Cationic Ring-Opening Polymerization of Spiroorthoester: Polymer Structure, Polymerization Mechanism, and Volume Change on Polymerization

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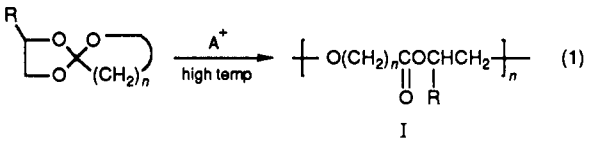
ABSTRACT: The polymer structure and polymerization mechanism of cationic polymerization of a spiroorthoester were studied, and the relationship between volume change on polymerization and polymer structure was examined. Spiroorthoester, 1,4,6-trioxaspiro[4.6]undecane (1), was polymerized with $SnCl_4$ (2 mol %) at various temperatures ranging from 0 to 120 °C. The polymer structure was dependent on polymerization temperature. The polymer obtained at 0 °C was entirely poly(cyclic orthoester), whereas the polymer obtained at 120 °C consisted of 25% poly(cyclic orthoester) and 75% poly(ether–ester). The unit ratio of poly(ether–ester) increased with rising polymerization temperature. The polymerization mechanism is discussed in terms of the relation between the yield and the structure of the polymer synthesized at 80 °C. It was suggested that the poly(ether–ester) unit was formed by acid-catalyzed intermolecular isomerization of the poly(cyclic orthoester) unit. Further, the volume change on polymerization was studied in relation to the polymer structure, and an increase of poly(ether–ester) units in the polymer suppressed shrinkage on polymerization.

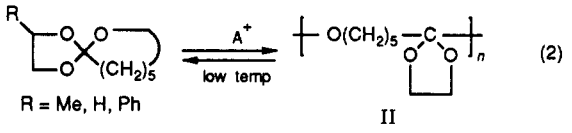
Introduction

Volume shrinkage is always observed in the polymerization of various monomers including thermosetting resins. In contrast to it, spiroorthocarbonates (SOCs),[1] bicycloorthoesters (BOEs),[2] and spiroorthoesters (SOEs)[3,4] show no shrinkage or sometimes an expansion in volume on polymerization. Among them SOE is the most useful monomer because of its easy preparation. Cationic polymerization of SOEs at high temperature (>100 °C) is reported to give poly(ether–ester) via a double-ring-opening process (eq 1), although there has been no detailed study of the polymer structure and polymerization mechanism. Recently we have found that the cationic polymerization of SOEs containing a seven-membered ether ring selectively affords poly(cyclic orthoester)s via single opening of the ether ring of SOE (eq 2) at low temperature (<10 °C).[5] This type of polymerization was originally suggested by Matyjaszewski.[6] In the single-ring-opening polymerization, no isomerized unit (I) was formed, as shown in eq 1.[5] In those studies, we have pointed out a strong influence of polymerization temperature on the polymer structure in the polymerization of SOEs. On the other hand, Hall reported that 2,6,7-trioxabicyclo[2.2.1]-heptane polymerizes with a cationic catalyst at room temperature to afford a single-ring-opened poly(orthoester) and at high temperature to afford double-ring-opened poly(ether formate). The single-ring-opening polymerization causes a volume shrinkage while a volume expansion is observed in the double-ring-opening polymerization to poly(ether formate).[7]



(1)

I



(2)

II

The results obtained so far prompt the following questions to the cationic polymerization of SOE:

(i) Does the polymer formed by the polymerization at high temperature consist only of structure I? Can structure II be excluded? A possible alternative can be a mixture of polymer structures I and II with a ratio depending upon the polymerization temperature.

(ii) Does the structural change from II to I take place during polymerization at high temperature? Since the reaction pathway to II (eq 2) is an equilibrium polymerization,[5] it may be difficult to determine the occurrence of the isomerization of II to I.

(iii) Is there any difference in volume change to be observed between the two polymerizations to I and II? The difference may be observed, since a quite small volume change characteristic of the polymerization of SOE is believed to come from the double-ring-opening polymerization. If the polymer consists of a mixture of the two units (I and II), how does the unit ratio affect the volume change?

This paper discusses the above-mentioned questions.

Experimental Section

Materials. Tin(IV) chloride (Wako Pure Chemical Industries, Ltd.; purity >97%) was distilled under dry nitrogen and stored in a glass tube under argon atmosphere. Spiroorthoester 1 was prepared from ethylene oxide (Capox 30; Nihon Gas Sakkin Kogyo Co., Ltd.; 30% diluted with carbon dioxide) and ϵ-caprolactone according to Bodenbenner's method.[3]

Synthesis of SOE (1): To a mixture of ϵ-caprolactone (0.2 mol) and BF_3OEt_2 (1.26 mL, 0.01 mol) in CCl_4 (40 mL) was added dropwise ethylene oxide (0.4 mol) in CCl_4 (40 mL) at 0 °C. The ethylene oxide solution in CCl_4 was prepared by bubbling the commercial mixture of ethylene oxide and carbon dioxide into CCl_4 at −30 °C. The reaction mixture was stirred for 4 h at 0 °C and then washed with 200 mL of 1 M NaOH. After separation of the organic layer and drying over anhydrous magnesium sulfate, the solvent was evaporated and the residual product was distilled under vacuum: yield 10.8 g (34% based on ϵ-caprolactone); bp 85–87 °C (9 mmHg) [lit.[8] bp 82 °C (8 mmHg)].

Cationic Polymerization. Typical procedure: 1 (0.316 g, 2 mmol) was heated to 80 °C in a Schlenk tube under argon

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atmosphere. Tin(IV) chloride (4.7 μL, 0.04 mmol) was added, and the mixture was stirred at 80 °C. After 1 h, triethylamine (0.5 mL) was added, and then the mixture was cooled to room temperature. CH_2Cl_2 (5 mL) was added to dissolve the product, and the resulting solution was washed with saturated $NaHCO_3$ solution and dried over anhydrous sodium sulfate. The solution was evaporated, and the residue was dissolved in 1 mL of CH_2Cl_2 and precipitated into 20 mL of *n*-hexane. The precipitated polymer was collected as viscous material by decantation. The redissolution–precipitation was repeated once more, and the obtained polymer was dried under vacuum: yield 0.259 g (82%), $\bar{M}_n$ = 2840, $\bar{M}_w/\bar{M}_n$ = 4.53 by GPC.

Reaction of Poly(cyclic orthoester) with Tin(IV) Chloride. Poly(cyclic orthoester) was prepared by the polymerization of 1 (0.633 g, 4 mmol) with $SnCl_4$ (9.4 μL, 2 mol %) at 0 °C according to the procedure described above: yield 0.543 g (86%), $\bar{M}_n$ = 16 900, $\bar{M}_w/\bar{M}_n$ = 3.44 by GPC. The obtained polymer (0.300 g, 1.90 mmol) was heated to 120 °C in a Schlenk tube under Ar atmosphere. Tin(IV) chloride (4.4 μL, 2 mol %) was added, and the reaction mixture was stirred at 120 °C for 1 h. Triethylamine (0.5 mL) was added, and then the mixture was cooled to room temperature. The polymer was dissolved by addition of CH_2Cl_2 (5 mL), and the resulting solution was washed with saturated $NaHCO_3$ solution and dried over anhydrous sodium sulfate. The solvent was then evaporated, and the residue was redissolved in 1 mL of CH_2Cl_2 and poured into 20 mL of *n*-hexane. The precipitated polymer was collected as viscous material by decantation. The same step was once repeated, and the obtained polymer was dried under vacuum: yield 0.190 g (63%), $\bar{M}_n$ = 2620, $\bar{M}_w/\bar{M}_n$ = 1.99 by GPC.

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

Results and Discussion

1. Polymer Structure. Cationic polymerizations of an SOE, 1,4,6-trioxaspiro[4.6]undecane 1, were carried out under argon atmosphere for 1 h at various temperatures to examine the effect of polymerization temperature on the structure of the polymer produced. The bulk polymerization of 1 with $SnCl_4$ (2 mol %) proceeded well at temperatures between 0 and 120 °C (Table I, entries 1–8). The yield of the polymer was independent of the polymerization temperature, while $\bar{M}_n$ decreased with rising temperature. The polymer obtained at 0 °C was entirely poly(cyclic orthoester) (2, R = H).[5] On the contrary, polymers obtained above 40 °C showed the typical carbonyl absorptions (1736 cm^{-1}) in FT-IR spectra, suggesting the existence of poly(ether–ester) type structures, e.g., I. The intensity of carbonyl absorption showed a strong increase with rising temperature. This fact suggests a temperature-dependent ring-opening isomerization and unambiguously reveals that the polymer so far believed to consist entirely of structure I is instead a mixture of the two structures I and II.

To determine the content of the poly(ether–ester) unit in the obtained polymer, ^{13}C NMR (125.65 MHz, inverse-gated decoupling) measurements enabling quantitative analysis were employed. In the ^{13}C NMR spectra, the peak areas of the orthoester center carbon (~124 ppm) of II and the ester carbonyl carbon (~173 ppm) of I were compared and the degree of isomerization (the content of the poly(ether–ester) structure in the polymer) was calculated. A typical ^{13}C NMR spectrum of the polymer obtained by the polymerization at 80 °C (entry 5) is shown in Figure 1. The ratio of the two peaks was 62:38, which corresponded to the unit ratio (a(m):b(n)). Interestingly,

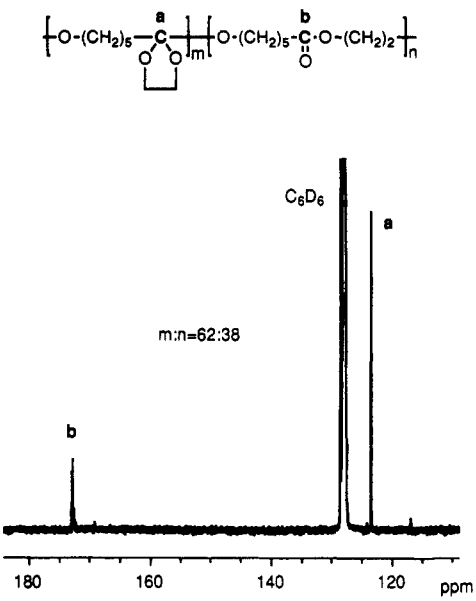


Figure 1. ^{13}C NMR spectrum (125.65 MHz, inverse-gated decoupling) of poly(SOE) obtained by cationic polymerization of 1 with $SnCl_4$ (2 mol %) in bulk at 80 °C for 1 h.

the presence of unit II was confirmed in the polymer obtained even at 120 °C. This result is in good accordance with the above IR study and demonstrates that to obtain a polymer with completely isomerized structure (I) is impossible or very difficult, because $\bar{M}_n$ of the polymer decreases seriously with rising polymerization temperature, presumably due to chain-transfer reactions (Table I).

The relationship between the polymerization temperature and the degree of isomerization is shown in Figure 2. The isomerization increasingly proceeded by raising the polymerization temperature; i.e., the degree of isomerization can be controlled by changing the polymerization temperature.

2. Polymerization Mechanism. The bulk polymerization of 1 was also performed at 80 °C, and the relation between the degree of isomerization and the polymerization time was studied (Table I, entries 5 and 9–11). The degree of isomerization increases with the polymerization time (Figure 3). However, the yield of the polymer shows no dependence on the polymerization time and is always considerably high. These results indicate that, at the beginning of the polymerization, poly(cyclic orthoester) is formed via a single-ring-opening process and is gradually isomerized to poly(ether–ester) by acid catalysis. The formation of poly(ether–ester) from poly(cyclic orthoester) can be explained by two possible pathways (Scheme I). Path A: Acid-catalyzed depolymerization of poly(cyclic orthoester) in the equilibrium yields SOE monomer, which then polymerizes to poly(ether–ester). Path B: Poly(cyclic orthoester) reacts directly to poly(ether–ester) via an acid-catalyzed intermolecular isomerization process. Although there is not enough evidence to distinguish between the two mechanisms, the result of Figure 3 seems to support path B as the actually occurring process. In path B, two routes (B-1 and B-2) are conceivable. We believe path B-1 to be predominant over path B-2, as generally exo C–O bonds are more prone to an acid-catalyzed cleavage than ring (endo) C–O bonds, e.g., mono(cyclic orthoester) with a dioxolane ring.[10]

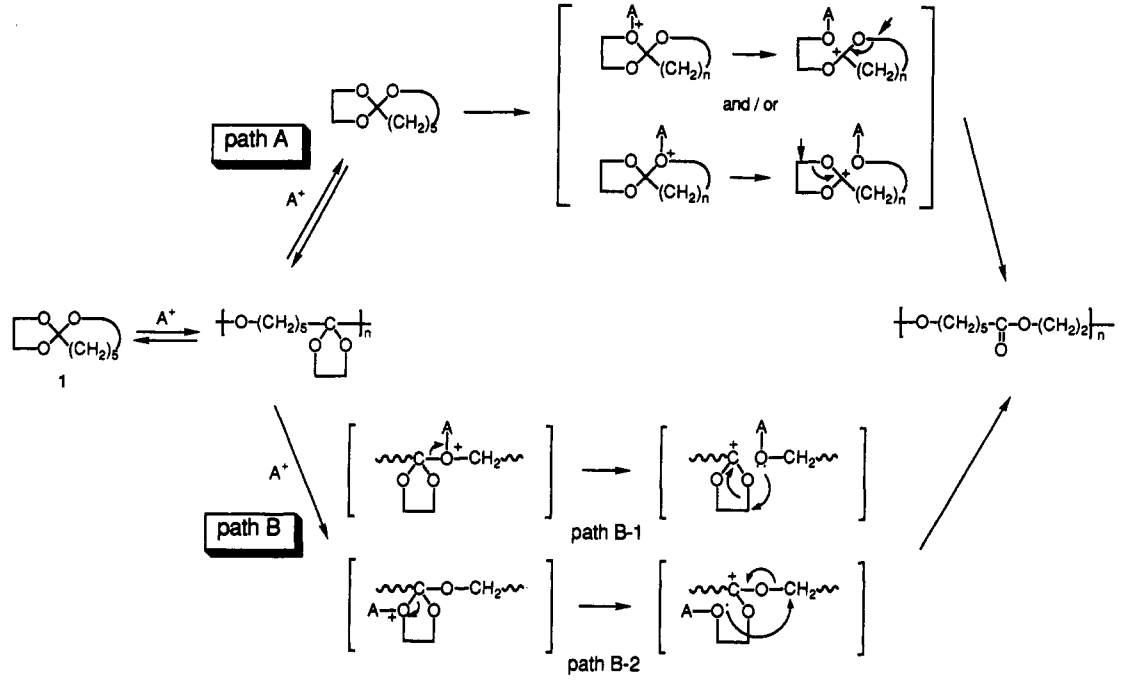
Furthermore, the structural change from II to I was studied using poly(cyclic orthoester) which was prepared under the same conditions as those for entry 1 (Table I).

Table I
Cationic Polymerization of 1[a]

entry	polymzn temp, °C	polymzn time, h	yield,[b] %	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[c]	degree of isomerization,[d] %	density of polym[e]	vol change on polymzn, %
1	0	1	84	14400 (4.69)	0	1.134	-2.6
2	40	1	64	7290 (2.91)	6	1.138	-3.0
3	60	1	70	6630 (3.51)	17	1.134	-2.6
4	70	1	84	3830 (4.20)	32	1.123	-1.6
5	80	1	82	2840 (4.53)	38	1.116	-1.0
6	90	1	73	2910 (3.15)	46	1.116	-1.0
7	100	1	79	1730 (3.74)	73	1.119	-1.3
8	120	1	79	1900 (2.95)	75	1.121	-1.4
9	80	5 min	81	6440 (3.25)	11		
10	80	4	81	3170 (2.57)	59		
11	80	12	87	2010 (2.07)	67	1.118	-1.2

[a] Bulk polymerization with $SnCl_4$ (2 mol %). [b] *n*-Hexane-insoluble part. [c] Estimated by GPC (eluent: THF, PSt standard). [d] Estimated by ^{13}C NMR (125.65 MHz, inverse-gated decoupling). [e] Measured with density gradient tubes at 25 °C. [f] (1 − density of polymer/density of monomer) × 100. Density of monomer: 1.105.

Scheme I



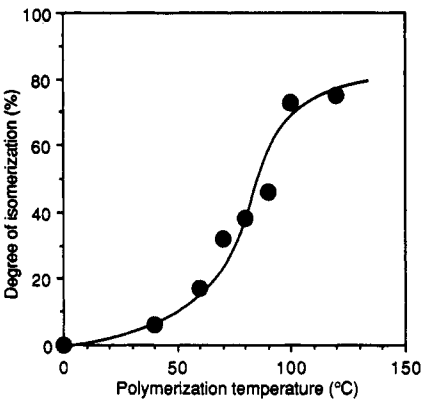


Figure 2. Relationship between the polymerization temperature and the degree of isomerization in the cationic polymerization of 1 with $SnCl_4$ (2 mol %) in bulk for 1 h.

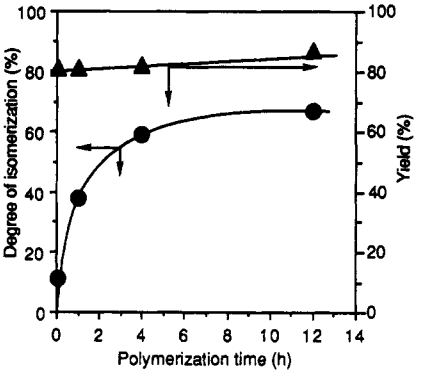


Figure 3. Time dependence of the degree of isomerization on the cationic polymerization of 1 with $SnCl_4$ (2 mol %) in bulk at 80 °C.

The obtained poly(cyclic orthoester) (yield 86%, $\bar{M}_n$ 16 900) was heated to 120 °C, and tin(IV) chloride (2 mol %) was added and kept at 120 °C for 1 h. The degree of isomerization of the recovered polymer (yield 63%, $\bar{M}_n$ 2620) was estimated to 54% by the ^{13}C NMR technique as described above. Although this value is rather low compared to that obtained by polymerization of 1 at 120 °C for 1 h (Table I, run 8), the result provides an additional evidence for the prediction that the poly(ether–ester) unit is formed via an intermediate poly(cyclic orthoester).

3. Volume Change on Polymerization. The above-mentioned polymerization behavior of SOE should result in volume changes during polymerization, since the specific nature of SOE is characterized by a double-ring-opening polymerization. Therefore, the volume change during the

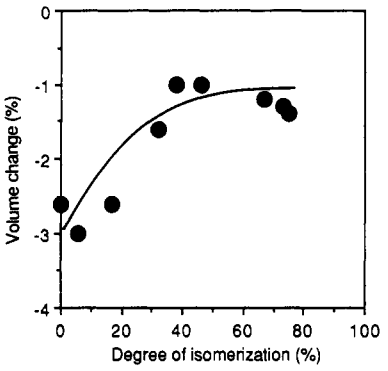
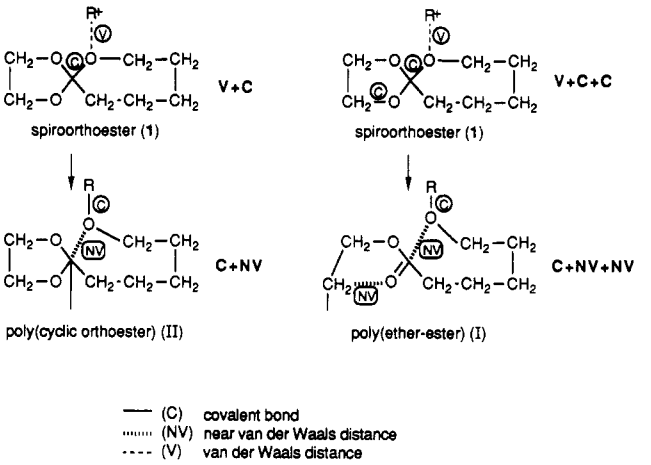


Figure 4. Relationship between the degree of isomerization and the volume change in the cationic polymerization of 1. The volume change was estimated by comparison of the densities of monomer (d = 1.105) and polymers.

polymerization of SOE was examined in relation to the degree of isomerization. The percentage of volume change was calculated from the densities of SOE and the obtained polymer which were measured with density gradient tubes. The density of 1 was 1.105. As shown in Table I, the density of the polymer ranged from 1.116 to 1.138. A relative volume change from −1.0 to −3.0%, i.e., a slight volume shrinkage, was observed during this study. During the conversion of SOE into II, a volume shrinkage of 2.6% was observed. The calculated volume change contains a maximum error of ±0.5%. The volume change (%) is plotted vs the degree of isomerization in Figure 4. The graph indicates the lowering of the volume shrinkage by enhancement of the degree of isomerization. This result can be easily understood since the essential factor of expandable monomers is reported to be the double ring opening of SOE.

According to Bailey's explanation,[11] one van der Waals distance (V) plus one covalent distance (C) is changed to one covalent distance (C) plus one near van der Waals distance (NV) in the conversion of SOE to structure II. Meanwhile, in the conversion of SOE to structure I, one van der Waals distance (V) plus two covalent distances (C) is changed to two near van der Waals distances (NV) plus one covalent distance (C). This explanation (Scheme II) is in good accordance with the experimental results. The difference of volume change between the conversion of SOE into II (−2.6%) and SOE into I (−1.0%) is 1.6%, which should result from the above-mentioned changes of the total bond distance generated by the two polymerizations. As shown in Scheme II, SOE → II causes (V + C) → (C + NV) while SOE → I results in (V + C + C) → (C + NV + NV). These results undoubtedly support the prediction that the pronounced volume change on polymerization originates from the double-ring-opening process of bicyclic or spirocyclic compounds. In the case of SOE, the volume change on polymerization can be

Scheme II



controlled by the degree of isomerization (content of unit II), or, in other words, by polymerization temperature, since the degree of isomerization depends upon temperature.

In this paper, the polymer structure of SOE which had been believed so far to consist solely of unit I has been found to consist of a mixture of the two units I and II. The mechanism of the cationic polymerization of SOE at high temperature was shown to involve initial conversion of SOE to poly(cyclic orthoester). The volume change on polymerization decreased in proportion to an increase of the degree of isomerization or polymerization temperature. With these studies the cationic polymerization of SOE was characterized in detail.

References and Notes

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Registry No. 1, 13043-49-7; 1 (homopolymer), 126493-57-0.