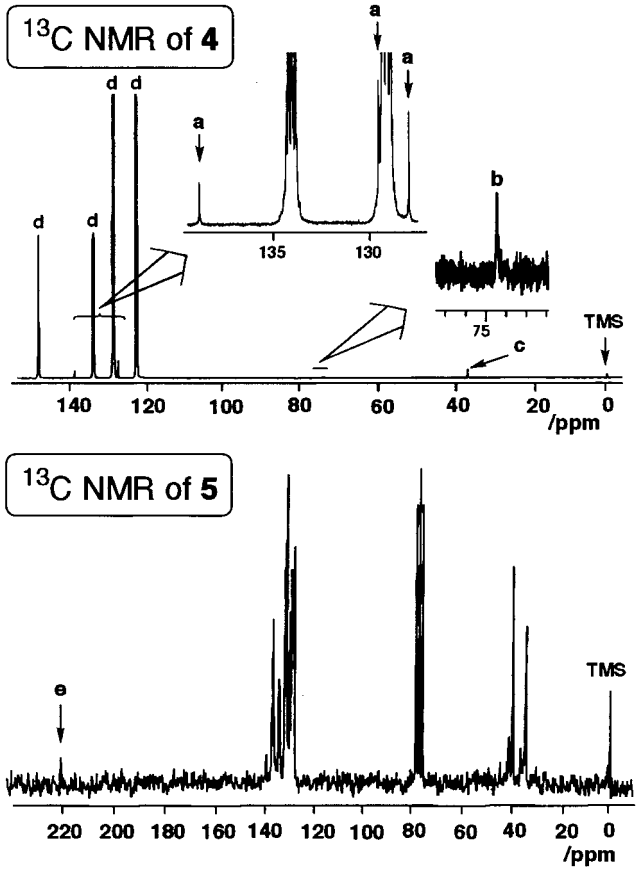


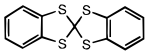
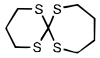
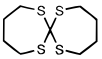
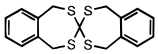
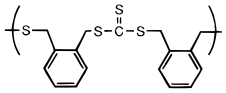
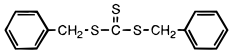
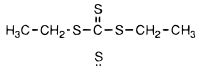
Figure 2. ^{13}C NMR spectra of monomer **4** (125 MHz, nitrobenzene-d_5, 85 °C) and polymer **5** ($CDCl_3$, 25 MHz, 27 °C): (a) signals in the aromatic region of **4**; (b) spiro carbon signal; (c) methylene carbon signal; (d) signals of solvent nitrobenzene-d_5; (e) trithiocarbonyl carbon signal.

modified Backer method (see Experimental Section). The structure of **4** was determined by the ^{1}H and ^{13}C NMR spectra and elemental analysis.

The ^{13}C NMR assignment of **4**, however, was not consistent with that already reported by Iwamura *et al.*,[9] who gave no experimental details of synthesis and identification of **4**, such as elemental analysis. Figures 1 and 2 show ^{1}H and ^{13}C NMR spectra of **4** in nitrobenzene-d_5. Each ^{13}C NMR signal of **4** is much weaker than that of the solvent (Figure 2) because of extremely low solubility of **4** and a long relaxation time of the spiro carbon.[9] The spiro carbon signal was not observed with 25 MHz ^{13}C NMR but was found at 74.7 ppm as a very weak signal by the high-resolution NMR measurement (125 MHz). The ^{1}H and ^{13}C NMR spectral characteristics are consistent with the proposed structure of **4**. However, Iwamura *et al.* reported 104.1 ppm for the spiro carbon chemical shift, which is significantly different from that observed for **4**. Other carbon signals reported are 36.2 ppm (benzyl methylene) and 138.9 ppm (ipso position), which are comparable to those obtained in this study (36.7 and 139.6 ppm, respectively). To determine the correct chemical shift, ^{13}C NMR spectra of various spirocyclic teterathioorthocarbonates were measured and their chemical shift data are summarized in Table 1 (top seven compounds).

The ^{13}C NMR chemical shifts of the spiro carbons of the STOCs including **4** are plotted *vs* the number of ring atoms (Figure 3). The plots of a series of unsubstituted STOCs give a clear V-shape curve having the six-membered ring at the bottom plot, although the reason for the ring size-dependent chemical shift is not clear.

Table 1. ^{13}C NMR Chemical Shifts of Spirocyclic Tetrathioorthocarbonates and Trithiocarbonates

Compound	^{13}C NMR Chemical Shift / ppm in $CDCl_3$ at r.t.	
	Spiro carbon / Trithiocarbonyl carbon	Others
	85.4	42.1[144][a]
	79.9	136.8, 126.3, 121.7
	71.7	40.8, 33.8, 23.5
	57.8 (58.9)[b]	28.8[139][a], 24.6[128][a] (28.9, 24.9)[b]
	66.6	33.6, 31.5, 31.3, 23.3
	78.4 (79.7)[b]	31.8[137][a], 31.0[126][a] (31.7, 31.1)[b]
	74.7[c]	139.6, 129.9, 128.2, 36.7[c]
	221.8	136.4~127.4, 39.2, 33.7
	222.0	134.7, 129.0, 128.5, 127.5, 41.3
	223.3	31.0, 13.1
	228.9	35.3

[a] Coupling constant J_{C-H} in Hz. [b] In benzene-d_6. [c] In nitrobenzene-d_5.

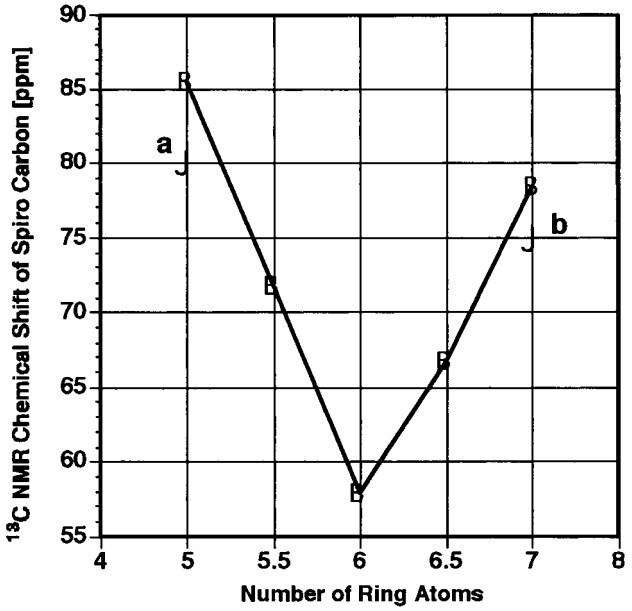
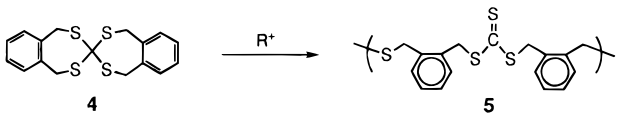


Figure 3. Relationship between the ^{13}C NMR chemical shift of the spiro carbon and the number of ring atoms of **4** and related unsubstituted spirocyclic tetrathioorthocarbonates (25 MHz, $CDCl_3$, 27 °C): (a) for dibenzo[2,3;7,8]-1,4,6,9-tetrathiaspiro[4.4]nonane; (b) for dibenzo[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]tridecane (**4**).

Points a and b of Figure 3 denote the chemical shifts of five- and seven-membered STOCs having two benzo groups, respectively. These values suggest that the benzo substitution does not largely cause the spiro carbon chemical shift. Therefore, the chemical shift value (74.7 ppm but not 104.1 ppm) is reasonably acceptable for the spiro carbon and the structure of **4** is concluded to be correct as proposed. The misassignment by Iwamura *et al.*[9] would come from the far lower solubility of **4** in ordinary organic solvents and the low S/N level of the instrument. Nitrobenzene was the best solvent of all tested to dissolve **4**, although the solubility of it was not very high, and thereby was chosen as the polymerization solvent.

Scheme 3



Cationic polymerization of **4** was carried out as follows: the heterogeneous mixture of **4** and latent thermal initiator BSH (3 mol %)[7] in nitrobenzene was heated at 150 °C for 30 min in a sealed tube. Besides unreacted monomer **4**, an *n*-hexane-insoluble and dichloromethane-soluble fraction was obtained in 53% yield as a black solid, which was soluble in many organic solvents such as dichloromethane, THF, benzene, and so on. The molecular weight of polymer **5** was $\bar{M}_n$ 1600.

If the tandem double ring-opening polymerization takes place, the polymer obtained should have the poly(thioether−trithiocarbonate) structure, as shown in Scheme 3. A weak IR absorption of $\nu_{C=S}$ due to the trithiocarbonate function was observed at 1060 cm^{-1}, while the ^{1}H NMR (Figure 1) showed two methylene signals at 3.67 and 4.63 ppm corresponding to two methylenes adjacent to thioether sulfur and trithiocarbonate sulfur, respectively. The ^{13}C NMR signal at 221.8 and a couple of signals at 39.2 and 33.7 ppm (Figure 2) were assigned as carbon signals of trithiocarbonate and two methylenes, respectively. In fact, the trithiocarbonate carbon signal certainly shows a chemical shift (221.8 ppm) similar to those of a few trithiocarbonates listed in Table 1. Elemental analysis data of the polymer were well consistent with the element composition of **5**, unambiguously suggesting the proposed poly(thioether−trithiocarbonate) structure.

The ring-opening polymerization of **4** was studied under varying conditions. Results are listed in Table 2. As shown in Table 2, the yield of *n*-hexane-insoluble polymer increased to 65% with an increase of reaction temperature, in accordance with the decrease of the chloroform-insoluble part, which contained mainly unreacted monomer **4**. To achieve 95% conversion of the monomer it takes more than 60 min at 150 °C. The molecular weight of the polymer was generally low, around $\bar{M}_n$ 1500, probably owing to the low solubility of the monomer in nitrobenzene and/or the fast transfer reaction due to the high reaction temperature. This can be confirmed in the ^{1}H NMR spectrum of polymer **5** (Figure 1), where the magnitude of the methylene signal adjacent to the thioether sulfur (3.67 ppm) is slightly larger than that adjacent to the trithiocarbonate sulfur (4.63 ppm). It may be explained by the presence of a terminal group like the mercapto group, which can induce a deshielding similar to that of the thioether group. The mechanism of the polymerization is discussed later.

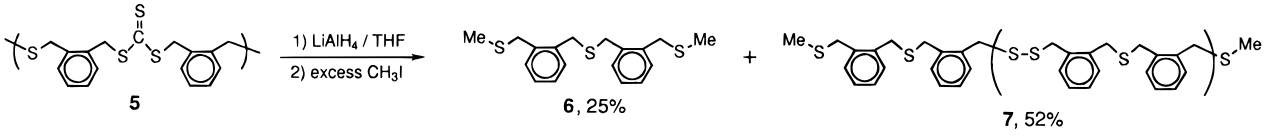
To further confirm the primary polymer structure, reduction of **5** with $LiAlH_4$ followed by methylation with methyl iodide was carried out. A few products were formed, probably via the reductive cleavage of the

Table 2. Cationic Polymerization of 4[a]

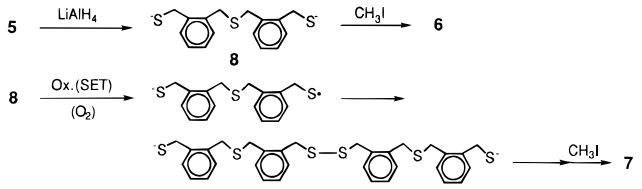
run	temp (°C)	time (min)	conv (%)	CH_2Cl_2 insol (%)[b]	n-hexane insol (%)	n-hexane sol (%)[c]	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$[d] *n*-hexane insol	$\bar{M}_n(\bar{M}_w/\bar{M}_n)$[d] *n*-hexane sol
1	120	120	34	52.9	12.8	30.3	1300 (1.54)	620 (1.54)
2	120	240	45	55.1	22.8	19.9	1600 (1.55)	430 (1.02)
3	150	15	79	17.0	23.0	59.8	1200 (2.61)	570 (1.71)
4	150	30	91	7.4	49.8	47.1	1600 (1.84)	230 (1.16)
5	150	60	94	4.7	51.6	39.1	1600 (1.87)	350 (1.12)
6	180	10	99	1.1	64.7	29.7	1600 (1.94)	330 (1.10)
7	180	30	100	0.4	60.4	34.7	2500 (2.42)	340 (1.10)

[a] Polymerization conditions: solvent, nitrobenzene (conc, 2 M); catalyst, benzyl tetramethylene sulfonium hexafluoroantimonate (3 mol %); degassed sealed pyrex tube. [b] Yield of chloroform-insoluble part. [c] Yields of *n*-hexane-soluble and -insoluble parts. [d] Molecular weight and molecular weight distribution estimated by gel permeation chromatography (eluent, THF; calibrated by polystyrene standards).

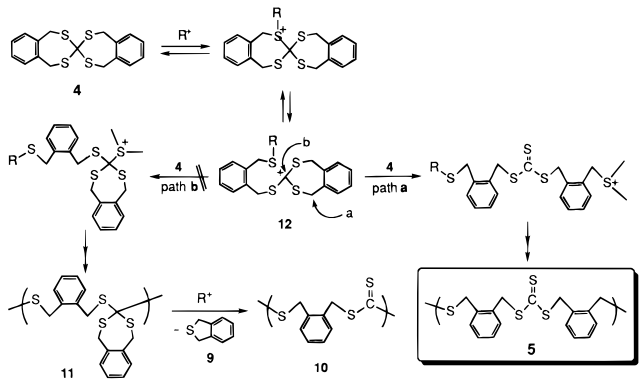
Scheme 4



Scheme 5



Scheme 6



trithiocarbonate group (Scheme 4). The monomeric methylated product **6** was isolated in 25% yield by preparative GPC and identified as bis[*o*-((methylthio)-methyl)benzyl] sulfide from the spectral data. In addition to **6**, low molecular weight polymer was also formed and was considered to have structure **7**, from the GPC result and NMR spectrum. Its average molecular weight calculated from the NMR was 1100. These results justify the poly(thioether−trithiocarbonate) structure of **5**.

Most probable mechanisms of the formation of **6** and **7** are simply illustrated in Scheme 5, in which dimercaptide **8** initially produced by the $LiAlH_4$ reduction of **5** reacts with 2 mol of methyl iodide to give **6**. Meanwhile, low molecular weight polymer **7** would be derived by single electron transfer (SET) to oxygen and successive radical dimerization followed by the methylation in both termini. The SET from thiolates to, *e.g.*, molecular oxygen is accelerated under basic conditions to yield thiyl radicals, which are eventually coupled to the corresponding disulfide.

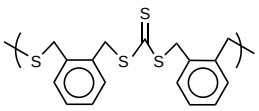
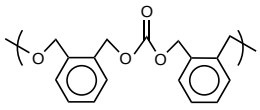
The hexane-soluble fraction of the polymerization of **4** was analyzed in detail for benzodihydrothiophene (**9**), which can be detected if the polymerization accompanying the formation of **9** as an elimination product takes place (Scheme 6), like in the case of **3c**, which is reported to polymerize with the formation of a 50% yield of tetrahydrothiophene at most. The GC−MS analysis indicated that less than 1% of **9** (*m*/*e* 134) is formed during the polymerization in some cases. Therefore, poly(thioether) **10** can be involved as a polymer unit, although it should be too small to be confirmed by NMR. Furthermore, detailed ^{13}C NMR analysis revealed that there is no single ring-opened structure **11** as a polymer unit, from the absence of ^{13}C NMR signal around 75 ppm. Spiro carbons of **3c** and **4** appear at 78.4 and 74.7 ppm, respectively, while a single ring-opened unit of a copolymer of **3c** with an SOC[10] is confirmed at 76.3 ppm. Further, usually no signal should appear around 75 ppm other than those of $CDCl_3$ in this system.

Thus, it is reasonable that the cationic polymerization of **4** is concluded to proceed via the tandem double ring-opening process to selectively afford poly(thioether−trithiocarbonate) **5**, as depicted in Scheme 6, which shows the polymerization mechanism. As shown in Scheme 6, the polymerization proceeds via single ring-opened tris(alkylthio)carbenium ion **12**, a key propagating species. This species is capable of being attacked by the second monomer to give each segment via path a or b. From the product structure determined and the several experiments mentioned above, the polymerization occurs mostly along path a. Therefore, formation of unit **10** and elimination of **9** are not taken into consideration. This mechanism can be compared with the mechanism of the polymerization of mother skeleton monomer **3c**, in which the elimination of tetrahydrothiophene is one of the main processes.[6]

The terminal structure of polymer **5** can be derived from the trithiocarbenium cation intermediate, which eventually reacts with some nucleophiles such as water to afford the mercapto terminal (Scheme 7). Since the mercapto group is much more stable toward oxygenation in acidic conditions than in alkaline conditions, most mercapto groups might remain unreacted after the polymerization.

Thermal properties of polymer **5** were examined and compared with those of the corresponding oxygen analog

Table 3. Thermal Properties of Polymer 5[a] (Comparison with Those of the Corresponding Oxygen Analog (13)[b]

polymer sample		$\bar{M}_n(\bar{M}_w/\bar{M}_n)$	T_g (°C)	T_m (°C)	T_{d10} (°C)
 **5**	Table 1, run 2	1600 (1.55)	25.1	146	196
 **13**	Table 1, run 4	1200 (2.08)	15.1	178	204
		5800 (2.40)	16.0	147	292

[a] Abbreviations: T_g, glass transition temperature; T_m, melting temperature; T_{d10}, 10% weight loss temperature. [b] This polymer was prepared by the cationic polymerization of **2** according to the reported method.[5]

Scheme 7

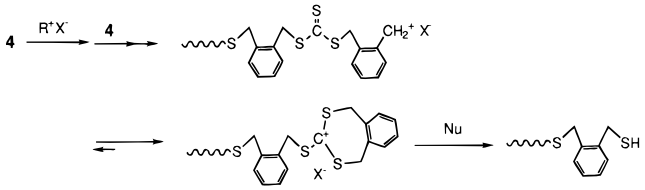
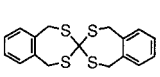
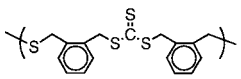
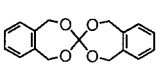
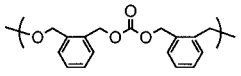
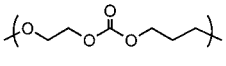


Table 4. Volume Change on Polymerization

Density,[*1] g/cm^3		Vol Change, %[*2]
Monomer	Polymer	
 1.424	 1.350	+5.2
 1.348	 1.258	+6.7
 1.31[*3]	 1.20[*3]	+8.4

[*1] Measured by density gradient tube method at 25°C.
[*2] Volume change [%] = $(d_{monomer} - d_{polymer})/d_{monomer} \times 100$.
[*3] Data obtained from ref. 3.

13 (polymer of **2**). Results are summarized in Table 3. Whereas T_g's of these polymers were rather low, around 20 °C, T_m's could be observed around 150 °C. The decomposition temperature of **5** was *ca.* 200 °C, somewhat lower than that of **13**. The low thermal stability of **5** might be caused by its low molecular weight.

On the other hand, to estimate the volume change on polymerization of **4**, densities of **4** (d_{25} 1.424) and **5** (d_{25} 1.350) were measured by the density gradient tube method. The density of **4** was greater than that of **5**, and hence it was concluded that the polymerization of **4** proceeds with a volume expansion of 5.2% (Table 4), indicating that **4** can be recognized as the first sulfur-based expanding monomer. The degree of volume expansion can be compared with that of **13** (6.7%) and the polymer of **1b**[3] (8.4%). An increase of molecular weight would enhance the degree of volume expansion, as expected from the mechanism of volume expansion.[1,2]

Thus, as described above, this work presents a new sulfur-containing monomer STOC **4** that undergoes selective tandem double ring-opening polymerization to afford poly(thioether−trithiocarbonate) **5** under cationic conditions. The selective formation of **5** is compared with the polymerization product of **3c** (Scheme 1). The successful polymerization of the sulfur analog of SOC should be attributed to the introduction of the benzo moieties into the unsubstituted seven-membered STOC skeleton, on the basis of the idea of enhancement of the electrophilic nature of the a ring carbon of the key propagating intermediate, the monocyclic trithiocarbenium ion, as expected from the results of the polymerization of **2**. And as a result, 5.2% volume expansion was observed.

The first sulfur-based expanding monomer, dibenzo-[3,4;10,11]-1,6,8,13-tetrathiaspiro[6.6]tridecane (**4**), is of special interest, but the problem remaining when it is used in an actual expanding system is the low molecular weight of the corresponding polymer. However, this can be resolved because we could obtain a higher molecular weight polymer ($\bar{M}_n$ 3200) by repeating the precipitation of the polymer with $\bar{M}_n$ 1500. Namely, it is possible for **4** to polymerize to a higher molecular weight polymer. So, it is suggested that a molecular design to enhance the solubility of such a monomer should cause production of a high molecular weight polymer, since the formation of low molecular weight polymer is believed to be attributed to the low solubility of the monomer. Further study based on this work will bring about useful sulfur-based expanding monomers.

References and Notes

(1) Takata, T.; Endo, T. *Prog. Polym. Sci.* **1993**, *18*, 839.
(2) Takata, T.; Endo, T. In *Expanding Monomers: Synthesis, Characterization, and Applications*; Sadhir, R. S., Luck, R. M., Eds., CRC Press: Boca Raton, FL, 1992; Chapter 3, p 63.
(3) Bailey, W. J.; Sun, R. L.; Katsuki, H.; Endo, T.; Iwama, H.; Tsushima, R.; Saigo, K.; Bitritto, M. M. In*Ring-Opening Polymerization;* Saegusa, T., Goethals, E., Eds.; ACS Symposium Series, No. 59; American Chemical Society, Washington, DC, 1977; p 38.
(4) For examples: (a) Sakai, S.; Fujinami, T.; Sakurai, S. *J. Polym. Sci., Polym. Lett. Ed.*, **1973**, *11*, 631. (b) Takata, T.; Ariga, T.; Endo, T. *Macromolecules* **1992**, *25*, 3829.
(5) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 900.
(6) Takata, T.; Endo, T. *Macromolecules* **1988**, *21*, 2314.
(7) Endo, T.; Kikkawa, A.; Uno, H.; Sato, H.; Hiza, M.; Takata, T. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 73.
(8) Backer, H. J.; Stedehouder, P. L. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 923.
(9) Smoliñski, M.; Balazy, M.; Iwamura, H.; Sugawara, T.; Kawada, Y.; Iwamura, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1106.

MA9700789