New Polymerization of Spiroorthocarbonate: Cationic Single Ring-Opening Polymerization of 2,3-Benzo-1,4,6,12-tetraoxaspiro[4.7]dodecane

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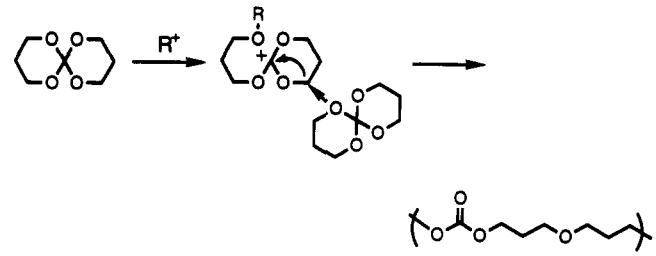
Received August 19, 1992
Revised Manuscript Received December 7, 1992

Six-membered spiroorthocarbonates (SOCs) undergo cationic ring-opening polymerization to afford poly(ether carbonate) via an isomerization process, during which a volume expansion is observed, unlike polymerization of common monomers.[1] The volume expansion is suggested to come from the characteristic polymerization through tandem double ring-opening isomerization as shown in Scheme I,[1,2] but the polymerization mechanism has not been clarified yet.[1a] A few SOCs have been reported, which polymerize by a clearly different mechanism involving initial decomposition of a SOC skeleton to a cyclic carbonate and an oxetane (Scheme II).[3,4] Analogous bicyclic (BOE) and spirocyclic *orthoesters* (SOE) are known to show no shrinkage or slight volume expansion by double ring-opening polymerization. The polymerization of SOEs[5] and BOEs[6] has been reported to occur in a single ring-opening mode to give poly(monocyclic orthoester)s with some volume shrinkage. However, similar single ring-opening polymerization of SOC has been believed not to occur, despite the fact that poly(monocyclic orthocarbonate)s can be prepared by an independent method.[7] It is important to study the polymerization behavior of SOC, because SOC is regarded as the most promising expanding monomer due to the highest degree of volume expansion of all. We have recently found SOCs (1 and 2) capable of undergoing cationic polymerization through a single ring-opening process.

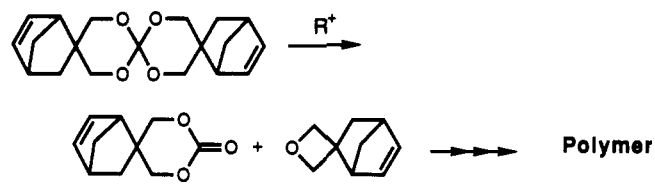
SOC 1[8] containing five- and eight-membered rings was treated with BF_3OEt_2 (5 mol %) in PhCl at 0 °C for 24 h under an argon atmosphere (Table I, run 1). By precipitation of the reaction mixture, a polymeric product (polymer A) was obtained as an *n*-hexane-insoluble fraction in 76% yield ($\bar{M}_n$ 4100 by GPC). From the *n*-hexane-soluble fraction, phenylene carbonate (benzo-1,3-dioxole-2-one) (3) was obtained in 7% yield, along with a small amount of low molecular weight polymer. In the IR spectrum of polymer A strong absorptions of ν_{C-O} and $\nu_{C=O}$ appeared at 1103–1261 and 1744 cm^{-1}, respectively. Two major signals corresponding to methylene protons were observed around 3.7 and 4.1 ppm in the ^1H NMR spectrum of the polymer A (Figure 1B).

When the polymerization of 1 with BF_3OEt_2 (5 mol %) at room temperature in $CDCl_3$ (run 2) was monitored directly by ^1H NMR, it was observed that the signal around 3.7 ppm was formed in the initial stage (in ca. 2 h) and gradually decreased to finally disappear in 30 h. Figure 1C exhibits the ^1H NMR spectrum of the final product (polymer B) obtained after 30 h. Similar results were obtained in the polymerization in chlorobenzene (run 3). A polymer showing ^1H NMR similar to that of the polymer A was obtained, when the polymerization at room temperature was stopped at 1.5 h (run 4) according to the result of the ^1H NMR monitoring. Further, when polymer A isolated was treated with BF_3OEt_2 (5 mol %) under the same conditions as those of run 1, formation of a polymer similar to polymer B was confirmed by ^1H NMR.

Scheme I



Scheme II



In order to analyze the structures of polymers A and B, a model compound, monocyclic orthocarbonate (2,2-dipentoxy-1,3-benzodioxole) (4), was prepared[9] and its ^1H NMR signals (Figure 2A) were compared with those of

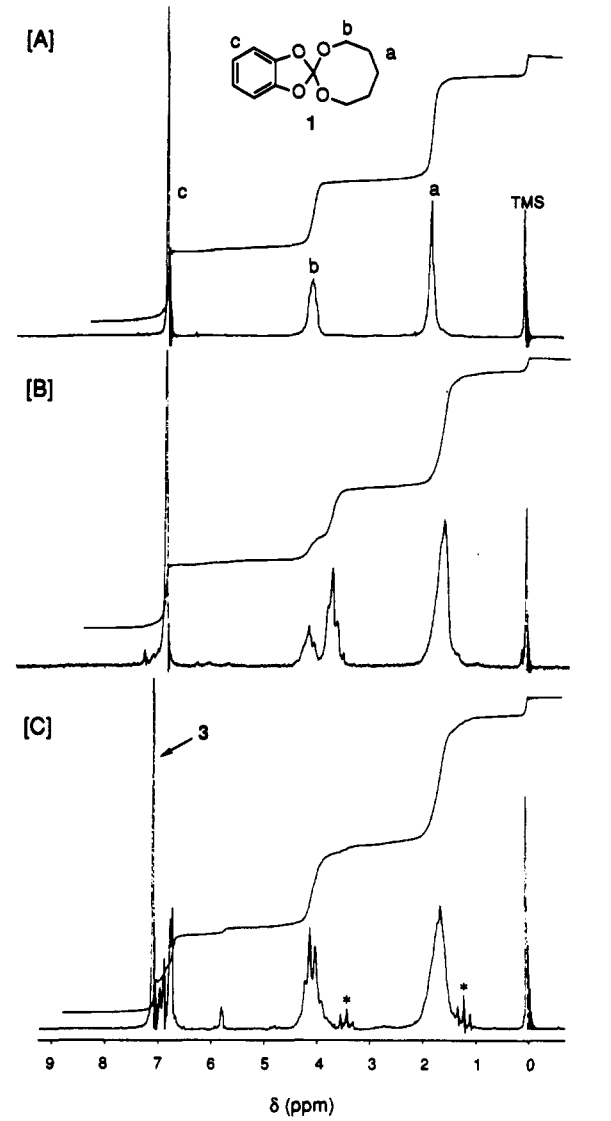


Figure 1. ^1H NMR spectra (solvent, $CDCl_3$; 60 MHz, at 27 °C) of [A] monomer 1, [B] polymer A (isolated by preparative HPLC), and [C] polymer B (crude product, containing 3 and other minor products). Asterisks in [C] denote signals derived from catalyst BF_3OEt_2.

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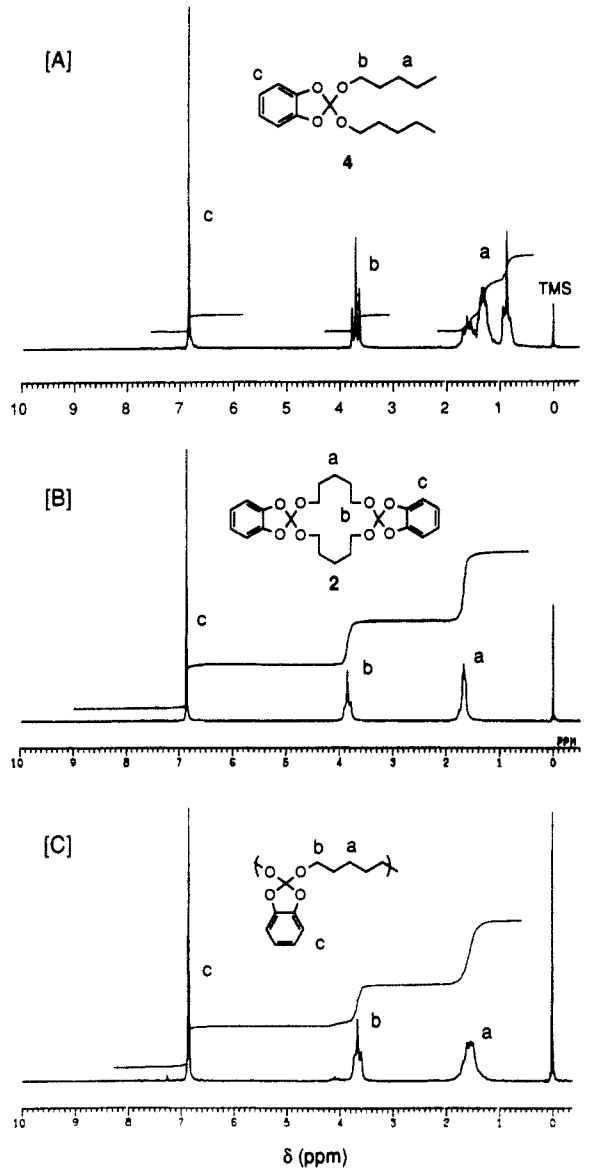


Figure 2. ^{1}H NMR spectra (solvent, $CDCl_3$; 90 MHz, at 27 °C) of [A] model compound 4, [B] monomer 2, and [C] polymer C (obtained by precipitation with *n*-hexane).

polymers A and B (Figure 1B,C). The signal around 3.7 ppm was tentatively assigned as the methylene protons adjacent to the ether oxygen of the monocyclic orthocarbonate. Further, 4 was treated with BF_3OEt_2 (5 mol %) at room temperature for 36 h when the conversion of 4 reached 100%. Isolated products were ether carbonate (5, 15%), diether (6, 10%), hydroxy ether (7, 24%), carbonate (8, 34%), 3 (22%), and orthocarbonate (9, 5%) of which structures were determined by NMR and IR spectra other than elemental analyses (Scheme III).

On the basis of the results of this model reaction in addition to the detailed ^{1}H NMR analyses of the polymers, polymer A was suggested to consist mainly of *poly(monocyclic orthocarbonate)* (unit a, Scheme IV), which probably involves the following four units in the ratio of a:(b + c):d = 68:25:7, whereas polymer B had no such unit. From the IR carbonyl absorption of 5 (1767 cm^{-1}), polymer A contained few unit b. Meanwhile, formation of an additional unit e was suggested in the ^{1}H NMR spectrum of polymer B but not in polymer A.

Monocyclic orthocarbonate unit a can be regarded to be formed by opening of only the aliphatic ring of 1, while unit b is the typical polymer unit of SOC produced by double ring-opening polymerization of 1.[1] Other units c–e

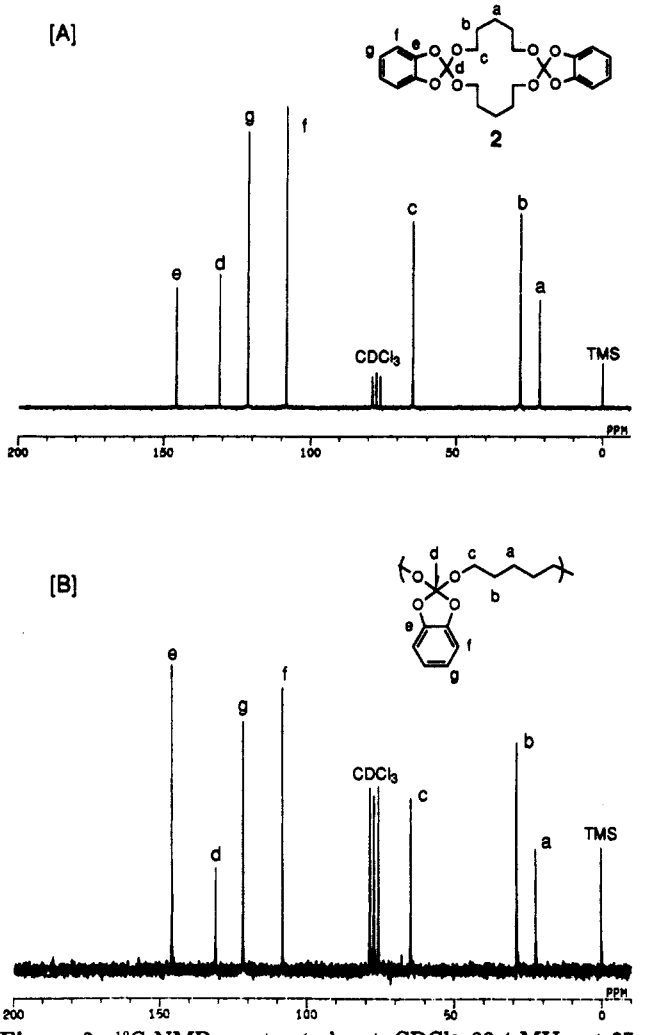


Figure 3. ^{13}C NMR spectra (solvent, $CDCl_3$; 22.4 MHz, at 27 °C) of [A] monomer 2 and [B] polymer C (obtained by precipitation with *n*-hexane).

might result by some complicated secondary reactions including elimination of 3. Since formation of poly(monocyclic orthocarbonate) like unit a has never been reported in polymerization of SOCs, the formation of unit a is very noteworthy as the first example, especially in the mechanistic aspect of polymerization of SOC which is not sufficiently clarified yet.[1]

In attempts to enhance the ratio of unit a in polymer A, a slightly higher content of unit a (a:(b + c):d = 77:15:8) was achieved by using *p*-toluenesulfonic acid as catalyst (run 5). The highest ratio of unit a (86%) was obtained in bulk polymerization with pyridinium *p*-toluenesulfonate (PPTS) at high temperature (120 °C), although the polymerization was slow (run 6). However, at higher temperatures than 120 °C, the ratio decreased (runs 7 and 8). Consequently, a polymer consisting only of unit a could not obtained from 1.

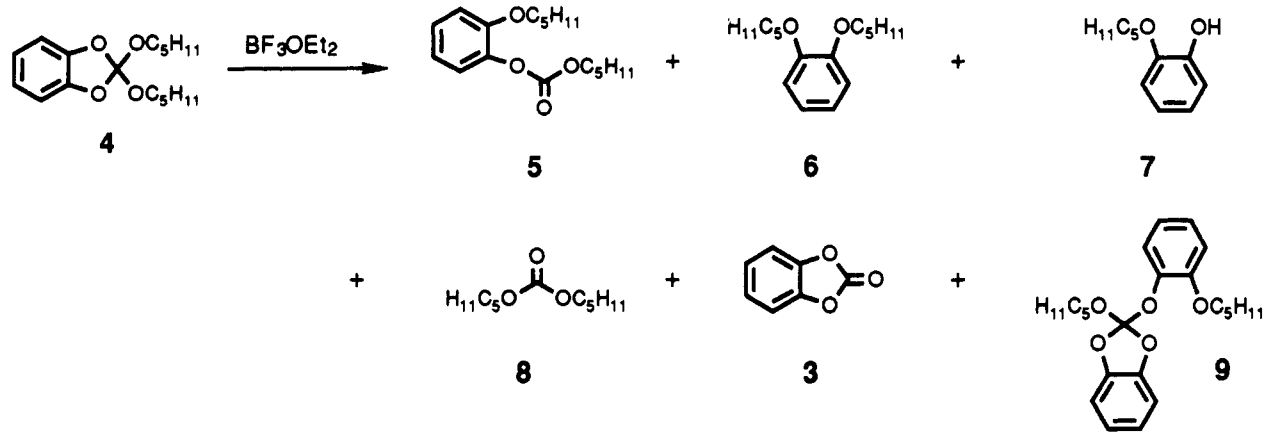
A polymer consisting mostly of unit a was obtained by cationic bulk polymerization of a 16-membered-ring-containing bis(spiroorthocarbonate) (2)[10] with pyridinium hydrochloride at 220 °C (run 10) (Scheme V). The polymerization proceeded slowly (conversion of 2: 79% for 12 h) to give 71% yield of the corresponding polymer C ($\bar{M}_n$ 12 700) with the ratio of unit a being ca. 95%, judging from its ^{1}H NMR spectrum (Figure 2C). Consistent with the proposed structure of the polymer C, the IR spectrum showed a strong ν_{C-O} absorption at 1005–1226 cm^{-1} along with an extremely weak carbonyl absorption at 1744 cm^{-1}. Furthermore, ^{13}C NMR (Figure 3B) spectra strongly

Table I
Cationic Polymerization of 1 and 2

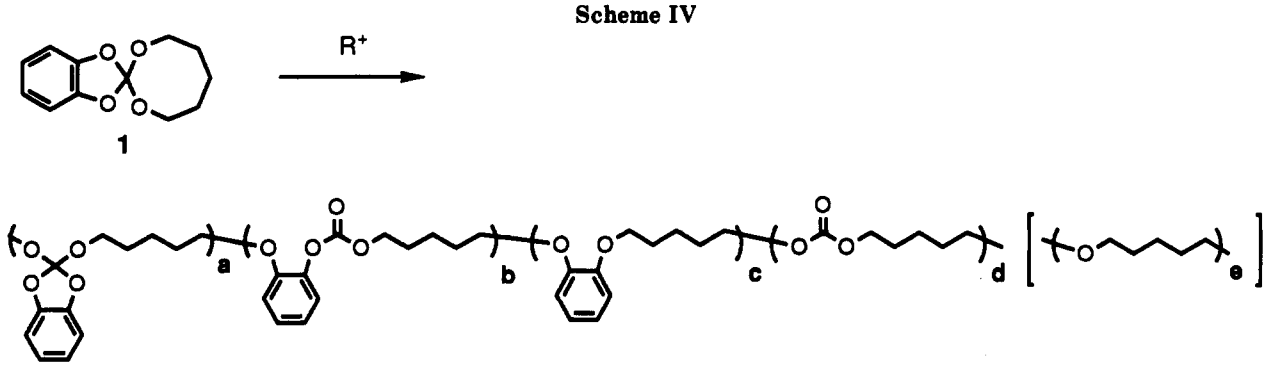
run	SOC	solv (M)	cat. (mol %)	temp, °C	time, h	conv,[a] %	yield,[b] %	$\bar{M}_w$[c]	$\bar{M}_n$[c]	structure[d] (a:(b + c):d:e), %
1	1	PhCl (2.5)	BF_3OEt_2 (5)	0	24	93	76	8800	4100	68:25:7:0
2	1	$CDCl_3$ (2.5)	BF_3OEt_2 (5)	rt	30	100	70[e]	2000	1280	0:54:38:8
3	1	PhCl (2.5)	BF_3OEt_2 (5)	rt	30	100	46	1600	1200	6:36:54:4
4	1	PhCl (2.5)	BF_3OEt_2 (5)	rt	1.5	87	85[e]	3600	1700	68:17:15:0
5	1	PhCl (2.5)	*p*-TsOH (5)	0	24	83	73	12300	7700	77:15:8:0
6	1	bulk	PPTS (5)	120	0.3	54	47	8300	5700	86:14:0:0
7	1	bulk	PPTS (5)	160	0.3	24	17	5500	3500	79:17:4:0
8	1	bulk	PPTS (5)	200	0.3	20	13	4400	2800	67:26:7:0
9	1	bulk	Py·HCl (1)	220	12	16	10	3700	2700	50:26:24:0
10	2	bulk	Py·HCl (1)	220	12	79	71	27800	12700	95:5:0:0
11	2	bulk	PPTS (10)	160	0.3	19	14	4700	3500	80:20:0:0
12	2	PhCl (1.3)	BF_3OEt_2 (10)	0	24	89	68	9500	3600	53:29:18:0

[a] Estimated by GC. [b] *n*-Hexane-insoluble polymer. [c] Estimated by GPC. [d] Estimated by ^1H NMR. [e] Polymer was separated by HPLC.

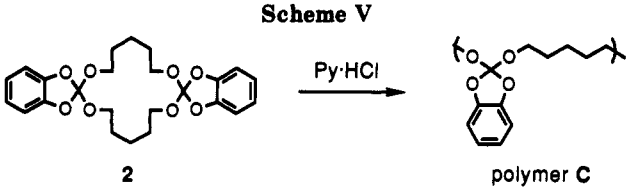
Scheme III



Scheme IV



Scheme V

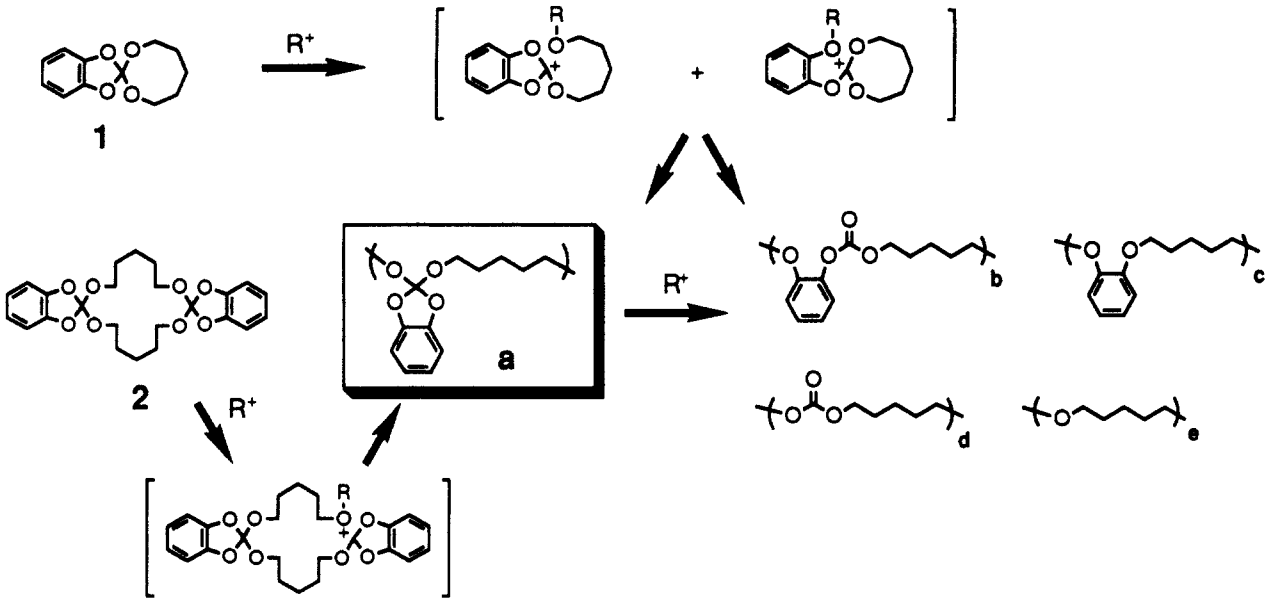


supported this monocyclic orthocarbonate structure. Thus, profoundly selective formation of poly(monocyclic orthocarbonate) was attained using **2**. Meanwhile, **1** was treated with pyridinium hydrochloride under conditions similar to those of **2**, but a polymer with a low content of unit a was obtained in only 10% yield (run 9). On the other hand, the polymerization of **2** was employed under the same conditions in which the high content of unit a was achieved in the case of **1**, but the ratio of unit a (80%) was not high (run 11). In addition, treatment of **2** with BF_3OEt_2 resulted in the formation of a polymer with a low unit a content (run 12). Consequently, unit a is favorably formed from **2** under conditions with high concentration at high temperature in the presence of weak cationic catalyst.

Major pathways of the polymerizations of **1** and **2** are, therefore, considered as follows from the obtained results (Scheme VI). Both **1** and **2** initially polymerize with a cationic catalyst to afford the poly(monocyclic orthocarbonate) or unit a, via a selective opening of the aliphatic ring but not the aromatic one. This polymer, once formed, slowly undergoes some complicated inter- and intramolecular reactions to eventually afford units b–e. Alternative pathways to units b–e via direct conversion of the monomers are also possible. Since reactivity of the two monomers would be fairly different, each highest ratio of unit a was attained under different conditions, and a polymer consisting nearly only of unit a was produced from **2**.

Thus, occurrence of a single ring-opening polymerization of SOC was first demonstrated in this work.[11,13] The obtained results should have an influence not only on the mechanism of polymerization of SOCs but also on their important function as expanding monomers.[14]

Scheme VI



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(8) A new monomer 1, 2,3-benzo-1,4,6,12-tetraoxaspiro[4.7]-dodecane, was prepared from 2,2-dichloro-1,3-benzodioxole and 1,5-pentanediol according to the method of Gross[9] with some modification. Yield: 7%. Mp: 106 °C.

(9) Gross, H.; Rusche, J.; Boruowski, H. *Justus Liebigs Ann. Chem.* **1964**, *675*, 142.

(10) A new compound 2 was prepared by the method similar to that of 1. Yield: 8%. Mp: 144–145 °C.

(11) In contrast to the polymerization behavior of 1, analogous benzo-substituted SOCs having aliphatic five- and six-membered rings (2,3-benzo-1,4,6,9-tetraoxaspiro[4.4]nonane and 2,3-benzo-1,4,6,10-tetraoxaspiro[4.5]decane) selectively polymerized to give corresponding poly(ether carbonate)s via tandem double ring-opening polymerization.[12]

(12) Komatsu, S.; Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1990**, *39*, 1532.

(13) This polymerization is also of special interest, because there has been no efficient polymerization of various aromatic and five-membered SOCs so far.

(14) The density[15] of monomers and polymers obtained in this study was measured, and an interesting result which suggested the volume expansion on polymerization to polymer consisting mainly of unit a was obtained. The details of volume change on polymerization will be reported elsewhere along with those of monomers shown in ref 11.

(15) Measured by density gradient tubes at 25 °C.