Novel Isomerization Polymerization of Glycidyl Acetate To Produce a Poly(ortho ester)

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ABSTRACT: A new mode of polymerization of glycidyl acetate (**1a**) to yield a poly(ortho ester), i.e., poly-[(2-methyl-1,3-dioxolane-4,2-diyl)oxymethylene] (**3a**), was explored. This new polymerization exclusively proceeded when a bulky Lewis acid, methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2a**), was employed as the catalyst. The polymerization of **1a** with 4 mol % of **2a** proceeded smoothly in toluene at 0 °C and gave **3a** in 82% after 1 h. The time-trace of the polymerization system revealed that this polymerization was completed within 3 min under these conditions. The polymerization mechanism is tentatively assumed as polyaddition of zwitterionic species produced from **1a** with the assistance of **2a**. The polymerization of glycidyl methacrylate (**1b**) with **2a** gave poly(ortho ester) **3b** in a similar manner.

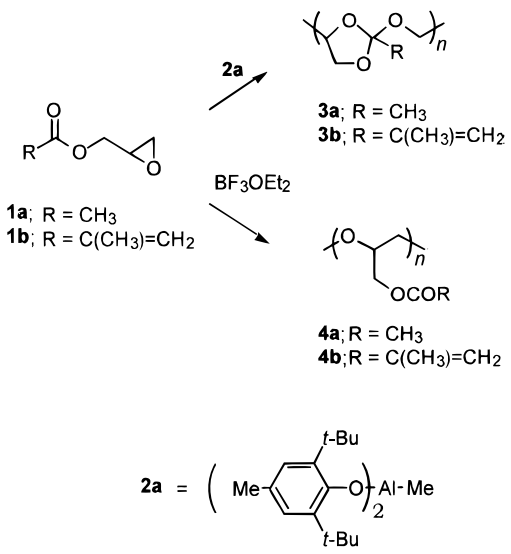
Introduction

Epoxide is a representative class of monomers in the field of ring-opening polymerization, and compounds bearing one or more epoxy group(s) are widely used for various industrial purposes.[1] Among these epoxides, glycidyl esters have high versatility since they are readily prepared from epichlorohydrin and carboxylic acids.[2] For example, bifunctional glycidyl esters are used for the preparation of epoxy resins, and glycidyl methacrylate (**1b**) is often chosen as a comonomer for the preparation of reactive polymers by radical copolymerization.[3,4] However, other monofunctional glycidyl esters, e.g., glycidyl acetate (**1a**), have received little attention from polymer chemists as well as polymer engineers.

The ring-opening polymerization of glycidyl carboxylate (**1**) with a conventional cationic initiator, such as BF_3, yields a ring-opening oligomer, oligo[oxy(1-acyloxymethyl)ethylene] (**4**).[5] The present paper, however, describes a novel mode of polymerization of **1** to yield poly(1,3-dioxolane-4,2-diyloxymethylene)s (**3**) (Scheme 1).

This new mode of polymerization occurred when a bulky Lewis acid, e.g., methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2a**), was employed as the catalyst. This type of bulky Lewis acid **2** was developed by Yamamoto et al. and has been used for the selective activation of a carbonyl group in the field of organic chemistry.[6] In the field of polymer chemistry, **2** has been applied successfully to the activation of acrylic monomers as well as lactones toward anionic polymerization.[7] In these studies, the basic structures of the resulting polymers were not affected by the presence of **2**, while the rates of polymerization were accelerated by the coordination of **2** to carbonyl groups of these monomers.[8] In the present case, on the other hand, **2a** induces a novel type of polymerization of **1** to give a new polymer.

Scheme 1



Experimental Section

Materials. Glycidyl acetate (**1a**) and isobutyrate (**1c**) were prepared by the condensation of the corresponding sodium carboxylate with epichlorohydrin.[2] Glycidyl methacrylate (**1b**) was commercially available. These monomers were distilled under reduced pressure and stored in nitrogen. Methylaluminum bis(2,5-di-*tert*-butyl-4-methylphenoxide) (**2a**) was prepared by the reaction between trimethylaluminum and 2,5-di-*tert*-butyl-4-methylphenol, which was purified by recrystallization from toluene.[6] Other aluminum derivatives, ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2b**), chloroaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2c**), methylaluminum 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxide) (**2d**), and ethylaluminum 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxide) (**2e**), were prepared in similar manner. They were used as toluene solutions. 1-Methyl-2,6,7-trioxabicyclo[2.2.1]heptane (**5b**) was prepared according the literature.[9] Solvents were commercially available, which were dried by the conventional methods, distilled under nitrogen, and stored over molecular sieves 3Å.

Measurements. ^{1}H NMR spectra were recorded on a 90 MHz JEOL JNM-FX90Q, a 200-MHz Varian XL200, or a 500-

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MHz Bruker ARX500 NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL JNM-FX90Q NMR spectrometer operated at 22.6 MHz. FT-IR spectra were obtained on a Jasco IR-810 infrared spectrometer. GPC analysis was performed using a Tosoh G2500H_{XL} column in chloroform. Number average molecular weights of the samples were measured by a vapor pressure osmometer (Corona Model 114) in chloroform at 35 °C.

Polymerization of 1. A typical procedure for the polymerization of **1** was as follows. All operations were carried out under nitrogen. In a test tube equipped with a three-way stopcock and a stir bar were placed 0.296 g (2.50 mmol) of **1a** and 1.38 mL of toluene. The mixture was cooled to 0 °C and 0.36 mL of 0.278 M toluene solution of **2** (0.10 mmol) was added to the mixture. The mixture was kept at 0 °C for 1 h with stirring. The content of the tube was added to hexane to precipitate the produced polymer, which was purified further by reprecipitation from chloroform to hexane. After drying in vacuum, 0.244 g of **3a** (82% yield) was obtained as white powdery solid.

3a: See Figures 2 and 3 concerning its NMR data. IR (KBr) 2992, 2940, 2885, 1382, 1220, 1130, 1057, 1028, 898 cm^{-1}.

3b: ^1H NMR ($CDCl_3$) δ 1.77 (s, 3 H, CH_3), 3.38−4.38 (m, 5 H, OCH_2 and OCH), 4.96 (bs, 1 H, C=CH, trans), 5.29 (bs, 1 H, C=CH, cis). ^{13}C NMR ($CDCl_3$) δ 17.65 (CH_3), 62.43 (*exo*-CH_2), 67.25 (C_5), 75.05 (C_4), 113.55 (C=*C*H_2), 121.36 (C_2), 140.62 (*C*=CH_2). IR (KBr) 2964, 2900, 1732 (trace, $\nu_{C=O}$), 1664 ($\nu_{C=C}$), 1462, 1309, 1132, 1028, 990, 924 cm^{-1}.

3c: ^1H NMR ($CDCl_3$) δ 0.94 (d, 6H, CH_3), 1.57−1.60 (m, 1H, CH_3CH), 3.60−4.38 (m, 5H, OCH_2 and OCH). ^{13}C NMR ($CDCl_3$) δ 17.21 (CH_3), 34.93 (*C*HCH_3), 61.58 (*exo*-CH_2), 68.15 (C_5), 76.00 (C_4), 125.30 (C_2). IR (KBr) 2973, 2934, 1732, 1476, 1238, 1119, 1069, 976 cm^{-1}.

Hydrolysis of 3a. In a 5 mm-i.d. NMR sample tube were placed 9.9 mg of **3a** and 1.0 mL of D_2O. The system was heterogeneous at the beginning but became transparent after 40 min as it was kept at room temperature. The ^1H NMR measurement showed the complete conversion of the polymer to glycerol and acetic acid at this point.

Results and Discussion

Isomerization Polymerization of 1a. This new isomerization polymerization of glycidyl esters catalyzed by **2a** was investigated by using glycidyl acetate (**1a**), methacrylate (**1b**), and isobutyrate (**1c**) as the monomers. In the present study, the polymerization of **1a** was mainly investigated because it gave the polymer of the simplest structure.

The polymerization of **1a** with 4 mol % of **2a** was carried out in toluene at 0 °C for 1 h. The system was homogeneous throughout the reaction and a polymeric product was obtained as a white solid by pouring the reaction mixture into hexane. The yield of the polymer was 82% and no improvement on the yield was achieved with prolonged reaction (vide infra).

The polymer was soluble in almost all solvents except water and hexane. The structure of the polymer was identified as poly[(2-methyl-1,3-dioxolane-4,2-diyl)oxymethylene] (**3a**) from ^1H and ^{13}C NMR and IR spectra.

In Figure 1, the IR spectrum of **3a** (Figure 1a) is compared with that of the usual ring-opening polymer of **1a** (**4a**) prepared with BF_3OEt_2 (Figure 1b). Obviously, the structures of these polymers are completely different from each other. The carbonyl stretching band of the ester group of **4a** is observed at 1738 cm^{-1} in Figure 1b, while the corresponding peak due to the carbonyl group is scarcely found in Figure 1a. Moreover, several strong peaks due to the ortho ester-type C−O−C stretching are observed in a region 1000−1300 cm^{-1} in Figure 1a, whereas two strong peaks are observed in this region Figure 1b at 1050 and 1220 cm^{-1}, which are characteristic for the acetoxy group.

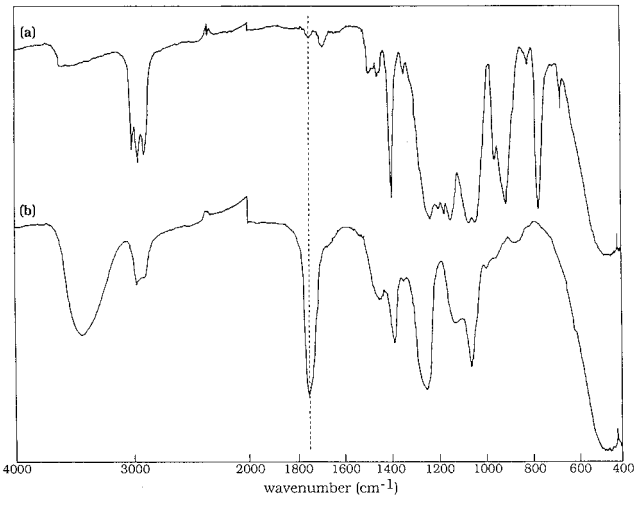


Figure 1. IR spectra of the polymers **3a** (a) and **4a** (b). The samples were casted on NaCl plates.

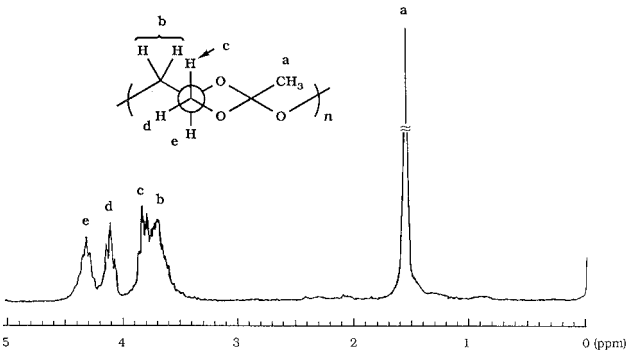


Figure 2. 200-MHz ^1H NMR spectrum of **3a** ($CDCl_3$/TMS).

The 200 MHz ^1H NMR spectrum of **3a** is shown in Figure 2, which again indicates the absence of an acetyl group in **3a**. The peak at δ 1.55 is ascribed to the methyl protons of ortho acetate. The ^{13}C NMR spectrum of **2a** (Figure 3) also shows the absence of a carbonyl group in the polymer: no peak due to carbonyl carbon is observed in the region 150−220 ppm and the peak at 121.9 ppm is ascribed to a quaternary ortho ester carbon (peak e). These spectroscopic data showed that the polymer **3a** was poly(ortho ester). The detailed assignment of the NMR spectra was done with the assistance of the HMQC spectrum of **3a** as well as the ^1H NMR data of unit models reported by Yokoyama et al.[9] In Figure 3, two OCH_2 carbons in the repeating unit of **3a** appear separately at δ 62.3 and 67.2, which indicates that the unit of **3a** has a five membered structure, poly-[(2-methyl-1,3-dioxolane-4,2-diyl)oxymethylene].

Although cis and trans configurations are possible for the unit of **3a**, its simple ^1H and ^{13}C NMR spectra suggest that **3a** exclusively consists of one of these isomers. With due consideration to the study by Yokoyama et al., we concluded that the configuration of **3a** was exclusively trans. The signals in the ^1H and ^{13}C NMR spectra (Figures 2 and 3) were assigned as indicated in these figures.

Hydrolysis of 3a. The structure of **3a** was also confirmed by hydrolysis. It is well-known that an ortho ester readily hydrolyzes in aqueous medium to produce a carboxylic acid and an alcohol. The hydrolysis of **3a** was examined in D_2O without adding any catalyst at room temperature. The polymer was insoluble in D_2O at the beginning, but the suspension gradually became homogeneous with stirring. After 40 min, a completely

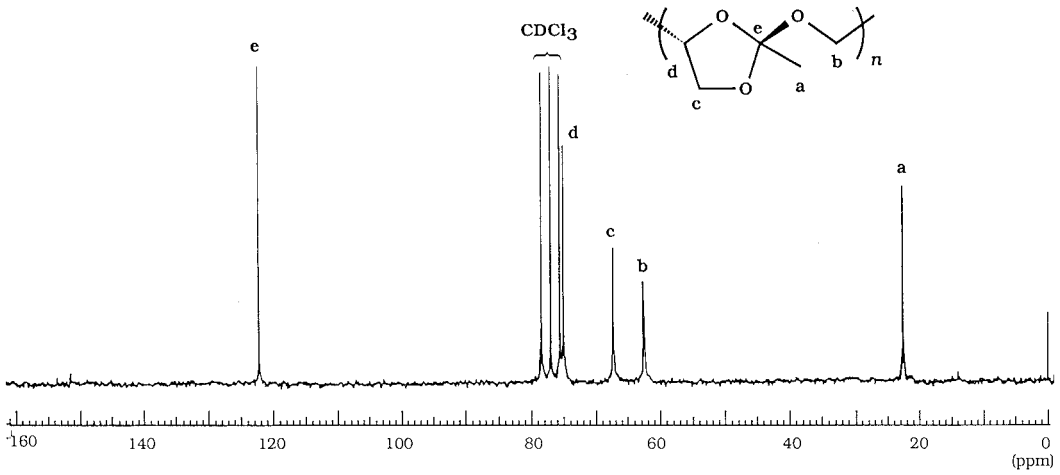


Figure 3. 22. 5-MHz ^{13}C NMR spectrum of **3a** ($CDCl_3$/TMS).

Table 1. Polymerization of 1a with 2a[a]

solvent	temp,[c] °C	time, h	3a yield, %	3a M_n[b]	3a M_w/M_n[b]
toluene	0	1	82	4600	2.6
benzene	0	1	46	1000	1.9
CH_2Cl_2	0	1	52	3800	2.0
THF	0	1	3	8800	1.9
CH_3CN	0	1	5	12000	1.5
nitrobenzene	0	1	4	7600	1.4
toluene	40	1	34	1400	2.3
toluene	rt	1	55	1700	3.3
toluene	rt	3	57	1500	2.6
toluene	−20	1	55	3800	2.3
toluene	−40	1	19	730	1.4
toluene	−78	1	8	1000	2.5

[a] [**2a**]/[**1a**] = 0.04; at 0 °C for 1 h. [b] Determined from GPC with polystyrene calibration. [c] rt = room temperature.

transparent solution was obtained and it was subjected to the ^1H NMR analysis, which showed that **3a** was completely hydrolyzed to acetic acid and glycerol.

Effect of Polymerization Conditions. This new polymerization of **1** proceeds in either a polar solvent or a nonpolar solvent as shown in Table 1, although it rather prefers nonpolar solvents: the polymerization in the polar solvent, acetonitrile and THF, produced **3a** in poor yields. Therefore, toluene was chosen as the solvent in the following experiments.

The polymerization of **1a** in toluene proceeded best at 0 °C and both yield and molecular weight of **3a** decreased upon increasing or decreasing the reaction temperature. No improvement was observed with prolonged reaction time (3 h).

The time conversion curve, the molecular weight, and the molecular weight distribution of **3a** are shown in Figure 4 for the polymerization of **1a** with **2a** carried out in toluene at 0 °C. The rate of polymerization was so fast that the polymerization was complete within 3 min. Although a small amount of **1a** remained in the system at this point, no further conversion of **1a** was observed during the reaction. The number average molecular weight of **3a** reached 4600 after 3 min and, then, decreased gradually with prolonged reaction. The weight average molecular weight of **3a** was not affected by the reaction time, but it decreased gradually from 9600 to 9000 during the reaction. These observations suggested that the polymerization of **1a** proceeded very quickly with accompanying termination. The decrease of the molecular weight during the reaction could be due to the slow hydrolysis of the produced polymer by water contaminating the system.

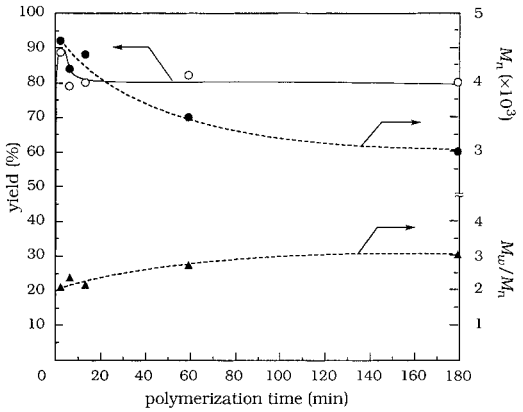


Figure 4. Time dependence curves for the yield, number average molecular weight, and polydispersity of **3a** ([**2a**]/[**1a**] = 0.04, in toluene, at 0 °C).

Table 2. Effect of Concentration of 2a on the Polymerization of 1a[a]

$[2a]_0/[1a]_0$	3a yield, %	3a M_n[b]	3a M_w/M_n[b]
0.1	93	470	1.13
0.06	75	1400	2.48
0.04	82	4600	2.58
0.03	11	1600	2.41
0.02	2		

[a] In toluene; at 0 °C for 1 h. [b] Determined from GPC with polystyrene calibration.

The molar ratio of **1** to **2** is an important factor in the present polymerization. Table 2 shows the effect of Lewis acid concentration on the polymerization. The polymer yield increased from 2% to 93% as $[2a]_0/[1a]_0$ increased from 2% to 10%. If **2a** is an initiator for this polymerization, *i.e.*, it directly attacks **1a** to initiate chain propagation and if chain transfer is negligible, the molecular weight of the polymer will decrease according to the increment of the initial feed ratio. If **2a** is an initiator and chain transfer frequently occurs, the molecular weight will be independent of the feed ratio and the polymer yield will decrease with the decrease of the feed ratio since the main factor determining the molecular weight is the ratio of rate of propagation to that of chain transfer. In the actual experiments, on the other hand, the molecular weight reaches a maximum in the run with 4 mol % of **2a**. It suggests that the role of **2a** is not as simple as that of conventional cationic initiators.

Table 3. Isomerization Polymerization of 1b and 1c[a]

monomer	$[\mathbf{2a}]_0/[\mathbf{1}]_0$	solv	product			
			3	yield, %	M_n[b]	M_w/M_n[b]
1b	0.04	toluene	**3b**	98[c]	7000[d]	1.8[d]
1b	0.02	toluene	**3b**	78	11000	1.5
1b	0.02	CH_2Cl_2	**3b**	78	10000	1.3
1b	0.02	acetonitrile	**3b**	33	6700	1.5
1c	0.04	toluene	**3c**	4	7000	1.4

[a] At 0 °C for 1 h. [b] Determined from GPC with polystyrene calibration. [c] The polymer containing chloroform soluble part (48% yield) and insoluble part. [d] Data for the chloroform soluble part.

Table 4. Polymerization of 1a with Other Lewis Acids[a]

Lewis acid	solvent	temp,[c] °C	time, h	polymer			
				structure	yield, %	M_n[b]	M_w/M_n[b]
BF_3OEt_2	toluene	−40	1	**4a**	15	450	1.3
2b	toluene	0	1	**3a**	78	1100	1.7
2b	toluene	rt	1	**3a**	62	730	1.6
2d	CH_2Cl_2	rt	3	**3a/4a**	84	740	1.1

[a] With 4 mol % of Lewis acid. [b] Determined from GPC with polystyrene calibration. [c] rt = root temperature.

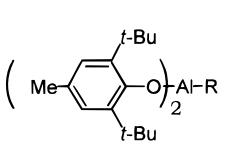
Polymerization of 1b and 1c. This new polymerization was successfully applied to glycidyl methacrylate (**1b**). The results for the polymerization of **1b** with **2a** are shown in Table 3. The polymerization of **1b** under the standard condition (with 4 mol % of **2a** in toluene at 0 °C for 1 h) gave a polymeric product quantitatively. However, it contained a significant amount of chloroform insoluble product. The structure of the chloroform soluble part of the polymer was determined as poly[(2-isopropenyl-1,3-dioxolane-4,2-diyl)oxymethylene] (**3b**) from the IR and NMR spectra. The IR spectrum of the chloroform insoluble part was essentially the same as that of the chloroform soluble part.

The polymerization of **1b** proceeded successfully even with 2 mol% of **2a** and gave a chloroform soluble polymer in 78% yield, whose number average molecular weight was determined as 11 000. No chloroform insoluble part was produced in this case. This is in contrast to the result that the yield of **3a** in the polymerization of **1a** with 2 mol % of **2a** was only 2%. The polymerization of **1b** in dichloromethane gave similar results: the polymer prepared with 4 mol % of **2a** was insoluble in chloroform, while that with 2 mol % of **2a** was soluble. The polymerization of **1b** proceeded successfully even in acetonitrile, although it was not suitable for the polymerization of **1a**.

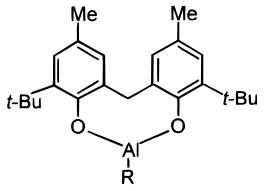
The present polymerization is exothermic and the temperature of the mixture rose just after the mixing of **1b** with **2a**. The coordination of **2a** to an acrylic monomer, e.g., MMA, has been known to enhance the reactivity of MMA toward the anionic polymerization. Therefore, the reaction of **2a** with **1b** at an elevated temperature may cause both vinyl and ring-opening isomerization polymerizations, concurrently. It is the reason why a cross-linked polymer was obtained in the runs with 4 mol % of **2b**. This will be the reason for the formation of the chloroform insoluble polymer.

The present polymerization was found to be sensitive to the bulkiness of acyl substituent of monomer. The polymerization of glycidyl isobutyrate (**1c**) under the standard condition gave poly[(2-isopropyl-1,3-dioxolane-4,2-diyl)oxymethylene] (**3c**) in a similar manner, but the yield was poor.

Effect of Lewis Acid on the Polymer Structure. The polymerization of **1a** with BF_3OEt_2 gave the ring-opening oligomer **4a** whose number average molecular weight was found as 450 from the GPC measurement. Obviously, the present polymerization is strongly influenced by the steric factor of the Lewis acid. To clarify this problem, a series of bulky Lewis acids **2b**−**e** was examined as the catalysts for the present polymerization.



2a; R = Me
2b; R = Et
2c; R = Cl



2d; R = Me
2e; R = Et

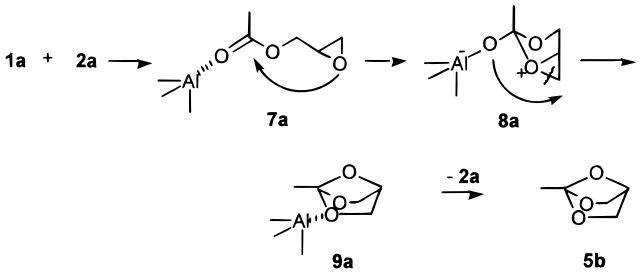
When ethylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2b**) was chosen as the Lewis acid instead of **2a**, the ortho ester-type polymer **3a** was also produced. The polymer yields were generally high, although the molecular weights of the polymers were significantly lower than those prepared with **2a** under similar conditions. The treatment of **1a** with chloroaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (**2c**), on the other hand, yielded no polymeric product. The polymerization of **1a** with methylaluminum 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxide) (**2d**) did not yield **3a**, but gave an oligomer composed of both **3a** and **4a** units, while the polymerization with ethylaluminum 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxide) (**2e**) yielded no polymeric product.

Possible Polymerization Mechanism. It is of interest to clarify the mechanism of this unique polymerization. However, we have no concrete evidence to determine it at present. At least it is clear that the present polymerization does not proceed via an ordinary mechanism, the cationic ring-opening polymerization of **1a** initiated by **2a** or the polycondensation between the ester moiety and the epoxide moiety of **1a** catalyzed by **2a**.[10] The former mechanism was refused by the fact that the polymerization of **1a** with the conventional cationic initiator BF_3OEt_2 did not yield **2a**, but **4a**. The latter was also ruled out since no polymerization of 3,4-epoxybutyl acetate (**11**) proceeded in the presence of 4 mol % of **2a** in toluene at 0 °C for 1 h. No polyaddition took place between diethylene glycol diacetate and ethylene glycol diglycidyl ether under the same conditions.

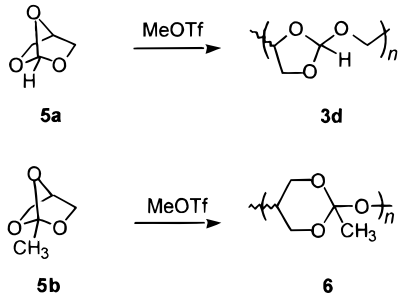
Determination of terminal structure of polymer or kinetic analysis of polymerization often gives important information concerning the polymerization mechanism. In the present case, the IR and NMR analyses of **3a** showed that it contained a small amount of acetyl group. However, it is difficult to determine whether the acetyl group was formed during the polymerization or was produced during and/or after workup by hydrolysis. A kinetic study could not be performed since the polymerization of **1a** progressed so fast at 0 °C as shown in Figure 4. At −20 °C, on the other hand, the monomer conversion reached ca. 15% at the very beginning of reaction and stayed around this value during the reaction. Therefore, the polymerization mechanism of **1a** with **2a** should be considered based on indirect evidences.

1a has two nucleophilic sites, the epoxide oxygen and the carbonyl oxygen, each of which can coordinate to a Lewis acid. In general, ether oxygen is more nucleo-

Scheme 2



Scheme 3



philic than ester-type carbonyl oxygen.[12] Therefore, a conventional Lewis acid such as BF_3OEt_2 is coordinated by the epoxy oxygen and induces the ring-opening polymerization of **1** to produce **4**. On the other hand, the coordination of **2a** by the epoxy oxygen is inhibited for a steric reason and, instead, **2a** is coordinated by the carbonyl oxygen. This is highly likely considering previous studies.[13] The complexation increases the electrophilicity of the carbonyl carbon of the adduct (**7a**) and, therefore, it can accept a nucleophilic attack.

A probable pathway, which seems to be adequate at first glance, is the isomerization/ring-opening polymerization pathway. An intramolecular attack of the epoxy oxygen of **7a** leads to the formation of a zwitterionic species **8a** having an oxiranium ring, which rapidly isomerizes to an adduct of 1-methyl-2,6,7-trioxabicyclo-[2.2.1]heptane (**5b**) with **2a** (**9a**). Then it dissociates to **2a** and **5b**, and the regenerated **2a** continues further isomerization of **1a** to **5b** (Scheme 2). In this pathway **5b** is the real monomeric species and its cationic ring-opening polymerization initiated by **2a** produces **3a**.

Although this route seems to be reasonable, the formation of **5b** in the polymerization system was not detected at all. To verify the appropriateness of this mechanism, the examination on the ring-opening polymerization of **5b** with **2a** is important. The polymerization of **5** has already been done by Yokoyama et al. and they reported that the cationic ring-opening polymerization of **5b** with methyl trifluoromethanesulfonate (MeOTf) yielded poly[(2-methyl-1,3-dioxane-2,5-diyl)oxy] (**6**) having a six-membered ring in its repeat unit (Scheme 3).[9] Our investigation on the polymerization of **5b** with **2a** or BF_3OEt_2 as the catalyst, however, leads to quite different results.

The polymerization of **5** was examined in CH_2Cl_2 under similar conditions to those of the polymerization of **1** (Table 5) with varying the feed ratio ([I]/[M]) from 0.01 to 0.1. The dependence of the polymer yield and molecular weight on the feed ratio in the polymerization of **5b** was similar to those in the case of **1a** as far as comparing the data in Tables 2 and 5, which suggests both polymerizations proceed via the same mechanism. With BF_3OEt_2 initiator, a polymer was produced only when 4 mol% of the Lewis acid was employed. In any case, the structure of the produced polymer was not **6**.

Table 5. Ring-Opening Polymerization of 5b[a]

		polymer		
Lewis acid	$[LA]_0/[\mathbf{5b}]_0$	yield, %	M_n[b]	M_w/M_n[b]
2a	0.1	85	1100	1.2
2a	0.04	80	3300	1.9
2a	0.01	2.8	1600	1.9
BF_3OEt_2	0.1	0		
BF_3OEt_2	0.04	46	1100	1.7
BF_3OEt_2	0.01	0		

[a] In CH_2Cl_2 at 0 °C for 1 h. [b] Determined from GPC with polystyrene calibration.

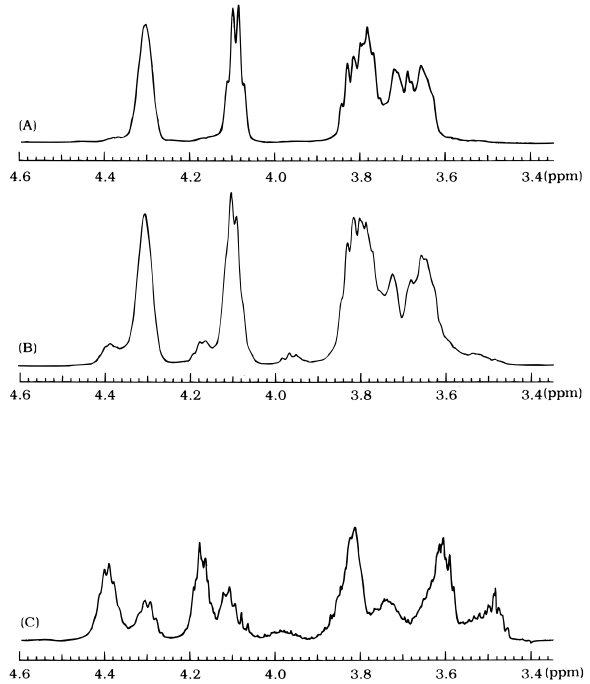


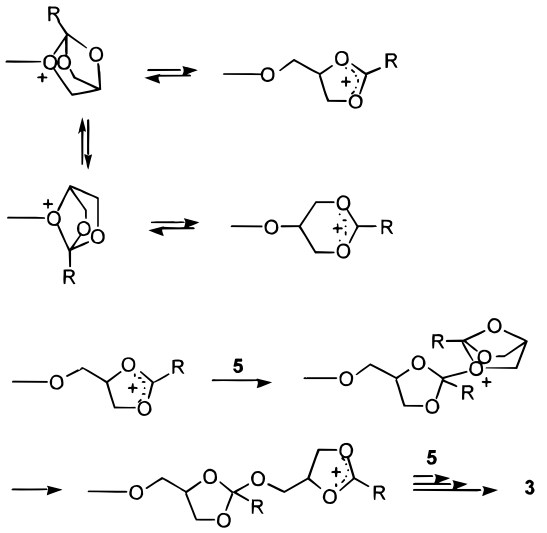
Figure 5. Comparison of the 500 MHz ^1H NMR spectrum of **3a** (A) with those of poly(**5**)s prepared with **2a** (B) and with BF_3OEt_2 (C) in the region δ 3.4−4.6 ($CDCl_3$/TMS in all cases).

In Figure 5 are compared a part of the 500 MHz ^1H NMR spectrum of **3a** (A) with that of the poly(**5**) prepared with **2a** (B). The coincidence of the main signals shows that the main structure of the poly(**5**) prepared with **2a** is **3a**. On the other hand, the spectrum of the poly(**5**) prepared with BF_3OEt_2 (C) differs significantly from the others, and it was assumed to contain both five- and six-membered units, although the exact assignment was not yet done.

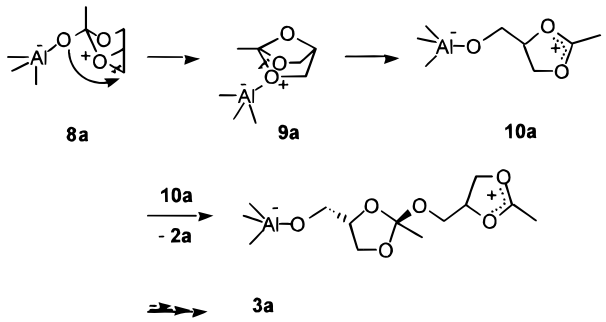
The mechanism for the ring-opening polymerization of **5** proposed by Yokoyama et al. was shown in Scheme 4. The attack of initiator occurs preferably at O_2 (or O_6) and an oxonium ion is once formed. It isomerizes to a 1,3-dioxolanium ion. In the case of **5a** (R = H), this kinetically preferred 1,3-dioxolanium ion concerns the subsequent propagation and produces **6**. In the case of **5b** (R = CH_3), on the other hand, the methyl substituent stabilized the 1,3-dioxolanium ion and it isomerized to a more thermodynamically favored 1,3-dioxanium ion. The propagation from the latter forms the polymer of five-membered ring structure.[9]

The above mechanism, however, does not explain the structural difference among the poly(**5**)s prepared with the different initiators, since the Lewis acid exists only at the initiating end of the polymer and will not influence the polymer structure. Moreover, the exclusive trans configuration of **3a** cannot be explained by

Scheme 4



Scheme 5



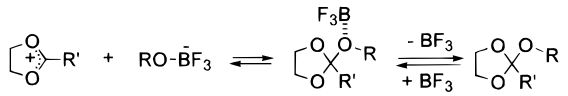
this mechanism: the polymerizations of **5a** and **5b** were not stereoselective and respectively gave **3c** and **6** of random configuration (cis:trans = ca. 1:1).[9] Therefore, it was highly likely that the ring-opening polymerization of **5** with Lewis acid as well as the polymerization of **1** with **2a** proceeds via a different route from the ring-opening polymerization of **5** with an alkylating agent.

The mechanism involving polycondensation of zwitterionic species **10a** shown in Scheme 5 seems to be more feasible to this polymerization at present. The zwitterion **10a** has the reactive 1,3-dioxolanium ring and its isomerization to another zwitterion having a six-membered 1,3-dioxanium ring as shown in Scheme 4 is conceivable. However, the attachment of the bulky **2a** moiety at the alkoxide oxygen will inhibit the backward cyclization sterically, and, therefore, the isomerization of **9a** to **10a** is considered to proceed irreversibly.

The polycondensation begins with the intermolecular condensation between two molecules of **10a**. In this step the bulky substituents attached to the aluminum atom will cover one side of the 1,3-dioxolanium ring, and, therefore, the attack of alkoxy aluminate moiety of another **10a** molecule to the 2-position of the ring exclusively occurs at the opposite side of the 1,3-dioxolanium ring to yield the trans **3a** unit. Thus, the exclusive trans configuration of **3a** can be explained reasonably according to this mechanism.

The formation of **10a** requires the generation of **7a**, **8a**, and **9a** in turn. If the isomerization reactions **8a** → **9a** → **10a** proceed fast enough, neither **8a** nor **9a** concern the propagation directly. Among these steps, the intramolecular cyclization of **7a** to produce **8a** seems to be the most important step, since no polymerization took place when **11** was employed as the monomer: in

Scheme 6



this case the cyclization requires the formation of a six-membered homologue of **8a**, which will be entropically less favorable.

The polymerization of **5b** with Lewis acid will proceed via essentially the same pathway as that of **1**. In the case with BF_3OEt_2 catalyst, however, the isomerization of a 1,3-dioxolanium-type zwitterion to a 1,3-dioxanium-type one will proceed to some extent to induce the complicated structure of the resulting polymer.

In the above polymerization pathway we are assuming polycondensation between zwitterionic molecules caused by the reaction of the alkoxyaluminate with the 1,3-dioxolanium cation. A similar reaction between an alkoxyborate with a 2-alkyl-1,3-dioxolanium cation was reported previously by Meerwein et al. (Scheme 6).[11] In this reaction the attack of alkoxyborate exclusively occurs at the 2-position of dioxolanium ring, although the 4-position attack is common in the ring-opening polymerization of 1,3-dioxolanes. Although this reaction is reversible, the retro-reaction can be avoided by the addition of a carbonyl compound into the system, which removes BF_3 from these equilibria.

In the present polymerization system, similar equilibria may exist in the polycondensation step. However, the equilibria will lie well to the right since the unreacted monomer removes **2a** from the equilibria and it ensures the successive polyaddition to produce **3a**.

The difference in the catalytic activity between **2** as well as that in the polymerization behavior of **1** are well explained by assuming the polycondensation mechanism. The low polymerizability of **1c** is explained by the fact that the polycondensation between zwitterionic species is difficult to proceed since it has a more bulky, secondary alkyl group at the 2-position of the dioxolanium ring. Similarly, the steric hindrance around the alkoxyaluminate end of zwitterionic species can be the reason for the low molecular weight of **3a** prepared with **2b**. The higher polymerizability of **1b** in comparison with either those of **1a** or **1c** will be due to the resonance stabilization of the 1,3-dioxolanium ring by the isopropenyl group, which prevents side reactions leading to termination.

When **2c** was chosen as the catalyst for the polymerization of **1a**, no polymerization of **1a** took place. This is explained as follows: the once produced zwitterionic species **8a** will readily loose a chloride anion, which attacks immediately the oxiranium cation to form a stable covalent species.

Although the above polycondensation mechanism seems to be the most suitable to explain the present polymerization, it is tentative, and detailed examination should be carried out on the polymerization of bicyclic ortho esters **5** with various Lewis acids to establish the mechanism. Even though the mechanism is not clear at present, the present polymerization is interesting not only from the view point of polymer chemistry but also from that of material science since the produced polymer can be called poly(monoglyceride): be aware that the hydrolysis of **3** gives the carboxylic acid and glycerol. It will be applicable, therefore, as a new class of biodegradable material usable in organisms: at least, the present pathway starting from **1** is superior to the

cationic polymerization of **5** to prepare poly(monoglyceride) because of the great difficulty in the synthesis of **5**.[9]

References and Notes

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(9) Yokoyama, T.; Padias, A. B.; DeBlauwe, F.; Hall, H. K., Jr. *Macromolecules* **1980**, *13*, 252
(10) Similar polycondensations between diepoxides and ditrifluoroacetates and between potassium perfluoroalkanoates and epibromohydrin catalyzed by quaternary ammonium salts were recently reported. (a) Kameyama, A.; Mochida, K.; Nishikubo, T. *Macromolecules* **1995**, *28*, 3490. (b) Kameyama, A.; Hashikawa, H.; Kijima, N.; Nishikubo, T. *Polym. J.* **1995**, *27*, 1068.
(11) Meerwein, H.; Borner, P.; Fuchs, O.; Sasse, H. J.; Spille, J. *Chem. Ber.* **1956**, *89*, 2060.
(12) *p*Ka values for conjugated acids of common esters were reported as around −6.5, while those for conjugated acids of common ethers were around −3.5. See for example: March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; Chapter 8. It has already been shown that **2** coordinates to the carbonyl oxygen of MMA[7b] and it does not induce the ring-opening polymerization of epoxide.[7c] See also refs 6−8.

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