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Cationic Ring-Opening Polymerizations of Five-Membered Spiro Orthocarbonates: Unsubstituted and 2,8-Diaryl-1,4,6,9-tetraoxaspiro[4.4]nonanes

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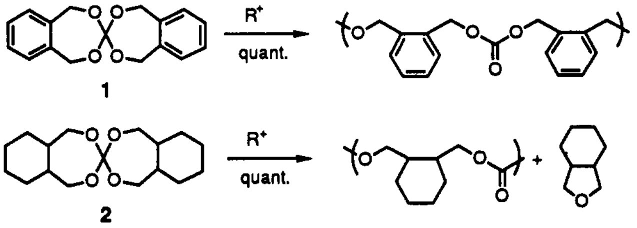
ABSTRACT: Cationic polymerizations of five-membered spiro orthocarbonates (SOCs), 1,4,6,9-tetraoxaspiro[4.4]nonane (**3**), 2,8-diphenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**4**), 2,8-bis(2-nitrophenyl)-1,4,6,9-tetraoxaspiro[4.4]nonane (**5**), were studied in detail. **4** and **5** were prepared in 74% and 17% yields, respectively, by the acid-catalyzed reactions of phenylethylene glycol and (2-nitrophenyl)ethylene glycol with tetramethyl orthocarbonate. Treatment of **4** with a catalytic amount of BF_3OEt_2 in CH_2Cl_2 at room temperature afforded phenylacetaldehyde (20%), phenylethylene carbonate (100%), and 2-benzyl-4-phenyl-1,3-dioxolane (25%), along with poly(phenylacetaldehyde) (30%). In a detailed ^1H NMR study of the reaction of **4** with BF_3OEt_2 we observed a fast reaction with complete elimination of phenylethylene carbonate. The reaction mechanism was discussed in terms of the products and their distribution. In the cationic polymerization of **5** the corresponding poly(ether–carbonate) was obtained in 50–60% yield along with cyclic carbonate (41%) without formation of (2-nitrophenyl)acetaldehyde. In the polymerization of **3**, ethylene carbonate was obtained in 70% yield along with a polymer consisting of both poly(ether–carbonate) and polyether units. In order to identify the key feature of the cationic polymerization of five-membered SOCs, the polymerization mechanism of **3** was proposed and compared with those of **4** and **5**.

Introduction

Spiro orthocarbonate (SOC) is a useful monomer which shows expansion in volume on cationic ring-opening isomerization polymerization to poly(ether–carbonate).[1–5] However, this characteristic behavior is limited to six-membered SOCs. The polymerization behavior of SOC depends clearly on its number of ring members. Previously, Sakai et al. studied cationic polymerizations of five- to seven-membered SOCs and proposed a general scheme which indicated the ring size-dependent attacks of monomer at three different positions of propagating stable cationic species.[6] In the polymerization of unsubstituted seven-membered ring SOC, poly(butylene carbonate) was selectively obtained along with tetrahydrofuran as an elimination product. We have recently studied the polymerization of new seven-membered SOCs, benzene ring-fused SOC **1** and cyclohexane ring-fused SOC **2**, and found that although the polymerization of **2** involves complete elimination of a tetrahydrofuran derivative like that of unsubstituted one, **1** polymerizes without such elimination to the corresponding poly(ether–carbonate) and shows 6.6% expansion in volume on polymerization (Scheme I).[7]

Thus, the selective ring-opening isomerization polymerization of SOC could be achieved with the seven-membered SOC as well as six-membered ones. Meanwhile, it is very significant to prepare five-membered SOCs which undergo selective ring-opening isomerization polymerization and thereby show volume expansion on polymerization, because readily available 1,2-diols can be used for their synthesis.[8] Up to now, however, no five-membered SOC monomer polymerizing via efficient ring-opening isomerization process has been reported. Only a report of polymerization of the unsubstituted five-membered SOC 1,4,6,9-tetraoxaspiro[4.4]nonane (**3**) has appeared so far,[6] in which ring-opening isomerization polymerization with elimination of a small molecule is observed. Now, we have examined the polymerization behavior of five-membered SOCs in detail in order to obtain the basis for molecular design of such useful SOCs capable of undergoing selective ring-opening isomerization polymerization. This study is also exhibited to exert some influence on the whole chemistry of SOCs. In this report, new five-membered SOCs having phenyl and 2-nitrophenyl groups

Scheme I



are synthesized and their polymerization behaviors are studied in comparison with that of **3**.

Experimental Section

^{1}H NMR spectra were recorded on JEOL PMX 60SI and FX-100 spectrometers, using tetramethylsilane (TMS) as internal standard in deuteriochloroform at 27 °C. FT-IR spectra were obtained with a JASCO FT/IR-3 instrument at 25 °C. Molecular weight ($\bar{M}_n$ and $\bar{M}_w$: number and weight average molecular weights) and its distribution ($\bar{M}_w/\bar{M}_n$) were estimated by gel permation chromatography (GPC) with a Toyo Soda HPLC CCP & 8000 system, equipped with polystyrene gel columns, using tetrahydrofuran as solvent, flow rate 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Solvents were purified by distillation according to the usual methods and stored over molecular sieves (4A). BF_3OEt_2 was distilled over CaH_2.

Synthesis of 3. To a heterogeneous mixture of tetramethyl orthocarbonate (1.36 g, 10 mmol) and ethylene glycol (1.24 g, 20.0 mmol) in dry xylene (33 mL) was added anhydrous *p*-toluenesulfonic acid (57 mg, 0.03 mmol). The mixture was heated at a bath temperature of 110 °C for 9 h. During the reaction methanol was removed by distillation. The resulting mixture was cooled to room temperature, and then a few drop of triethylamine was added to it. The mixture was washed with aqueous $NaHCO_3$ and extracted with ether. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated. The residual solid material was recrystallized from methanol: yield 50%; mp 121–121.5 °C (MeOH); ^{1}H NMR ($CDCl_3$, ppm) δ 4.13 (s); IR (KBr, cm^{-1}) 2912, 1568, 1367, 1257, 1217, 1059, 1006, 948.

Synthesis of 4. To a mixture of tetramethyl orthocarbonate (2.04 g, 15.0 mmol) and phenylethylene glycol (4.15 g, 30 mmol) in dry xylene (30 mL) was added anhydrous *p*-toluenesulfonic acid (57 mg, 2 mol %). The resulting mixture was stirred for a few minutes at room temperature and methanol was promptly distilled off under reduced pressure (50 mmHg) at room temperature. To the residual mixture was added a few drops of triethylamine. The mixture was evaporated, and the residual crude product was purified by column chromatography on silica gel (Wako gel-C200) (solvent, benzene): yield 74% (white crystal); mp 58 °C (benzene/hexane). ^{1}H NMR ($CDCl_3$, ppm) δ 4.00 (m, 2 H), 4.43 (m, 2 H), 5.33 (m, 2 H), 7.38 (m, 10 H); IR (KBr, cm^{-1}) 2900, 1499, 1454, 1311, 1288, 1188, 1107, 1014, 941; Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.07; H, 5.77.

Synthesis of 5. To a mixture of tetramethyl orthocarbonate (0.80 g, 5.85 mmol) and (2-nitrophenyl)ethanediol (2.14 g, 11.7 mmol) in dry benzene (70 mL) was added anhydrous *p*-toluenesulfonic acid (42.6 mg, 0.23 mol %). The mixture was heated at a bath temperature of 80 °C for 3 h. During the reaction methanol was removed by distillation. The resulting mixture was cooled to room temperature, and a few drop of triethylamine was added to it. The mixture was washed with aqueous $NaHCO_3$ and extracted with ether. The organic layer was dried over anhydrous $MgSO_4$ and then evaporated. The residual solid material was recrystallized from methanol: yield 17% (white crystal); mp 175–176 °C (benzene); ^{1}H NMR ($CDCl_3$, ppm) δ 4.17 (dd, J = 7 Hz, 9 H, 2 H), 4.95 (dd, J = 7 Hz, 9 Hz, 2 H), 6.00 (dd, J = 7 Hz, 2 H), 7.20–8.20 (m, 8 H); IR (KBr, cm^{-1}) 2900, 1612, 1528, 1336, 1198, 1070, 955; Anal. Calcd for $C_{17}H_{14}O_8N_2$: C, 54.50; H, 3.74; N, 7.48. Found: C, 54.10; H, 3.50; N, 7.48.

Cationic Polymerization. The polymerization of **3**–**5** was carried out in either a two-necked flask or an NMR sample tube.

Typical Procedure. 3 (132 mg, 1.00 mmol) and stirrer bar were placed in an argon-purged two-necked flask to which was introduced catalyst BF_3OEt_2 (6.5 μl, 5 mol %) dissolved in CH_2Cl_2 (0.5 mL) by a syringe, and the flask was sealed off. The mixture was stirred at a set temperature for 3 h. The polymerization was terminated by adding a few drop of triethylamine. The resulting mixture was diluted with CH_2Cl_2 (2–4 mL) and precipitated with ether (100 mL). The ether-insoluble part was isolated by centrifugal separation. The ether-soluble part was concentrated by evaporation under reduced pressure.

When the polymerization was carried out in an NMR sample tube, monomer and BF_3OEt_2 (**3**, 5 mol %; **4**, 1–3 mol %) dissolved in the solvent (500 μL) were introduced by syringe under an argon atmosphere.

Products of the Polymerization of 3. Ethylene carbonate and dioxane were identified by ^{1}H NMR spectroscopy in comparison with their authentic samples. Ethylene carbonate was isolated from the water-soluble fraction in 70% yield. IR, NMR, and $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) data for the ether-insoluble fraction were as follows: ^{1}H NMR ($CDCl_3$, ppm) δ 3.60 (s), 3.69 (br), 4.29 (br); IR (neat, cm^{-1}) 1745, 1265, 1108, 1040; $\bar{M}_n$ 1000; $\bar{M}_w/\bar{M}_n$ 1.27.

Products of the Polymerization of 4. Phenylacetaldehyde (**7**) and 2-benzyl-4-phenyl-1,3-dioxolane (**8**) were identified by ^{1}H NMR spectroscopy in comparison with their authentic samples prepared independently. Phenylethylene carbonate (**6**) was isolated from the reaction mixture by distillation and identified by physical and spectral data (mp 56 °C). Poly(phenylacetaldehyde) (**9**) was identified by comparison with its authentic sample prepared independently by the polymerization of **7** with BF_3OEt_2.

Products of the Polymerization of 5. Polymer **14** and (2-nitrophenyl)ethylene carbonate (**15**) were separated by preparative HPLC. The yield of **15** was 41% from ^{1}H NMR analysis of the reaction mixture. **15** was identified by its spectral data: ^{1}H NMR ($CDCl_3$, ppm) δ 4.35 (dd, J = 6 Hz, 7.8 Hz, 1 H), 5.25 (dd, J = 6 Hz, 1 H), 6.37 (dd, J = 6 Hz, 7.8 Hz, 1 H), 7.5–8.5 (m, 4 H); IR (KBr, cm^{-1}) 1805, 1620, 1512, 1350, 1056.

2,5-Diphenyl-1,4-dioxane (12). Phenylethylene oxide (30.0 g, 0.25 mmol) was dropped into a solution of stannic chloride (0.57 mL, 5 mmol) in benzene (17.8 mL) at 0 °C for 30 min, and then the solution was stirred for 6 h at the same temperature. The mixture was washed with 10% NaOH solution and then water. The organic layer was dried, evaporated, and distilled under a reduced pressure. From the collected distillate (bp 160–163 °C/0.17–0.9 mmHg, 1.20 g), colorless crystals were isolated (1.00 g, 4%) by filtration and recrystallized from benzene: mp 169–170 °C (lit. 167–169 °C[13,14]); ^{1}H NMR ($CDCl_3$, ppm) δ 3.67 (dd, J = 9.9 Hz, 11.4 Hz, 2 H), 4.05 (dd, J = 2.8 Hz, 11.4 Hz, 2 H), 4.70 (dd, J = 9.9 Hz, 11.4 Hz, 2 H); IR (KBr, cm^{-1}) 2862, 1495, 1451, 1119, 902, 745.

2-Benzyl-4-phenyl-1,3-dioxolane (8). To a mixture of phenylacetaldehyde dimethyl acetal (5 g, 36.1 mmol) and phenylethylene glycol (5 g, 36.2 mmol) was added anhydrous *p*-toluenesulfonic acid (34.4 mg, 1.81 mmol). The mixture was heated and methanol formed during the reaction was removed by distillation. The mixture was diluted with CH_2Cl_2 (20 mL) and washed with diluted Na_2CO_3 solution and then water. After the mixture was dried over anhydrous $MgSO_4$, the solvent was removed, and the product was distilled under a reduced pressure. Pale yellow liquid (7.82 g) was obtained: yield 90%; bp 128 °C/0.2 mmHg (lit.[10,11] 187 °C/14 mmHg); ^{1}H NMR ($CDCl_3$, ppm) δ 3.13 (d, J = 5 Hz, 2 H), 3.63 (dd, J = 6.4 Hz, 7.3 Hz, 1 H), 4.10 (dd, J = 7.3 Hz, 8.2 Hz, 1 H), 4.93 (dd, J = 7.3 Hz, 8.2 Hz, 1 H), 5.23 (t, J = 5 Hz, 1 H); IR (neat, cm^{-1}) 3063, 2878, 1496, 1134, 1081, 1041, 756.

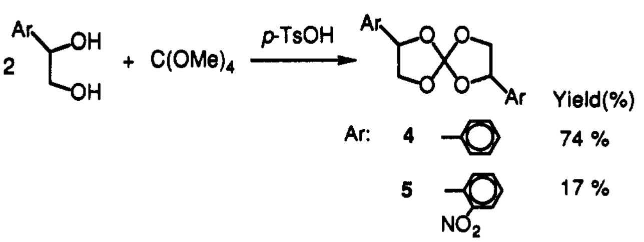
Poly(phenylacetaldehyde) (9). Phenylacetaldehyde (96 mg, 0.80 mmol) was placed in an argon-purged NMR sample tube. BF_3OEt_2 (0.04 mmol, 5 mol %) dissolved in deuteriochloroform (500 μL) was added to it. The tube was allowed to stand at 25 °C for 6 h. After the addition of a few drop of triethylamine to the mixture followed by removal of the solvent under a reduced pressure, the residual viscous liquid was subjected to measurements by ^{1}H NMR and IR spectroscopy: ^{1}H NMR ($CDCl_3$, ppm) δ 2.67 (br), 7.20 (br); IR (neat, cm^{-1}) 3029, 2924, 1604, 1495, 1140, 1046.

Reaction of SOC 4 with Phenylacetaldehyde (7). To a mixture of 0.14 g (0.50 mmol) of **4** and 0.03 g (0.25 mmol) of **7** placed in an argon-purged NMR sample tube was added BF_3OEt_2 (0.04 mmol, 5 mol %) dissolved in deuteriochloroform (500 μL). The tube was allowed to stand at 25 °C for 5 h. In the ^{1}H NMR spectrum of the mixture, 2-benzyl-4-phenyl-1,3-dioxolane (**8**) was confirmed and the yield of **8** was calculated to be 40%.

Results and Discussion

Previously, we have postulated that the efficient isomerization polymerization of **1** can result from the selective attack of monomer at the benzylic carbon of the propa-

Scheme II



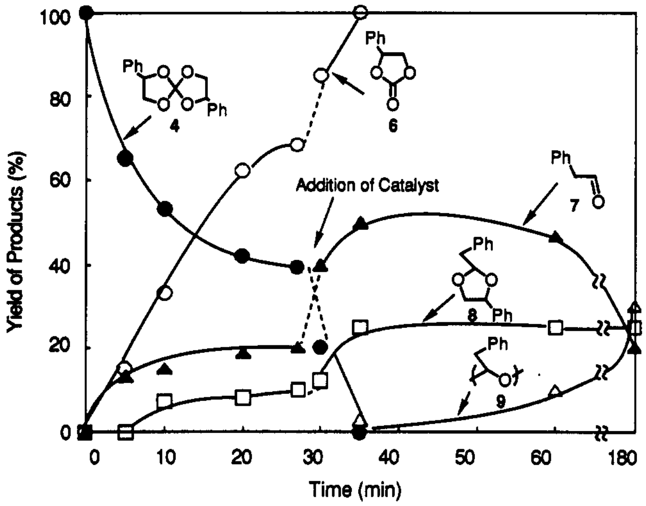


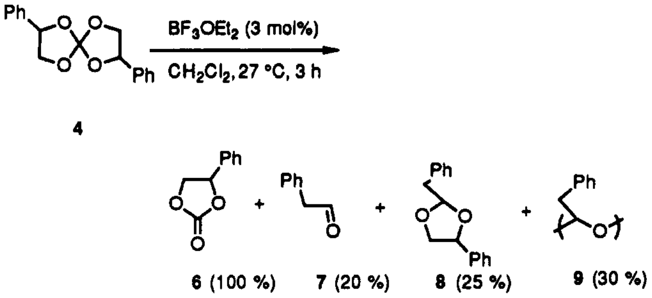
Figure 1. Time-yield of curves of the cationic polymerization of 4 with BF_3OEt_2 in $CDCl_3$ (0.5 M) at 27 °C. The first addition of BF_3OEt_2 (1 mol %) was followed by further addition of BF_3OEt_2 (2 mol %) after 30 min. Key: (●) SOC 4; (○) phenylethylene carbonate (6); (▲) phenylacetaldehyde (7); (□) 2-benzyl-4-phenyl-1,3-dioxolane (8); (△) poly(phenylacetaldehyde) (9).

gating cationic species, like those of six-membered SOCs.[7] If it is actually operative in other systems, a five-membered SOC having a phenyl group on the ring (i.e. having a benzylic ring carbon capable of being attacked) should also undergo the desired isomerization polymerization. Thus a new SOC monomer, 2,8-diphenyl-1,4,6,9-tetraoxaspiro[4.4]nonane (4), was prepared by the acid-catalyzed condensation of phenylethylene glycol and tetramethyl orthocarbonate at room temperature in the presence of p-toluenesulfonic acid. Since 4 was not so stable under the reaction conditions, short reaction time and prompt workup are required. Characterization of 4 was easily accomplished by the physical and spectral data as well as elemental analysis data, which are listed in the Experimental Section.

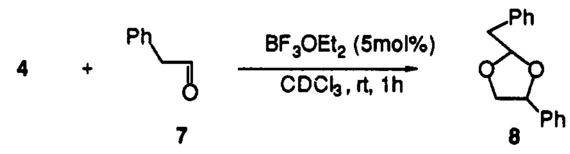
SOC 4 was treated with 5 mol % of BF_3OEt_2 in CH_2Cl_2 ([C] = 3.9 M) in a sealed tube at room temperature. 4 was consumed within 1 h and phenylethylene carbonate (6) was obtained quantitatively. Other products were phenylacetaldehyde (7, 20%) and 2-benzyl-4-phenyl-1,3-dioxolane (8, 25%) including a low molecular weight polymer with a number-average molecular weight of 470 by GPC. The polymer appeared to be poly(phenylacetaldehyde) (9), because the ^1H NMR spectrum of the reaction mixture showed a characteristic proton signal at 2.5 ppm corresponding to the methylene of the benzyl group.

To clarify details of the reaction, time-yield curves of the products were drawn from the results of the ^1H NMR study of the reaction at 25 °C in $CDCl_3$ (Figure 1). There was no essential difference between solvents CH_2Cl_2 and $CDCl_3$ in the reaction progress and the final product distribution.

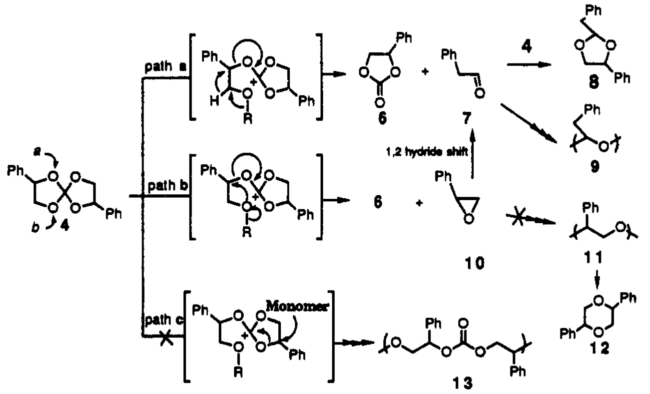
Scheme III



Scheme IV



Scheme V

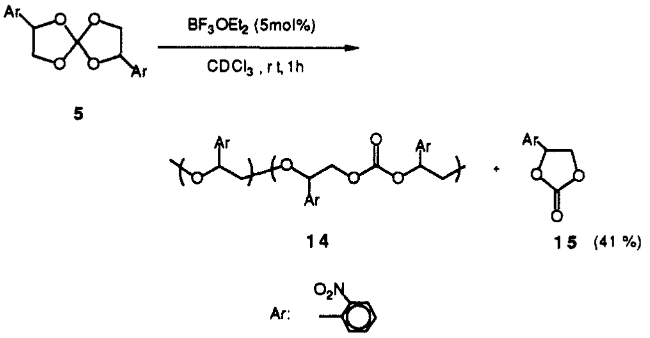


Under the conditions with 1 mol % of BF_3OEt_2, the consumption of 4 stopped at ca. 30 min, probably due to a certain termination. After addition of additional BF_3OEt_2 (2 mol %, total 3 mol %), as shown in Figure 1, 4 disappeared immediately, and accordingly, the yields of the products were suddenly changed. An increase of the yield of 6 is exactly proportional to the decrease of that of 4, clearly indicating quantitative direct formation of 6 from 4. Phenylacetaldehyde (7) is formed from the beginning of the reaction, and its yield increases according to the progress of the reaction, but is not corresponding directly to the conversion of 4. Formation of dioxolane (8) and the polymer 9 is confirmed after certain induction periods.

The results of Figure 1 and the following experimental result suggest that the product 8 is formed by acid-catalyzed reaction of the product 7 with residual 4. Namely, the reaction of 7 with 4 in the presence of BF_3OEt_2 (5 mol %) in CH_2Cl_2 at room temperature for 3 h gave the dioxolane 8 in 32% yield. This reaction is consistent with Barton's result[12] that 3 serves as an acetalization agent for carbonyl compounds in the presence of a Lewis acid. Consequently, 8 is a secondary product derived from 4 and 7. Similarly, the polymer 9 is formed as a secondary product by cationic polymerization of 7. These results agree with the presence of the induction period in the formation of 8 and 9 in Figure 1.

Thus, the mechanism of the reaction of 4 can be illustrated in Scheme V. The above observations undoubtedly demonstrate no occurrence of the ring-opening isomerization polymerization leading to poly(ether-carbonate) (13) (path c). Therefore, the acid-catalyzed reaction of 4 proceeds along two possible pathways (path a and path b). Path b involves acid-catalyzed decomposition to 6 and phenylethylene oxide (10) via a or b attack at 4, whereas path a gives 6 and 7 through decomposition with a 1,2-hydride shift. On the other hand, Lewis acid-

Scheme VI



catalyzed rearrangement of 10 to 7 is a known process.[13] Furthermore, 7 can react with 10 to yield 8, because acid-catalyzed reaction of epoxide and aldehyde is reported to give the corresponding acetal.[14,15] In fact, BF_3OEt_2-catalyzed reaction of 7 with 10 produced 8, along with polymeric products (probably 9 and/or 11).

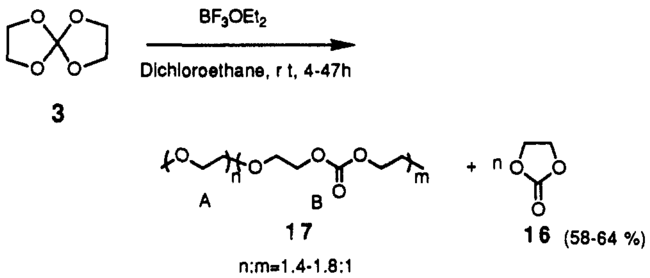
Therefore, both paths a and b are somewhat feasible. However, path b can be ruled out by the following observation and control experiment. Cationic polymerization of 10 is reported to afford 2,5-diphenyl-1,4-dioxane (12) as a byproduct other than poly(phenylethylene oxide) (11). Meanwhile, when 10 was treated with BF_3OEt_2 under the same conditions, phenylacetaldehyde (7) was mainly formed (20%) and 10 remained (20%) at the initial stage (ca. 10 min). At the last stage, both acetal 8 and polymer 9 were detected besides 7. Although 10 should be observed if 10 is actually formed, neither 10 nor 12 was detected in the reaction mixture of 4. Therefore these results obviously exclude the intervention of path b. Thus, the BF_3OEt_2-catalyzed reaction of 4 is concluded to proceed only along path a.

Lack of polymerizability of 4 obtained by introduction of a phenyl group to 3 seems to come from the formation of the stable benzylic cation in the treatment with a Lewis acid, followed by a hydride shift to eventually produce phenylacetaldehyde (7) and phenylethylene carbonate (6) (Scheme V, path a). In order to confirm it, SOC having a 2-nitrophenyl group (5), which would be expected to destabilize the benzylic cation, was synthesized in 17% yielded by the same procedure as 4 (Scheme II).

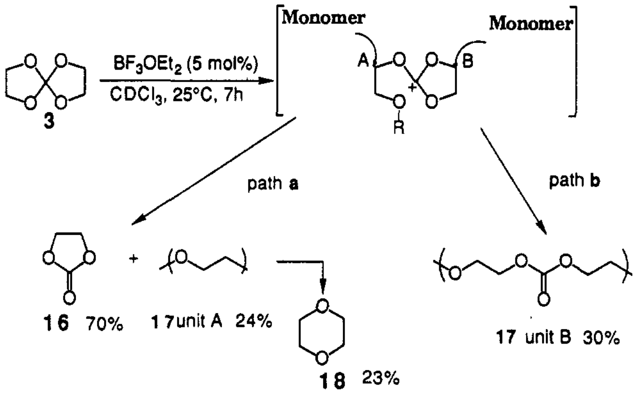
Cationic polymerization of 5 with BF_3OEt_2 (5 mol %) in $CDCl_3$ (2 M) afforded a low molecular weight polymer (14, $\bar{M}_n$ = 500–600) along with corresponding five-membered cyclic carbonate 15, but no aldehyde product was detected by ^1H NMR spectroscopy and HPLC. The polymer 14 had an absorption at 1740 cm^{-1} (C=O) in the IR spectrum and a multiplet methylene signal adjacent to ether oxygen at 3.5–4.0 ppm in the ^1H NMR spectrum. From these spectral data for 14, it is concluded that 14 has both polyether and poly(ether–carbonate) units. Although the exact ratio of these units could not be determined from the ^1H NMR data due to the broad signals, polyether: poly(ether–carbonate) was estimated to be 40:60–50:50 from the slightly larger signal at 3.5–4.8 ppm of methine and methylene protons bound to the ether oxygen than that at 5.0–5.8 ppm assignable to the methine and methylene protons adjacent to the carbonate oxygen. This result suggests the isomerization polymerization of 5 predominated over the polymerization with elimination of cyclic carbonate.

As a result, introduction of a 2-nitrophenyl group to 3 prevents formation of aldehyde and eventually causes partial isomerization polymerization of 5 by making the corresponding benzylic cation unstable. The polymerization behavior of 5 which involved isomerization polymerization along with elimination of five-membered cyclic carbonate is similar to that of alkyl-substituted five-membered SOCs.[16] Thus, as expected, the formation of the benzyl cation consequently results in the elimination of phenylacetaldehyde (7) in the cationic polymerization of 4.

Scheme VII



Scheme VIII



Previously, Sakai et al. communicated that, in BF_3OEt_2-catalyzed polymerization of 3, a viscous polymer ($\bar{M}_n$ ca. 1000) was obtained in 10–80% yield in 4–47 h, which consisted of two units A (17) and B (19) (Scheme VII) in a molar ratio of 1.4–1.8:1 (i.e., 58:42–64:36).[6] Namely, ring-opening isomerization polymerization of 3 actually takes place but the results are rather complicated and details are unclear.[6] In order to investigate the polymerization behavior of 3 thoroughly, we have studied it in detail and compared the results with those of 4 and 5.

Cationic polymerization of 3 with BF_3OEt_2 (5 mol %) was carried out in CH_2Cl_2 (1 M) at room temperature for 7 h in which time 3 completely disappeared. Ether-insoluble polymer (34 % yield) with $\bar{M}_n$ ca. 1000 (by GPC) was obtained. In the ^1H NMR spectrum of the polymer appeared a singlet at 3.60 ppm, which was attributed to the signal of poly(ethylene oxide) (unit A), and two broad signals at 3.69 and 4.29 ppm assignable to two methylenes adjacent to ether and carbonate oxygens of poly(ether–carbonate) (unit B), respectively (Scheme VII). IR absorptions at 1745 cm^{-1} (C=O), 1108, and 1040 cm^{-1} (C—O), in addition to these ^1H NMR data, agreed with the polymer structure consisting of the above two subunits. As a result, the unit ratio n:m was 56:44, being almost the same as that reported by Sakai et al.[2] From the unimodal GPC peak of the polymer, the two repeating units (A and B) undoubtedly form a single copolymer in which these units are involved in a random manner, since both paths a and b most likely have the common propagating cationic species shown as Scheme VIII. From the ether-soluble fraction, ethylene carbonate (16) was collected in 70% yield, while 1,4-dioxane (3.36 (s) ppm in ^1H NMR spectrum) was detected in a yield of 23%, as determined by ^1H NMR analysis. 1,4-Dioxane (18) should be produced by acid-catalyzed reaction of poly(ethylene oxide) once

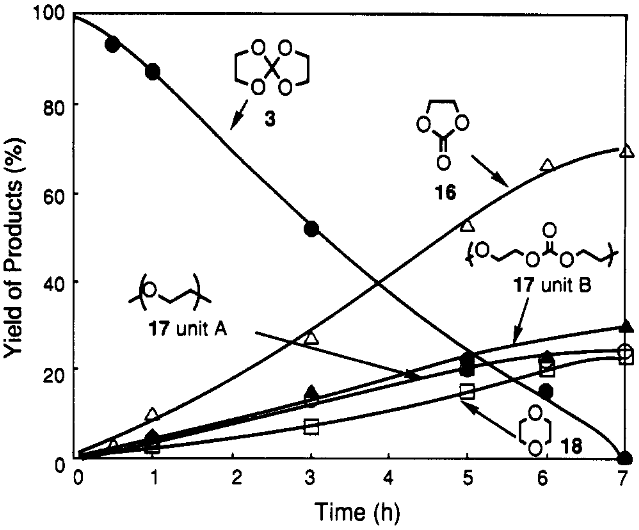


Figure 2. Time-yield curves of the cationic polymerization of **3** with BF_3OEt_2 (1 mol %) in $CDCl_3$ at 27 °C. Key: (●) SOC **3**; (△) ethylene carbonate (**16**); (○) polyether unit **17** unit A; (□) 1,4-dioxane (**18**); (▲) poly(ether–carbonate) unit **17** unit B.

produced (unit A), as reported.[17] Consequently, as shown in Scheme VII, the polymerization of **3** is concluded to proceed via both paths a and b in the ratio of 3:7.

Figure 2 indicates time-yield curves drawn up from the results of ^1H NMR study of the reaction of **3** with BF_3OEt_2 in $CDCl_3$ at 25 °C. The reaction profile was entirely similar to that of the reaction employed in CH_2Cl_2. In accordance with the above discussion, the yield of ethylene carbonate (**16**) increased in proportion to the conversion of **3**. Formation of 1,4-dioxane (**18**) suggests existence of a fast equilibrium between **17** unit A and **18** in the presence of such acid catalyst, because **18** would be observed early in the reaction. A similar result is reported in the cationic polymerization of ethylene oxide.[17]

In comparison of the polymerization behaviors of the three monomers **3–5**, **3** and **5** react much slower than **4**. Unsubstituted six-membered SOC, 1,5,7,11-tetraoxaspiro[5.5]undecane, which undergoes perfect ring-opening isomerization polymerization, polymerizes very sluggishly (16 h) under similar conditions.[6] Therefore, the slower reaction seems to result in the ring-opening isomerization polymerization, while the faster reaction might involve decomposition processes like paths a of Schemes V and VII. In other words, these two reactions can be competitive. If it is actually operative, no ring-opening isomerization should be observed in the case of **4**. In fact, no corresponding polymer was obtained. Namely, decomposition of **4** via a 1,2-hydride shift leading to phenylacetaldehyde (**7**) is so fast due to the presence of the cation-stabilizing phenyl group that slow isomerization polymerization is exclusively suppressed, giving no polymer derived by ring-opening isomerization polymerization of **4**. This would be consistent with the fact that no corresponding aldehyde like phenylacetaldehyde found in the case of **4** was detected in the cationic polymerization of **5** having a 2-nitrophenyl group as a cation-destabilizing group, in which the corresponding polymer **14** was formed through a ring-opening isomerization process.

Thus, in this work characteristic features of the cationic polymerization of five-membered SOCs could be clarified. As a result, the introduction of aryl groups on the five-membered rings did not result in the selective ring-opening isomerization polymerization of five-membered SOCs. The results obtained in this study, therefore, suggest that the successful ring-opening isomerization polymerization of the seven-membered SOC (**1**)[7] may not be enhanced by the introduction of a benzylic group. Consequently, new five-membered SOCs are envisaged on the basis of this new idea. Further studies based on new molecular designs are in progress in which novel five-membered SOCs capable of undergoing selective ring-opening isomerization polymerization will be synthesized.

References and Notes

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Registry No. **3**, 24471-99-6; **3** (homopolymer), 97917-19-6; **4**, 134110-57-9; **4** (homopolymer), 141510-26-1; **5**, 141510-24-9; **5** (homopolymer), 141510-27-2; **6**, 4427-92-3; **7**, 122-78-1; **8**, 4362-20-3; **9** (homopolymer), 33724-68-4; **12**, 24407-16-7; **15**, 141510-25-0; $HO(CH_2)_2OH$, 107-21-1; tetramethyl orthocarbonate, 1850-14-2; (2-nitrophenyl)ethanediol, 51673-59-7; ethylene carbonate, 96-49-1; dioxane, 123-91-1; phenylacetaldehyde dimethyl acetal, 101-48-4; phenylethylene glycol, 93-56-1.