

Copolymerization Utilizing an Equilibrium Polymerization System: Cationic Copolymerizations of 1,4,6-Trioxaspiro[4.6]undecane with 2-Methyl-1,4,6-trioxaspiro[4.5]decane and 2-Methyl-1,4,6-trioxaspiro[4.4]nonane

Satoyuki Chikaoka, Toshikazu Takata, and Takeshi Endo*

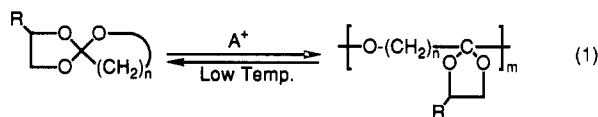
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received November 29, 1990; Revised Manuscript Received May 17, 1991

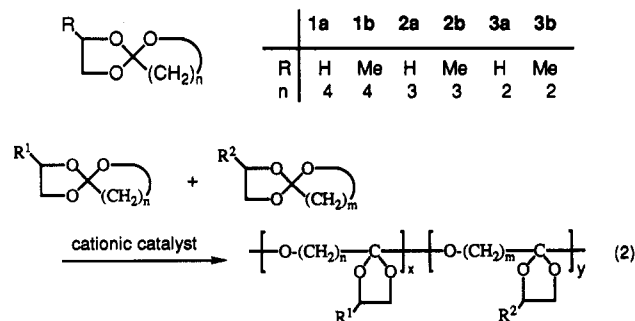
ABSTRACT: The cationic copolymerization of nonhomopolymerizable spiroorthoesters with a spiroorthoester as a comonomer capable of affording a homopolymer, poly(cyclic orthoester), was studied. The spiroorthoesters (SOEs) 2-methyl-1,4,6-trioxaspiro[4.5]decane (**2b**) and 2-methyl-1,4,6-trioxaspiro[4.4]nonane (**3b**), which could not give any homopolymer, were copolymerized with 1,4,6-trioxaspiro[4.6]undecane (**1a**) under cationic conditions. The incorporation of the **2b** or **3b** unit into the obtained copolymer was confirmed by ^1H NMR spectroscopy. The content of **2b** or **3b** in the copolymers was varied by changing the feed ratio. **3b** showed a higher copolymerizability toward **1a** than did **2b**. The structure of the obtained copolymers was suggested as poly(cyclic orthoester), which was formed via single ring opening of the ether rings of the SOEs, from the spectral data, the structure of the homopolymer of **1a**, and the results of the reactions of the SOEs (**1**, **2**, and **3**) with acetyl chloride.

Introduction

Spiroorthoesters (SOE) are known as monomers which show no shrinkage on polymerization affording poly(ether ester)s.¹ Recently, we have found a new polymerization in which SOEs polymerize cationically at low temperature ($<-40^\circ\text{C}$) to give a single ring-opened poly(cyclic orthoester)s (eq 1).^{2,3} In this case the SOE having a seven-membered ether ring ($n = 5$) can undergo a single ring-opening polymerization, although the SOEs having six- and five-membered ether rings ($n = 4$ or $n = 3$) afforded no corresponding polymers.



The ring size dependent polymerizability is explained in terms of a difference of strain energy of the SOEs,^{2,4} since the release of strain energy is considered as the driving force of the polymerization. Furthermore, we have suggested that the single ring-opening polymerization of SOE belongs to one of the equilibrium polymerizations.² The inertness of the SOEs having six- and five-membered ether rings toward acid catalyst can be attributed to the equilibrium polymerization: The equilibrium in the polymerization of these SOEs is largely shifted to the left side (monomer state), and consequently no polymer can be observed, although the ring opening of the SOEs certainly occurs. If this is actually operative, SOEs having no homopolymerizability may be incorporated into a polymer by copolymerization with a homopolymerizable SOE monomer. This type of copolymerization is achieved to actually give the corresponding copolymer,^{5,6} for example, between 2,2-bis(chloromethyl)oxetane and tetrahydropyran.⁷ In this paper, we describe the results of the cationic copolymerization of SOEs (**2** and **3**) having no homopolymerizability with SOE (**1**) having homopolymerizability.



Experimental Section

Materials. Tin(IV) chloride (Wako Pure Chemical Industries, Ltd., >97%) was distilled under nitrogen and stored in an ampule tube under an argon atmosphere. SOEs (**1a**, **1b**, **2a**, **2b**, **3a**, and **3b**) were prepared from ethylene oxide (Capox 30, Nihon Gas Sakkin Kogyo Co., Ltd., 30% content, diluted with carbon dioxide) or propylene oxide (Tokyo Kasei Kogyo Co., Ltd., >98%), and the corresponding lactones (Tokyo Kasei Kogyo Co., Ltd., >98%) were prepared according to Bodenbenner's method with some modifications.⁸

Synthesis of SOE: General Procedure. Ethylene oxide or propylene oxide (0.4 mol) dissolved in CCl_4 (40 mL) was added dropwise at 0°C to a mixture of a lactone (0.2 mol) and $\text{BF}_3\cdot\text{OEt}_2$ (1.26 mL, 0.01 mol) in CCl_4 (40 mL). The CCl_4 solution of ethylene oxide was prepared by bubbling gaseous ethylene oxide containing carbon dioxide into CCl_4 at -30°C . The mixture was stirred for 4 h at 0°C and then was washed with 1 M aqueous NaOH. The organic layer was dried over anhydrous magnesium sulfate and was evaporated. The residue was distilled under vacuum.

1a: yield 10.8 g (34% based on ϵ -caprolactone); bp $85-86^\circ\text{C}/9$ mmHg (lit.⁹ bp $82^\circ\text{C}/8$ mmHg).

1b: yield 17.9 g (52% based on ϵ -caprolactone); bp $49^\circ\text{C}/0.6$ mmHg (lit.¹⁰ bp $75^\circ\text{C}/5$ mmHg).

2a: yield 16.9 g (59% based on δ -valerolactone); bp $75^\circ\text{C}/12$ mmHg; ^1H NMR (60 MHz, in CCl_4) δ 1.23-1.92 (m, 6 H, CH_2), 3.57-4.13 (m, 6 H, OCH_2); FT-IR (neat) 2947, 1376, 1200, 1073, 1041, 1022 cm^{-1} . Anal. Calcd for $\text{C}_7\text{H}_{12}\text{O}_3$: C, 58.32; H, 8.39. Found: C, 57.97; H, 8.51.

2b: yield 17.4 g (55% based on δ -valerolactone); bp $70^\circ\text{C}/7$ mmHg (lit.² bp $70^\circ\text{C}/7$ mmHg).

3a: yield 7.9 g (30% based on γ -butyrolactone); bp 64 °C/12 mmHg (lit.⁸ bp 64–67 °C/14 mmHg).

3b: yield 8.9 g (31% based on γ -butyrolactone); bp 58 °C/6 mmHg (lit.⁸ bp 67–69 °C/15 mmHg).

Copolymerization: Typical Procedure. To a mixture of **1a** (0.158 g, 1 mmol) and **2b** (0.158 g, 1 mmol) cooled to –30 °C in a Schlenk tube under an argon atmosphere was added tin(IV) chloride (9.4 μ L, 0.08 mmol), and the mixture was stirred at –30 °C. After 1 h, triethylamine (0.5 mL) in CH_2Cl_2 (10 mL) was added to the mixture. The resulting solution was washed with saturated NaHCO_3 solution and dried over anhydrous sodium sulfate. The CH_2Cl_2 solution was evaporated, and the obtained polymer was dissolved in 1 mL of CH_2Cl_2 and precipitated with 20 mL of *n*-hexane. The polymer was collected as a viscous material by decantation. The precipitation was repeated twice, and the collected polymer was dried under vacuum.

Poly(1a-co-2b): yield 0.124 g (39%); $\bar{M}_n = 3660$, $\bar{M}_w/\bar{M}_n = 2.08$ by gel permeation chromatography (GPC); IR (neat) 2947, 2895, 1464, 1354, 1220, 1065, 950 cm^{-1} (in addition to these absorptions, a weak carbonyl absorption was observed at 1736 cm^{-1}); ^1H NMR, see Figure 1A.

Poly(1a-co-3b): IR (neat) 2947, 2895, 1464, 1354, 1220, 1065, 950 cm^{-1} (similarly to poly(1a-co-2b), a weak carbonyl absorption appeared at 1736 cm^{-1}); ^1H NMR, see Figure 1B.

Reaction of SOE with Acetyl Chloride: Typical Procedure. To a solution of **1a** (0.475 g, 2 mmol) in CHCl_3 (5 mL) was added acetyl chloride (213 μ L, 2 mmol), and the mixture was stirred for 3 days. The mixture was evaporated, and the residue was separated by preparative HPLC (Japan Analytical Industry Co., Ltd., Model LC-908 with columns JAIGEL-1H and JAIGEL-2H) with CHCl_3 as eluent.

4: yield 0.511 g (72%); ^1H NMR (90 MHz, in CDCl_3) δ 1.20–1.90 (m, 6 H, CH_2), 2.04 (s, 3 H, CH_3), 2.38 (t, $J = 6.9$ Hz, 2 H, CH_2COO), 3.68 (dd, $J = 6.4$ and 4.8 Hz, 2 H, CH_2Cl), 4.06 (t, $J = 6.3$ Hz, 2 H, $\text{CH}_3\text{COOCH}_2$), 4.34 (dd, $J = 6.4$ and 4.8 Hz, 2 H, $\text{COOCH}_2\text{CH}_2\text{Cl}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (22.4 MHz, in CDCl_3) δ 20.9 (CH_3), 24.5, 25.5, 28.3, 33.9, 41.7, 63.9, and 64.2 (CH_2), 171.1 and 173.0 (C=O); FT-IR (neat) 2950, 1738, 1388, 1366, 1241, 1162 cm^{-1} . Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{O}_4\text{Cl}$: C, 50.74; H, 7.24; Cl, 14.98. Found: C, 50.17; H, 7.30; Cl, 14.98.

5: yield 0.245 g (37%); ^1H NMR (90 MHz, in CDCl_3) δ 1.60–1.80 (br, 4 H, CH_2), 2.05 (s, 3 H, CH_3), 2.25–2.55 (br, 2 H, CH_2COO), 3.69 (dd, $J = 6.4$ and 4.8 Hz, 2 H, CH_2Cl), 4.00–4.20 (m, 2 H, $\text{CH}_3\text{COOCH}_2$), 4.34 (dd, $J = 6.4$ and 4.8 Hz, 2 H, $\text{COOCH}_2\text{CH}_2\text{Cl}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (22.4 MHz, in CDCl_3) δ 20.9 (CH_3), 21.4, 28.0, 33.5, 41.6, 63.9, and 64.0 (CH_2), 171.1 and 172.9 (C=O); FT-IR (neat) 2960, 1736, 1389, 1367, 1240, 1163 cm^{-1} . Anal. Calcd for $\text{C}_9\text{H}_{15}\text{O}_4\text{Cl}$: C, 48.55; H, 6.79; Cl, 15.92. Found: C, 48.27; H, 7.06; Cl, 16.33.

6: yield 0.283 g (45%); ^1H NMR (90 MHz, in CDCl_3) δ 1.80–2.20 (m, 2 H, CH_2), 2.05 (s, 3 H, CH_3), 2.46 (t, $J = 7.4$ Hz, 2 H, CH_2COO), 3.70 (dd, $J = 6.4$ and 4.8 Hz, 2 H, CH_2Cl), 4.12 (t, $J = 6.2$ Hz, 2 H, $\text{CH}_3\text{COOCH}_2$), 4.35 (dd, $J = 6.4$ and 4.8 Hz, 2 H, $\text{COOCH}_2\text{CH}_2\text{Cl}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (22.4 MHz, in CDCl_3) δ 20.9 (CH_3), 24.0, 30.6, 41.7, 63.3, and 64.1 (CH_2), 170.9 and 172.5 (C=O); FT-IR (neat) 2964, 1738, 1389, 1367, 1240, 1167 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{13}\text{O}_4\text{Cl}$: C, 46.05; H, 6.28; Cl, 16.99. Found: C, 45.81; H, 6.35; Cl, 17.12.

Measurements. NMR spectra were obtained with JEOL JNM-EX-90 and JNM-PMX-60Si spectrometers. FT-IR spectra were recorded with JASCO FT/IR-3 and JEOL JIR-5300 spectrometers. Number-average (\bar{M}_n) and weight-average molecular weights (\bar{M}_w) were estimated by GPC, which was performed with a Toyo Soda CCP&8000 with a data processing system (eluent: THF; calibration: polystyrene standards).

Results and Discussion

According to the recently reported method,² bulk polymerization of 1,4,6-trioxaspiro[4.6]undecane (**1a**) with SnCl_4 (4 mol %) was carried out at –30 °C for 1 h. The corresponding homopolymer, poly(cyclic orthoester) [poly(**1a**), $\bar{M}_n = 9310$, $\bar{M}_w/\bar{M}_n = 2.98$], was obtained as an *n*-hexane-insoluble fraction in 67% yield. Among four non-homopolymerizable SOEs (**2** and **3**) prepared, **2b** and **3b**

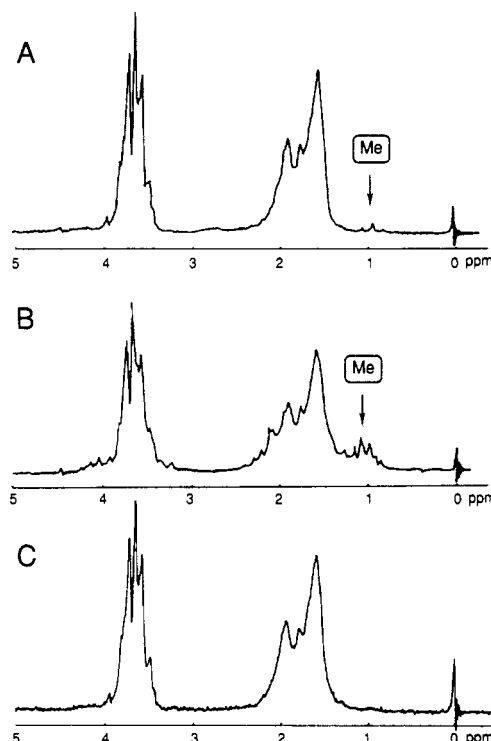


Figure 1. ^1H NMR spectra (60 MHz, in C_6D_6 at 27 °C) of (A) copolymer of **1a** with **2b**, (B) copolymer of **1a** with **3b**, and (C) homopolymer of **1a**.

were selected as comonomers for **1a** for easy determination of copolymer composition by ^1H NMR. The copolymerization of 2-methyl-1,4,6-trioxaspiro[4.5]decane (**2b**) with an equimolar amount of **1a** was conducted at –30 °C for 1 h in the presence of SnCl_4 (4 mol %). The copolymerization was stopped after 1 h because the reaction mixture became so viscous within a few minutes that no further polymerization seemed to proceed. The *n*-hexane-insoluble fraction was collected as a viscous product [poly(1a-co-2b), yield 39%]. The ^1H NMR spectrum of the product was measured (Figure 1A). A small signal of the methyl group from **2b** was observed, in comparison of its ^1H NMR spectrum with that of the homopolymer of **1a** (Figure 1C). GPC showed a unimodal peak ($\bar{M}_n = 3660$, $\bar{M}_w/\bar{M}_n = 2.03$). The FT-IR spectrum of poly(1a-co-2b) was almost the same as that of poly(**1a**), probably because of the low content of the **2b** unit and the structural similarity of the **1a** and **2b** units. These results indicated that, though it was small, the **2b** unit was certainly incorporated into the polymer by the copolymerization. Thus, it is clarified that **2b** does not undergo homopolymerization but can copolymerize with an appropriate monomer such as **1a** having homopolymerizability.

A similar copolymerization of 2-methyl-1,4,6-trioxaspiro[4.4]nonane (**3b**) with **1a** (molar ratio = 50:50) was carried out under the same conditions. The ^1H NMR spectrum (Figure 1B) of the obtained copolymer [poly(1a-co-3b), yield 48%] showed that the methyl group from **3b** could be observed more clearly than that from **2b**. From the NMR spectrum, the content of the **3b** unit in the copolymer was calculated as 18%. In this case the GPC curve was unimodal and the IR spectrum was nearly same as that of poly(1a-co-2b).

The copolymerizabilities of the SOEs were estimated by changing the monomer feed ratio. First, as a control experiment, the copolymerization of two homopolymerizable SOEs with seven-membered ether rings, 2-methyl-1,4,6-trioxaspiro[4.6]undecane (**1b**) and **1a**, was performed

Table I
Copolymerization of 1b, 2b, and 3b with 1a^a

entry	comonomer	feed ratio comonomer:1a	<i>n</i> -hexane-insoluble part			composition comonomer:1a, mol %
			yield, %	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	
1	1b	25:75	55	6350	2.35	27:73
2	1b	34:66	46	9650	3.13	40:60
3	1b	51:49	58	5100	2.47	50:50
4	1b	63:37	46	10040	2.17	70:30
5	1b	100:0	55	7300	1.91	100:0
6	2b	34:66	53	7450	2.41	c
7	2b	50:50	39	3660	2.08	c
8	2b	66:34	30	5560	1.97	c
9	3b	25:75	29	3360	2.34	c
10	3b	33:67	53	6760	2.95	9:91
11	3b	50:50	48	6070	2.34	18:82
12	3b	67:33	32	5140	2.40	20:80
13	3b	0:100	67	9310	2.98	0:100

^a Bulk polymerization with SnCl₄ (4 mol %) at -30 °C for 1 h. ^b Estimated by GPC (eluent: THF, PSt standard). ^c 2–5% of the comonomer unit was observed in ¹H NMR.

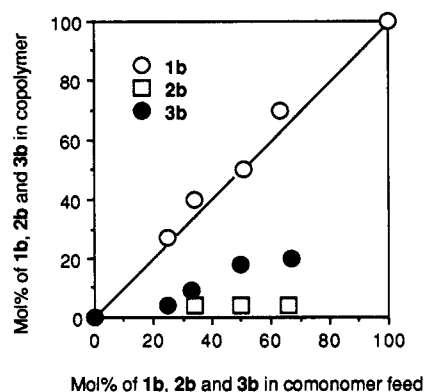


Figure 2. Feed ratio-copolymer composition curves of the copolymerizations of 1b, 2b, and 3b with 1a in bulk at -30 °C for 1 h in the presence of SnCl₄ (4 mol %).

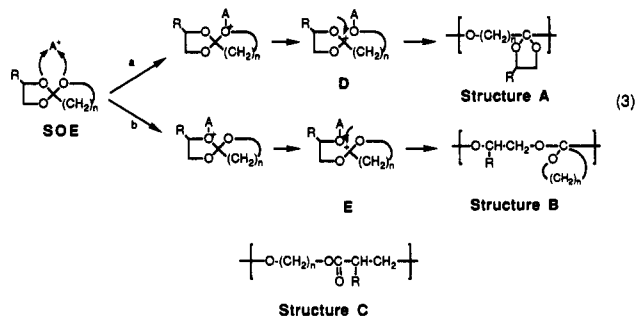
in various feed ratios at -30 °C for 1 h with SnCl₄ (4 mol %). The content of the 1b unit in poly(1a-co-1b) was estimated from the ¹H NMR spectra of the *n*-hexane-insoluble polymers obtained (Table I, entries 1–5). The copolymer composition was plotted vs the feed ratio. Although the conversions of the monomers are high, it would not affect so seriously the plots since the polymerization is an equilibrium polymerization.² The content of the 1b unit increases in good proportion to its feed ratio (Figure 2 (○)), indicating the formation of an almost random copolymer. Meanwhile, in these polymerizations, it is possible for the methyl group of 1b to exert some influence on the polymerizability of 1b in comparison with that of 1a, but the obtained good copolymerizability demonstrates that the methyl group has no influence on the copolymerizability. Therefore, the methyl groups of 2b and 3b would not affect the copolymerization with 1a.

The copolymerizations of 2b with 1a in the feed ratios of 34:66 to 66:34 gave the corresponding copolymers containing the 2b moiety in the polymer backbone in the range of 2–5%. However, the exact content of the 2b unit could not be obtained from the ¹H NMR spectrum because of its low content [Table I (entries 6–8), Figure 2 (□)]. On the other hand, in the similar copolymerization of 3b with 1a, the unit ratio of 3b increased to ca. 20% with increase of the feed ratio of 3b (from 25 to 67%) [Table I (entries 9–12), Figure 2 (●)]. Of course, 2b or 3b alone (feed ratio 100%) gave no polymer as they had no homopolymerizability.² Therefore, the order of copolymerizability toward 1a is 1b ≫ 3b > 2b, in good agreement with the order of the strain energy of the SOEs, 1b ≫ 3b > 2b.⁴ This appears to indicate that the polymerizability may be attributable to the ease of ring opening of the ether ring, i.e., the strain

energy of the SOEs. In the case of the copolymerization of 3b (M₁) with 1a (M₂), the reactivity ratio was estimated from Figure 2 by means of a curve-fitting method, and *r*₁ = 0.1 (±0.1) and *r*₂ = 5 (±1) were obtained. These values are reasonable and are compared with those of the copolymerization of 1b (M₁) and 1a (M₂) (probably *r*₁ = *r*₂ = ca. 1).

Table I shows the yield, molecular weight, and molecular weight distribution of the copolymers obtained as the *n*-hexane-insoluble fraction in the copolymerizations. The *n*-hexane-soluble part contained mainly low molecular weight polymer in the copolymerization of 1b with 1a, whereas 2b or 3b remaining as unreacted monomer was the main component of the *n*-hexane-soluble part in the copolymerizations of 2b or 3b with 1a. Therefore, as shown in entries 6–8 (2b) and 10–12 (3b) of Table I, the copolymer yield decreases as the feed ratio of 2b or 3b increases. However, no such tendency was observed in the case of homopolymerizable 1a and 1b. The molecular weight (\bar{M}_n) and its distribution (\bar{M}_w/\bar{M}_n) were in the ranges 3000–10 000 and 2–3, respectively.

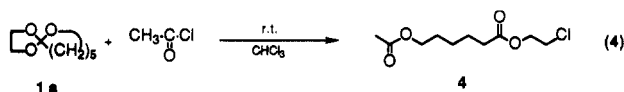
For the copolymer structure, two unit structures are possible to be formed, i.e., structures A and B (eq 3), although structure A is suggested to be more likely from the results of the homopolymerization.²



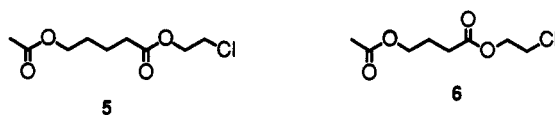
Structure A is formed by nucleophilic attack of the cyclic ether oxygen of the SOE at the cationic center of the di-alkoxycarbenium ion (D) (path a), while structure B is obtained by nucleophilic attack of the cyclic acetyl oxygen at that of E (path b). Meanwhile, the isomerization structure (structure C) is also a possible structure which is obtained in the polymerization at high temperature (>60 °C) but would not be involved in the copolymers. Because the IR spectra of the copolymers only showed similar carbonyl absorption to that of the homopolymer [e.g., poly(1a)],^{2,3} both structures B and C were ruled out for the structure of the homopolymer.² Therefore, the copolymers

are reasonably presumed to consist of two similar cyclic orthoester units containing five-membered acetal rings as shown in eq 2.

It is difficult to completely deny that the unit structure derived from 2 or 3 is neither structure B nor structure C, because the detailed NMR study did not clarify this unit structure due to its low content. Thus, we tried to obtain additional evidence for the structure by comparison of the reactivity of the SOEs (1, 2, and 3) using an electrophile, acetyl chloride. SOEs without methyl groups were used for easy assignment of NMR spectra. Reaction of 1a with an equimolar amount of acetyl chloride in CHCl_3 was carried out at room temperature for 3 days until no further change was observed in the ^1H NMR spectrum. The product (72% yield) was separated by preparative HPLC, and its structure was confirmed as a diester (4) by ^1H NMR, IR, and elemental analyses (eq 4). In addition to



4, oligomeric products were obtained as byproducts. Furthermore, the reaction of 1,4,6-trioxaspiro[4.5]decane (2a) with acetyl chloride gave the similar adduct 5 in 37% yield, although several minor byproducts were formed but not identified. Similarly, the reaction of 1,4,6-trioxaspiro[4.4]nonane (3a) with acetyl chloride also afforded adduct 6 in 47% yield.



Formation of the major products (4, 5, and 6) reveals that the reactions with acetyl chloride proceed along a similar mode but undergo double ring opening with isomerization. Accordingly, their product structures are different from those of the copolymerization where single ring opening takes place. This difference should be explained by the difference of the nucleophiles; i.e., in the cationic polymerizations the nucleophile is the ether oxygen of SOE but in the reactions with acetyl chloride it is chloride anion, a stronger nucleophile. The structures of the products suggest that the acetyl cation is first attacked selectively by the cyclic ether oxygen and then chloride anion attacks at the β -position of the dialkoxycarbenium carbon once formed (D in eq 3) (but not at the carbenium carbon itself), eventually leading to double ring opening with isomerization. However, whether the reaction of the SOEs with acetyl chloride can be regarded as a model

reaction of the polymerization or not seems to depend on whether the reaction proceeds along a similar mode to that of the polymerization or not, although it is not specified.

Consequently, these results suggest the possibility of the ring opening of the ether ring via path a in eq 3 independently of the ring size of the ether ring, and therefore the copolymers seem to have unit structures similar to that of the homopolymer of 1a, poly(cyclic orthoester).^{2,4}

In this study, SOEs incapable of homopolymerizing could be incorporated into a polymer by the copolymerization with a homopolymerizable SOE. These results not only exemplify the possibility of the copolymerization of monomer having no homopolymerizability but also support our prediction that SOEs such as 2 and 3 endowed with no homopolymerizability can apparently undergo ring opening of their cyclic ether rings, although the corresponding homopolymers cannot be obtained because of largely left side shifted equilibrium under the polymerization conditions. However, the study on this copolymerization appears to suffer from analytical and technical difficulties which result from the fact that both monomer and comonomer are able to form equilibrium polymerization systems. Further study will be needed to clarify the whole reactivity of SOEs using new SOEs, e.g., seven-membered acetal ring containing derivatives.¹¹

References and Notes

- (1) (a) Bailey, W. J. *J. Elastoplast.* **1973**, *5*, 142. (b) Endo, T. *Polym. Prepr. Jpn.* **1984**, *33*, 39. (c) Tagoshi, H.; Endo, T. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *77*.
- (2) (a) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules* **1991**, *24*, 331. (b) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules*, preceding paper in this issue.
- (3) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules*, submitted for publication.
- (4) Chikaoka, S.; Takata, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3101.
- (5) Lussi, H. *Makromol. Chem.* **1967**, *100*, 68.
- (6) For a review, see: Penczek, S.; Kubisa, P.; Matyjaszewski, K. *Adv. Polym. Sci.* **1985**, *68/69*, 30, 236.
- (7) For example: Tsuda, T.; Yamashita, Y. *Makromol. Chem.* **1966**, *99*, 297.
- (8) Bodenbenner, K. *Ann.* **1959**, *625*, 183.
- (9) Inokawa, S.; Ogata, T.; Yoshida, H.; Suzuki, S.; Suzumura, H.; Yamase, Y. *Nippon Kagaku Zasshi* **1967**, 1100.
- (10) Suzuki, S.; Yoshida, H.; Ogata, T.; Inokawa, S. *Nippon Kagaku Zasshi* **1968**, 988.
- (11) A referee has suggested studying the reactivity of such new SOEs with seven-membered acetal rings, but we have not succeeded in synthesizing them.

Registry No. 1a, 13043-49-7; 1a-co-1b (copolymer), 136805-48-6; 1a-co-2b (copolymer), 136805-49-7; 1a-co-3b (copolymer), 136805-50-0; 2a, 177-26-4; 3a, 176-37-4; 4, 136805-45-3; 5, 136805-46-4; 6, 136805-47-5; acetyl chloride, 75-36-5.