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New Aspects of Cationic Polymerization of Spiroorthoester: Cationic Single Ring-Opening Polymerization and Equilibrium Polymerization

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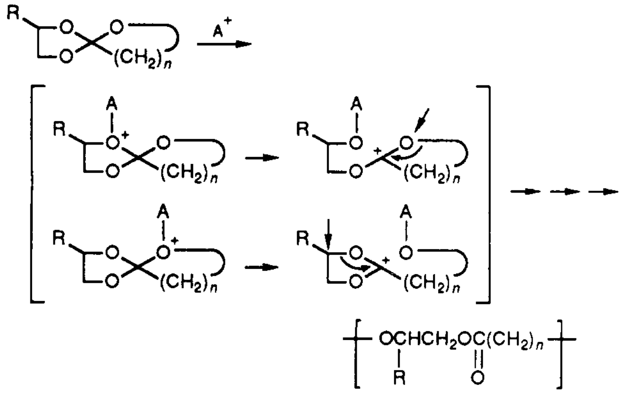
ABSTRACT: A new type of cationic polymerization of spiroorthoester, which proceeded via a single ring-opening process to give poly(cyclic orthoester), was studied. Furthermore, the polymerization was found to be a typical equilibrium one. Spiroorthoesters, 2-methyl-1,4,6-trioxaspiro[4.6]undecane (**1a**), 2-phenyl-1,4,6-trioxaspiro[4.6]undecane (**1b**), 1,4,6-trioxaspiro[4.6]undecane (**1c**), and 2-(bromomethyl)-1,4,6-trioxaspiro-[4.6]undecane (**1d**), polymerized under cationic conditions at low temperature to afford the corresponding poly(cyclic orthoester)s **2** (for example, under the conditions with 2 mol % of $SnCl_4$ at 0 °C and for 1 h; yields 78, 40, 84, and 56%; $\bar{M}_{ns}$ 7700, 4080, 14 400, and 8580, respectively) through single ring opening of their seven-membered ether rings. The obtained polymers **2** easily depolymerized upon treatment with hydrogen chloride at room temperature, and the starting monomers were recovered in good yields. The polymerizations were suggested to be typical equilibrium polymerizations, to which the Dainton's equation could be applied. Enthalpy changes ($\Delta H°$) and entropy changes ($\Delta S°$) of the polymerizations were calculated from the data, and hypothetical ceiling temperatures for the monomers **1** were also calculated by using their $\Delta H°$ and $\Delta S°$ values. $\Delta H°$ [kJ/mol], $\Delta S°$ [J/mol·deg], and the ceiling temperature (T_c [°C]) were −8.0, −30.7, and 254 for **1a**, −6.7, −25.7, and 258 for **1b**, −10.6, −39.6, and 172 for **1c**, and −5.0, −20.8, and 498 for **1d**, respectively.

Introduction

Spiroorthoesters (SOEs) polymerize with cationic catalyst to yield poly(ether–ester)s via a tandem ring-opening process with isomerization (eq 1).[1] No shrinkage in volume is observed on this polymerization. In contrast, we have recently found that 2-methyl-1,4,6-trioxaspiro[4.6]undecane (**1a**) polymerizes with $Al(acac)_3$ as a catalyst at room temperature to give poly(cyclic orthoester) **2a** which can be regarded as being formed via a selective single ring opening of the seven-membered ether ring (eq 2).[2] **1a** as well as a repeating unit of **2a** can have four possible isomeric structures in which two pairs are distinguishable by NMR. In this case, the ratio of the two pairs of **1a** is different from that of **2a**. This result seems to suggest the formation of a planar tricoordinated carbon species in the transition state. If, for this carbon species, a cationic species is predicted as the most feasible one, SOEs are expected to polymerize with a general cationic catalyst under conditions similar to those employed in the case of $Al(acac)_3$ to afford the same poly(cyclic orthoester).



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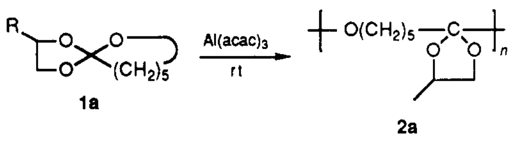

(2)

However, there is no report describing the formation of polymers other than poly(ether–ester) in the cationic polymerization of SOE. Only a report by Matyjaszewski describes a possible single ring opening in the cationic polymerization of a five-membered SOE,[3] in which the corresponding intermediate cationic carbon species are

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observed in NMR spectra. We have considered that polymerization temperature is the most important factor in the determination of the polymerization mode, i.e., either ring-opening isomerization or single ring opening, because bicycloorthoester cationically polymerizes to give either of two kinds of polymers strongly depending on the polymerization temperature.[4]

In this paper, the authors report two new aspects of the cationic polymerization of SOE: (1) cationic polymerization of SOEs at low temperature selectively affords single ring-opened poly(cyclic orthoester)s, and (2) the polymerization is one of the typical equilibrium polymerizations.[5]

Experimental Section

Materials. Tin(IV) chloride (Wako Pure Chemical Industries, Ltd.; >97%) and boron trifluoride ethyl ether complex (Tokyo Kasei Kogyo Co., Ltd.) were distilled under dry nitrogen and stored in glass tubes under argon atmosphere. Spiroorthoesters (**1a**–**d**, **3**, and **4**) were prepared from propylene oxide (Tokyo Kasei Kogyo Co., Ltd.; >98%), styrene oxide (Tokyo Kasei Kogyo Co., Ltd.; >95%), ethylene oxide (Capox 30; Nihon Gas Sakkin Kogyo Co., Ltd.; 30% mixture with carbon dioxide), or epibromohydrine (Tokyo Kasei Kogyo Co., Ltd.; >98%) and the corresponding lactones (Tokyo Kasei Kogyo Co., Ltd.; >98%) according to the Bodenbenner's method.[6] Dry CH_2Cl_2 for depolymerization and polymerization was obtained by refluxing over P_2O_5 and distillation.

Synthesis of SOE. General procedure: To a mixture of a lactone (0.2 mol) and BF_3OEt_2 (1.26 mL, 0.01 mol) in CCl_4 (40 mL) was added dropwise an oxirane (0.4 mol) in CCl_4 (40 mL) at 0 °C. In the case of ethylene oxide, a CCl_4 solution of it was prepared by bubbling the mixture of ethylene oxide and carbon dioxide into CCl_4 which was cooled to −30 °C. The reaction mixture was stirred for 4 h at 0 °C and then washed with 200 mL of 1 M NaOH. The organic layer was dried over anhydrous magnesium sulfate, the solvent was evaporated, and the residual oil was distilled under vacuum.

1a: yield 17.9 g (52% based on ϵ-caprolactone); bp 49 °C (0.6 mmHg) [lit.[7] bp 75 °C (5 mmHg)].

1b: yield 20.6 g (44% based on ϵ-caprolactone); bp 130–136 °C (0.09 mmHg); ^1H NMR (60 MHz, in CCl_4) 1.50–1.93 (br, 6 H, $-CH_2-$), 1.93–2.33 (br, 2 H, $(-O-)_3CCH_2-$), 3.50–4.50 (m, 4 H, $-OCH_2-$), 4.78–5.30 (m, 1 H, $-OCHPhCH_2-$), 7.17–7.43 (br, 5 H, −Ph); FT-IR (neat) 2933, 2858, 1454, 1365, 1238, 1176, 1134, 1072, 1041, 964 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.61; H, 7.79.

1c: yield 10.8 g (34% based on ϵ-caprolactone); bp 85–87 °C (9 mmHg) [lit.[8] bp 82 °C (8 mmHg)].

1d: yield 21.7 g (43% based on ϵ-caprolactone); bp 92 °C (0.5 mmHg) [lit.[9] bp 85–86 °C (0.6 mmHg)].

3: yield 17.4 g (55% based on δ-valerolactone); bp 70 °C (7 mmHg) [lit.[2] bp 70 °C (7 mmHg)].

4: yield 8.9 g (31% based on γ-butyrolactone); bp 58 °C (6 mmHg) [lit.[6] bp 67–69 °C (15 mmHg)].

Cationic Polymerization. Typical procedure: **1a** (0.344 g, 2 mmol) was cooled to 0 °C in a Schlenk tube under an argon atmosphere. Tin(IV) chloride (4.7 μL, 0.004 mmol) was added, and the mixture was stirred at 0 °C. After 1 h, triethylamine (0.5 mL) was added to quench the polymer, and then CH_2Cl_2 (5 mL) was added to dissolve the polymer. The solution was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous sodium sulfate. The solution was evaporated, and the residual material was dissolved in 1 mL of CH_2Cl_2 and precipitated with 20 mL of *n*-hexane. Precipitated polymer was collected as a viscous material by decantation. Similar precipitation was repeated once more, and the polymer **2a** was dried under vacuum. Yield 0.271 g (78%); $\bar{M}_n = 7700$, $\bar{M}_w/\bar{M}_n = 1.82$.

Reaction of Poly(cyclic orthoester) 2 with Hydrogen Chloride. A total of 0.10 g (0.58 mmol) of poly(cyclic orthoester) **2a** ($\bar{M}_n = 4200$, $\bar{M}_w/\bar{M}_n = 2.27$) was dissolved in 10 mL of dry distilled CH_2Cl_2 at 25 °C. An anhydrous solution of hydrogen chloride (2 mol %) in CH_2Cl_2 was added, and the mixture was stirred at 25 °C. A gel permeation chromatogram of the mixture withdrawn at an interval was obtained.

Table I
Cationic Polymerization of Spiroorthoesters in Bulk[a]

entry	monomer	initiator[b]	yield,[c] %	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	**1a**	$SnCl_4$	78	7700	1.82
2	**1b**		40	4080	1.62
3	**1c**		84	14400	4.69
4	**1d**		56	8580	2.32
5	**1a**	BF_3OEt_2	83	7190	1.89
6	**1b**		44	5080	1.77
7	**1c**		85	8020	2.96
8	**3**	$SnCl_4$	0		
9	**4**		0		

[a] At 0 °C for 1 h. [b] 2 mol % was used. [c] *n*-Hexane-insoluble part. [d] Estimated by GPC (eluent, THF; PSt standards).

To isolate the product, a large-scale experiment was performed. **2a** (1.89 g, 10.9 mmol) reacted with hydrogen chloride under the same conditions. After 14 h, the reaction was quenched by adding triethylamine (40 μL) and the resulting mixture was evaporated and distilled under vacuum. Yield of **1a** was 0.98 g (52%); bp 59.5 °C (1.6 mmHg) [lit.[6] bp 75 °C (5 mmHg)].

Solution Polymerization in CH_2Cl_2 for the Determination of Thermodynamic Parameters. Typical procedure: **1a** (0.344 g, 2 mmol) was dissolved in 0.5 mL of CH_2Cl_2 and cooled to −50 °C. $SnCl_4$ (4.7 μL, 0.04 mmol) dissolved in 0.5 mL of CH_2Cl_2 was added to the solution, and the mixture was stirred for 1 h at that temperature. After addition of 0.5 mL of triethylamine, the reaction mixture was evaporated. The conversion of **1a** was 60.2%, which was calculated by gel permeation chromatography (GPC) using a GPC sensitivity ratio of **1a** to **2a** in refractive index.

Measurements. Densities of monomers and polymers were measured with density gradient tubes at 25 °C with a Shibayama Kagaku Kikai Seisakusho Model A. NMR spectra were recorded with JEOL JNM-PMX-60Si, JNM-EX-90, JNM-GX-270, and JNM-GX-500 spectrometers. FT-IR spectra were recorded with Jasco FT/IR-3 and JEOL JIR-5300 spectrometers. GPC was performed with a Toyo Soda CCP&8000 with a data processing system by RI detector (eluent, THF; calibration, polystyrene standards).

Results and Discussion

A. Single Ring-Opening Polymerization. Four spiroorthoesters (SOEs) having seven-membered ether rings, 1,4,6-trioxaspiro[4.6]undecane (**1c**) and its 2-methyl (**1a**), 2-phenyl (**1b**), and 2-bromomethyl (**1d**) derivatives, were prepared according to Bodenbenner's method.[6] Cationic polymerizations of the SOEs were performed with $SnCl_4$ (2 mol %) in bulk at 0 °C under an Ar atmosphere. Polymerization was stopped in 1 h by addition of triethylamine in any case because the viscosity of the system became very high in a few minutes. Results are shown in Table I (entries 1–4). The highest yield of the polymer obtained as an *n*-hexane-insoluble fraction was achieved in the polymerization of **1c**, and the substituent (Me, **1a**; Ph, **1b**; CH_2Br, **1d**) seemed to lower the polymer yield. The molecular weight ($\bar{M}_n$) of the polymer also decreased by the substitution. The molecular weight distribution of polymer **2c** was remarkably high (for **2c**, $\bar{M}_w/\bar{M}_n = 4.69$, whereas for **2a**; $\bar{M}_w/\bar{M}_n = 1.82$, for **2b**; $\bar{M}_w/\bar{M}_n = 1.62$, and for **2d**, $\bar{M}_w/\bar{M}_n = 2.32$). This can be explained by very insufficient stirring of the system due to the formation of a sticky solid product in the case of **1c**. In contrast, the polymers obtained from **1a**, **1b**, and **1d** were viscous liquid.

Structures of the polymers **2** were examined by IR and NMR spectra. FT-IR spectra of the polymers obtained by polymerization of **1a**–**c** were shown in Figure 1. The polymers showed little ester carbonyl absorption around 1720 cm^{-1}. No carbonyl carbon was observed in ^{13}C NMR spectra of the polymers at all. Only a few ester carbonyls (less than ca. 5%) would exist in the polymer. These results

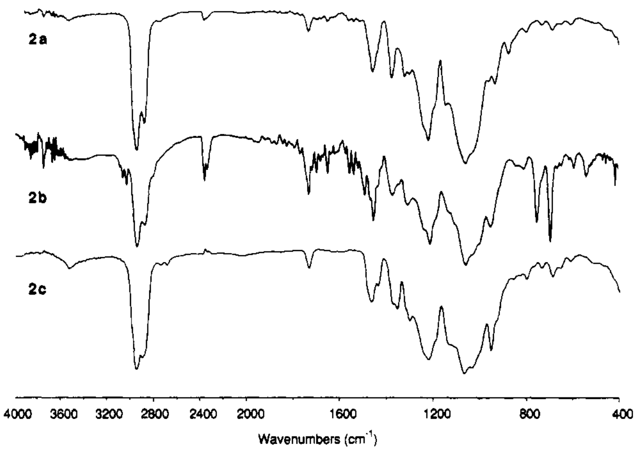


Figure 1. FT-IR spectra of poly(cyclic orthoester)s **2a–c** obtained by the cationic polymerization with $SnCl_4$ (2 mol %) in bulk at 0 °C (**2a**,**b**, neat; **2c**, film).

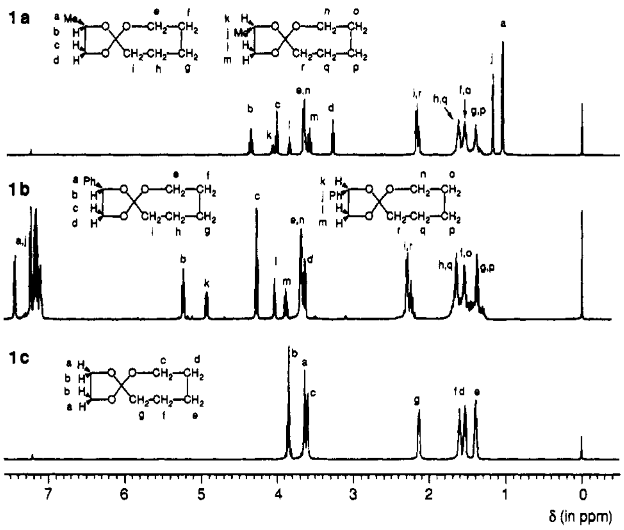
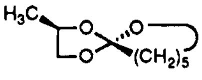
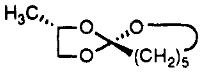
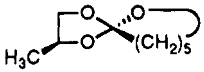


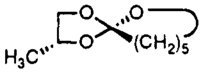
Figure 2. 500-MHz ^1H NMR spectra of spiroorthoesters **1a–c** in C_6D_6 at 27 °C.

suggest that the structure of the polymer is unambiguously different from poly(ether–ester) as shown in eq 1. The weak carbonyl absorption in the IR spectra can result from partial hydrolysis with moisture, a small amount of isomerization, or possible terminal structure, but they are not specified. However, isomerization during polymerization would be ruled out because the strength of the carbonyl absorption is not changed in the temperature range from 50 to 10 °C and the degree of isomerization is calculated by ^{13}C NMR study to be 5–6% at 40 °C polymerization and 15–20% at 60 °C polymerization as shown in the study on temperature-dependent isomerization polymerization of SOEs.[10] The structure, therefore, is confirmed to be different from a poly(ether–ester) and suggested to be a poly(cyclic orthoester) which can be formed by a single ring-opening polymerization of either a seven-membered ether ring or a five-membered acetal ring. Meanwhile, the polymerization of SOEs with $Al(acac)_3$ is reported to involve the selective single ring opening of a seven-membered ether ring by detailed ^1H NMR analysis.[2] Then, NMR spectra of the monomers (**1**) and polymers (**2**) were analyzed in detail in order to estimate which ring was opened. At first, ^1H NMR spectra (500 MHz) of the monomers **1a–c** were recorded (Figure 2), and the assignments of the spectral signals were carried out by using the ^1H–^1H COSY technique. Each couple of A and C and B and D in the four possible stereoisomers of **1** consists of a mixture of two enantiomers which are indistinguishable by NMR, but the ratio of (A + C):(B + D) can be calculated. For example, in the case of **1a** the ratio was 63:37 by ^1H NMR integration.

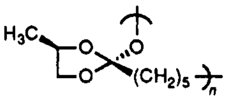

1a–A

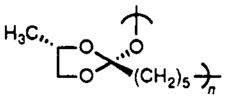

1a–B

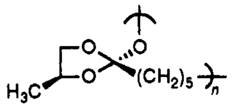

1a–C

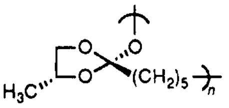

1a–D

^1H NMR spectra of the polymers **2a–c** are shown in Figure 3. The spectrum of **2a** (top) was completely the same as that of the polymer obtained in the polymerization with $Al(acac)_3$.[2] So, **2a** is concluded to be the same poly(cyclic orthoester) as that in the polymerization with $Al(acac)_3$ and should be formed by the single ring opening of a seven-membered ether ring in the cationic polymerization of **1a** at low temperature. For **2b** and **2c**, their methylene signal patterns of the seven-membered ether rings were nearly the same as that of **2a**, revealing that **1b** and **1c** polymerized similarly. A polymer unit of **2a** or **2c** can also have four possible isomeric structures, and the ratio of (A + C):(B + D) for **2a** is calculated to be 56:44 from the integration ratio of methyl groups in the ^1H NMR spectrum (270 MHz).


2a–A

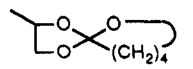

2a–B


2a–C


2a–D

The ratio is in good agreement with the ratio 57:43 for the polymer obtained with $Al(acac)_3$. This agreement suggests that the polymerization with $Al(acac)_3$ proceeds by a cationic mechanism. The fact that cationic polymerization of SOEs at low temperature affords single ring-opened poly(cyclic orthoester)s while tandem double ring-opening polymerization takes place at high temperature to give poly(ether–ester)s shows that isomerization polymerization to poly(ether–ester) requires a rather large energy. Similar results were obtained for **1d**.

Cationic polymerization with BF_3OEt_2 was performed under the same conditions (Table I, entries 5–7), but no significant difference between $SnCl_4$ and BF_3OEt_2 was observed, where the same polymers were obtained. Meanwhile, SOEs with different numbers of ether ring members, 2-methyl-1,4,6-trioxaspiro[4.5]decane (**3**) and 2-methyl-1,4,6-trioxaspiro[4.4]nonane (**4**), were subjected to cationic polymerizations under the same conditions (Table I, entries 7 and 8). However, both SOEs did not afford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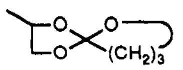
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any polymer but were recovered completely. This result is in good accordance with the reactivity of the SOEs in the polymerization with $Al(acac)_3$. The different polymerizabilities of the three SOEs **1a**, **3**, and **4** can be explained by the different strain energies of their ether rings, as discussed previously.[2]

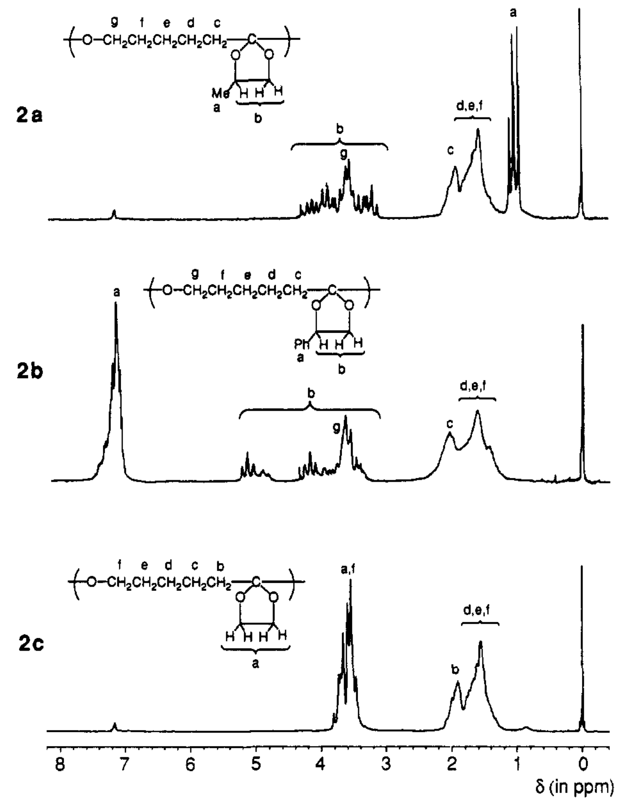
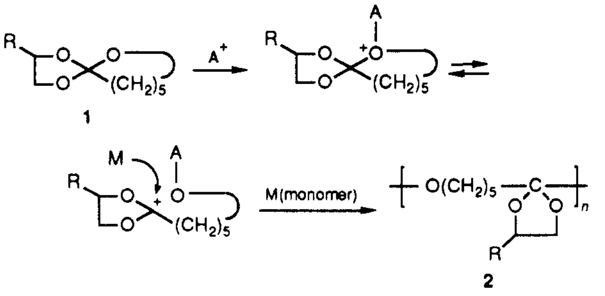


Figure 3. 90-MHz ^1H NMR spectra of poly(cyclic orthoester)s **2a–c**, obtained by the cationic polymerization with $SnCl_4$ (2 mol %) in bulk at 0 °C, in C_6D_6 at 27 °C.

Thus, SOE 1 polymerizes to produce poly(cyclic orthoester) 2 but not poly(ether–ester) under cationic polymerizations at low temperature. This behavior is independent of catalyst, solvent, and monomer structure, indicating a general behavior of SOE with a seven-membered ether ring. The product structure and monomer selectivity were the same as those in the polymerization with $Al(acac)_3$. Although the correct mechanism of the polymerization with $Al(acac)_3$ is not clear, the results obtained in this study seem to suggest the cationic mechanism as an adequate candidate. If it is correct, the mechanism of the two polymerizations can be accounted for by eq 3. Namely, an initially formed oxonium species is changed to a carbenium species which is attacked by a new monomer molecule to yield eventually poly(cyclic orthoester). The mechanism is clearly different from that involving ring-opening isomerization as shown in eq 1 which yields poly(ether–ester). The results described in this study present the problem of whether isomerization to poly(ether–ester) takes place from a monomer state like in eq 1 or from poly(cyclic orthoester) obtained here. This subject will be discussed in detail elsewhere.[10]



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B. Equilibrium Polymerization. Depolymerization. During the study of the above-mentioned polymerizations, it was found that the obtained poly(cyclic orthoester)s easily decomposed to the starting monomers when they were dissolved into $CDCl_3$ for recording of the NMR spectra. Since $CDCl_3$ usually contains a small amount of DCl as an impurity, DCl is considered to act as an acid catalyst which decomposes the poly(cyclic orthoester)s. To confirm it, the decomposition of the polymer **2a** was carried out by adding HCl positively. To **2a** ($\bar{M}_n$ = 4000, $\bar{M}_w/\bar{M}_n$ = 2.27) dissolved in CH_2Cl_2 (58 mM) was added HCl (2 mol %) dissolved in CH_2Cl_2 of which concentration was determined by titration. In a large-quantity experiment, the yield of product **1a** was determined to be 82% by GLC (isolated yield by vacuum distillation was 52%). The decomposition process was monitored by GPC (Figure 4). The decomposition immediately started by adding HCl, and the monomer **1a** was formed at the beginning of the reaction. This result evidently demonstrates that the decomposition proceeds to give the monomer via a zipping mechanism (eq 4).[11] It is reasonable to consider that the cleavage of C–O bond starts not only from the end of the polymer chain to form directly the monomer (eq 4) but also from any point of the polymer chain to form lower molecular weight polymer but not the monomer directly (eq 5).

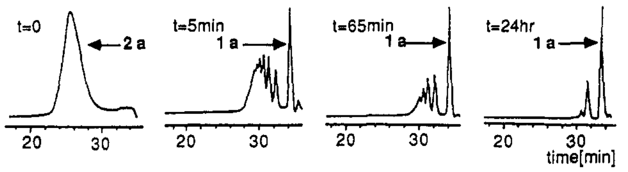
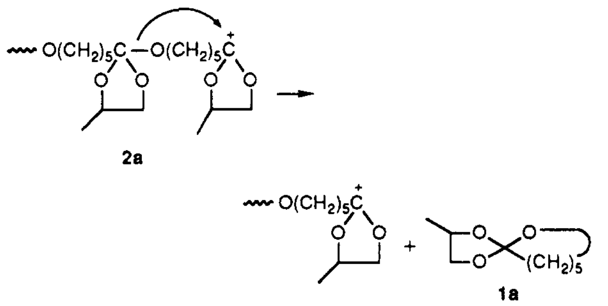


Figure 4. GPC change in the depolymerization of poly(cyclic orthoester) **2a** (concentration, 58 mM) with HCl (2 mol %) at 25 °C in CH_2Cl_2.



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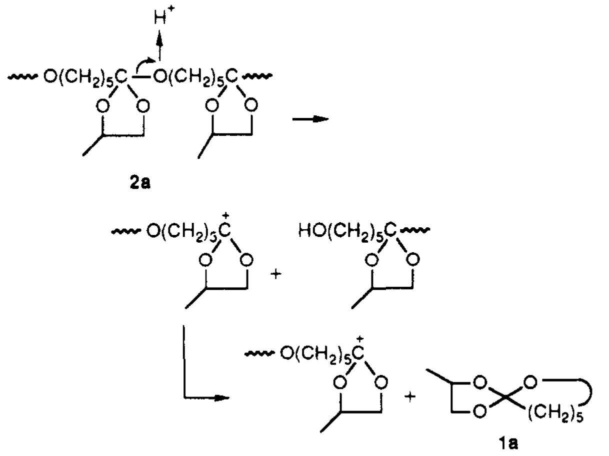

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Equilibrium Polymerization. Since polymer 2 is prepared under cationic conditions, the zipping depolymerization with HCl suggests the existence of an equilibrium process in polymerization. To clarify whether the polymerization is an equilibrium polymerization or not, dependence of the conversion of the SOEs on the polym-

Table II
Solution Polymerization of Spiroorthoesters[a]

entry	monomer	polymerizn temp, °C	convn,[c] %	$\bar{M}_n$[d]	$\bar{M}_w/\bar{M}_n$[d]
1	**1a**	-50	60.2	9770	1.89
2		-40	56.2	8710	2.05
3		-30	52.5	6220	1.69
4[b]		-20	43.3	5760	1.68
5[b]		-15	35.7	4750	1.60
6[b]		-10	30.6	4230	1.48
7[b]		-5	25.3	2480	1.66
8[b]		0	24.0	1010	2.17
9[b]		5	19.0	850	2.01
10	**1b**	-50	64.1	8840	1.75
11		-40	58.8	6360	1.64
12[b]		-30	45.8	4310	1.59
13[b]		-20	37.8	2710	1.36
14[b]		-15	30.4	1390	1.82
15[b]		-10	28.8	1150	1.83
16	**1c**	-30	58.5	1660	2.41
17		-20	55.5	1330	2.17
18[b]		-10	41.0	1420	1.59
19[b]		-5	34.2	1180	1.84
20[b]		0	30.2	1140	1.79
21[b]		5	23.0	1110	1.89
22[b]	**1d**	-35	34.6	5080	1.59
23[b]		-15	17.4	3170	1.37
24[b]		-10	18.0	1520	1.70
25[b]		-5	12.5	2050	1.30

[a] Initiator, $SnCl_4$ (2 mol %); solvent, CH_2Cl_2, conc, 1, 2 mmol/1 mL of CH_2Cl_2. [b] These data were used to calculate $\Delta H°$ and $\Delta S°$. [c] Calculated from the ratio of the peak area of the monomer to the polymer in a GPC chart. [d] Estimated by GPC (eluent; THF; PSt, standards).

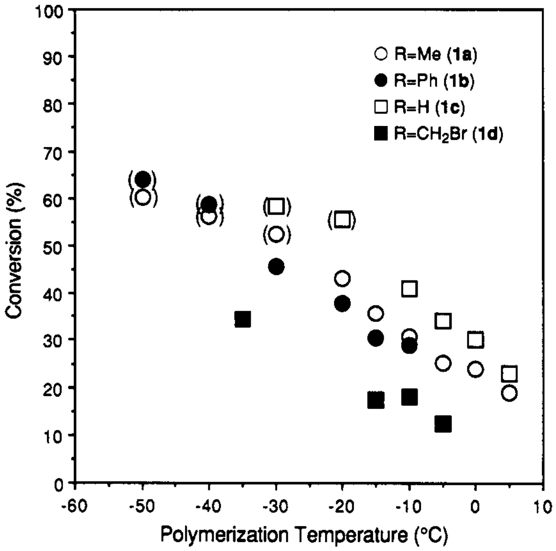

Figure 5. Temperature–conversion curves of the polymerizations of **1a**–**d** in CH_2Cl_2 (1, 2 mmol/1 mL of CH_2Cl_2) with $SnCl_4$ (2 mol %) for 1 h.

Table III
Densities of Monomer and Polymers[a]

monomer	density	polymer	density
1a	1.057	**2a**	1.101
1b	1.125	**2b**	1.147
1c	1.105	**2c**	1.134
1d	1.413	**2d**	1.444

[a] Data were measured with density gradient tubes at 25 °C.

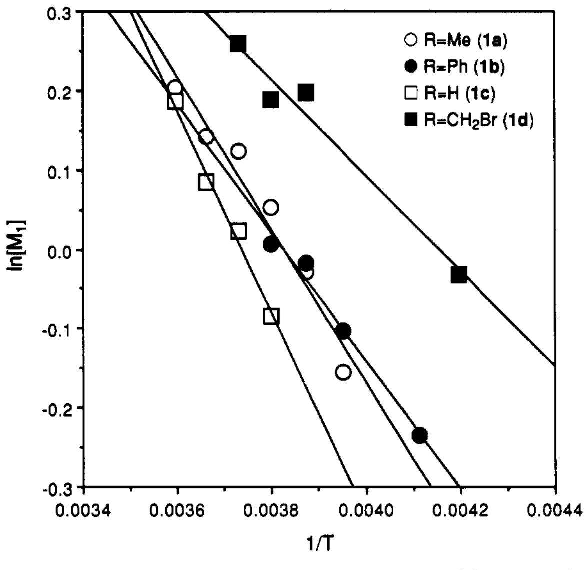

Figure 6. Plots of ln $[M_1]$ vs $1/T$ in the equilibrium polymerization of **1a**–**d** in CH_2Cl_2 (1, 2 mmol/1 mL of CH_2Cl_2) with $SnCl_4$ (2 mol %) for 1 h.

erization temperature was examined. Generally, in the equilibrium polymerization, conversion decreases by increasing polymerization temperature, and at a certain temperature, i.e., the ceiling temperature, only monomer exists.

Solution polymerizations of **1a**–**d** were performed in CH_2Cl_2 (concentration of **1**: 2 mmol/1 mL of CH_2Cl_2) with $SnCl_4$ (2 mol %) at various temperatures. Polymerization was stopped in 1 h because the polymerization system became viscous in any case within a few minutes and no further change of the conversion was observed. Conversion of the monomers was measured from the ratio of the peak areas of the monomer to the polymer in a GPC chart of the polymerization mixture. The sensitivity ratio of the monomers to the corresponding polymers was obtained in advance. The results are summarized in Table II. Polymerization temperature–conversion curves are shown in Figure 5. As shown in Table II and Figure 5, the conversion of **1** as well as the molecular weights of **2** decreased with an increase of the temperature, suggesting a typical equilibrium polymerization. To this type of equilibrium polymerization can be applied Dainton's equation[12] (eq 6 or eq 6′) where T, $[M_1]$, $\Delta H°$, and $\Delta S°$ are the

$$T = \Delta H°/(\Delta S° + R \ln [M_1]) \qquad (6)$$

$$\text{or } \ln [M_1] = \Delta H°/RT - \Delta S°/R \qquad (6')$$

polymerization temperature, the concentration of monomer at an equilibrium, the enthalpy change in the appropriate standard state, and the entropy change in the appropriate standard state, respectively. If plots of ln $[M_1]$ vs $1/T$ show a straight line, this is an equilibrium polymerization, and thermodynamic parameters $\Delta H°$ and $\Delta S°$ can be calculated. Densities of the monomers and the polymers, which were required to calculate $[M_1]$ from the conversion, were measured with density gradient tubes (Table III). In the application of Dainton's equation, the conversions higher than 50% were not used in order to exclude the viscosity effect, because a considerable increase of viscosity was observed at high conversion even in the solution polymerization. The obtained plots of ln $[M_1]$ vs $1/T$, as shown in Figure 6, were all in good linear lines ($r > 0.98$), suggesting the equilibrium polymerizations. From the plots, the corresponding $\Delta H°$ and $\Delta S°$ were calculated (Table IV). The values of $\Delta H°$ were in the order of **1c** < **1a** < **1b** < **1d**.

By using the $\Delta H°$ and $\Delta S°$ values thus obtained, ceiling temperatures of **1a**–**d** for *bulk polymerizations* were calculated by extrapolation (Table IV). In this calculation, the monomer should be regarded as solvent, but the effect

Table IV
ΔH° and ΔS° for the Equilibrium Polymerization of 1

	1a (R = Me)	**1b** (R = Ph)	**1c** (R = H)	**1d** (R = CH_2Br)
ΔH°, kJ/mol	-8.0	-6.7	-10.6	-5.0
ΔS°, J/mol·deg	-30.7	-25.7	-39.6	-20.8
T_c,[a] °C	254	258	172	498

[a] Values for bulk polymerization, obtained by extrapolation.

by changing the solvent from CH_2Cl_2 to the monomers is neglected. As a result, **1c** had its ceiling temperature of 172 °C, whereas two-substituted derivatives (**1a–d**) had rather higher ceiling temperatures over 250 °C. Namely, introduction of the substituent enhances the T_c value, and the order of the T_cs is the same as that of the ΔH° values. The orders of the ΔH° and T_c values of **1a–d** seem to follow that of the size of the substituent (H < Me < Ph < CH_2Br) on the dioxolane ring (at the 2-position) of 1 in this case, although the dioxolane ring is not directly taking part in the polymerization. A phenyl group is sterically more bulky than CH_2Br in most cases,[13] but steric hindrance of CH_2Br may be due to the flexible structure in comparison with that of Ph. The order can be simply explained by the stability difference between the polymers and the monomers. In the polymer state steric repulsion would be generated possibly between the substituents and/or between the substituent and the polymer main chain. It should be noted that the T_c values are obtained by extrapolation for bulk polymerization where effects of density change by both change of temperature and change from solution polymerization to bulk polymerization are neglected. ΔS° values decrease similarly, indicating that the entropy difference between the polymer and the monomer is in reverse proportion to the size of the substituent.

In the equilibrium polymerizations molecular weight distribution should be 2 when the degree of polymerization reaches infinity.[14] Our results demonstrated in Table II in which $\bar{M}_w/\bar{M}_n$s lie around 2 show accordingly characteristics of the common equilibrium polymerization.

Thus, we clarified that the cationic polymerization of SOEs at low temperature (<10 °C) selectively affords poly(cyclic orthoester)s through the single ring-opening polymerization. By this finding, Matyjaszewski's proposal[3] was evidently proven, although his study was carried out with an SOE having a five-membered ether ring.[3] Meanwhile, the polymerization of 1 was a typical equilibrium polymerization. Thermodynamic parameters (ΔH° and ΔS°) and imaginary T_c values were calculated and simply discussed on the basis of the substituent effect. The new polymers and polymerization behaviors demonstrated in this study would be significant in the fields of polymer synthesis, functional polymers, and so on.

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Registry No. 1a, 21511-66-0; **1b**, 130904-43-7; **1c**, 13043-49-7; **1d**, 84298-08-8; **2a**, 130572-36-0; **2b**, 136805-19-1; **2c**, 126493-57-0; **2d**, 84298-08-8; **3**, 130839-53-1; **4**, 3539-02-4; HCl, 7647-01-0.