Polymerization of Epoxide and β-Lactone Catalyzed by Aluminum Porphyrin. Exchange of Alkoxide or Carboxylate Group as Growing Species on Aluminum Porphyrin

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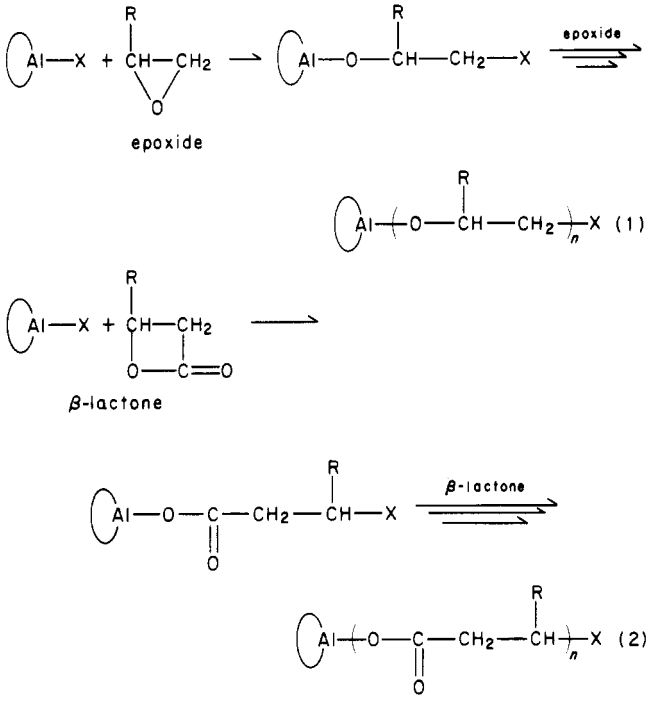
ABSTRACT: In the polymerization of epoxide or β-lactone catalyzed by aluminum porphyrin, exchange of alkoxide or carboxylate group as the growing species on aluminum porphyrin was directly confirmed by ^1H NMR spectroscopy by using combinations of two types of aluminum porphyrin with different alkoxide or carboxylate groups. A much faster rate for the exchange of the alkoxide or carboxylate group compared with the insertion of epoxide or β-lactone into aluminum–alkoxide or aluminum–carboxylate bonds was also confirmed by the unimodal, narrow molecular weight distribution of the polymer formed by using the mixture of two different aluminum porphyrins as catalyst.

Introduction

An aluminum porphyrin such as (tetraphenylporphinato)aluminum chloride (**1a**) is an excellent catalyst for the polymerization of epoxide[1] and β-lactone[2] and for the alternating copolymerization of epoxide and cyclic acid anhydride when coupled with quaternary ammonium or phosphonium salt.[3] The resulting polymers or copolymers are characterized by a narrow molecular weight distribution. The polymerization of epoxide or β-lactone proceeds by the repeated insertion of epoxide or β-lactone into aluminum–alkoxide bonds or aluminum–carboxylate bonds of the aluminum porphyrin, regenerating (porphinato)aluminum alkoxide or (porphinato)aluminum carboxylate, respectively.[4,5]

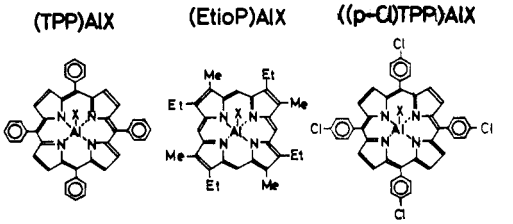


In these polymerization reactions, the number of polymer molecules is equal to the number of aluminum atoms. These facts appear to indicate that each alkoxide or carboxylate group on aluminum porphyrin has been fixed on a respective aluminum atom throughout the successive insertion reactions. In order to examine this possibility, we investigated whether or not alkoxide or carboxylate group X is exchanged in the system involving the mixture of two types of aluminum prophyrin with different alkoxide or carboxylate groups, Por^1AlX^1 and Por^2AlX^2. To our surprise and contrary to expectation, fairly rapid exchange of these groups was observed by ^1H NMR spectroscopy, as described here. The relation of the exchange to the insertion reaction is also discussed on the basis of the observation made as to the molecular weight distribution of the polymer formed by using the mixture of two different aluminum porphyrins as catalyst.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) and 5,10,15,20-tetrakis(*p*-chlorophenyl)porphine ((*p*-Cl)$TPPH_2$) were synthesized from pyrrole and benzaldehyde or *p*-chlorobenzaldehyde, respectively, in propionic acid and recrystallized from chloroform/methanol.[6] Etioporphyrin I ($EtioPH_2$) was synthesized from *tert*-butyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate, as reported by Barnett and Smith.[7] Dichloromethane (CH_2Cl_2) was washed successively with sulfuric acid, water, and aqueous sodium bicarbonate, dried over calcium chloride, and distilled over calcium hydride in nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) was distilled over calcium hydride in nitrogen atmosphere. Triethylaluminum (Et_3Al) and diethylaluminum chloride (Et_2AlCl) were purified by distillation under reduced pressure in nitrogen atmosphere. Methanol and ethanol were dried over magnesium sulfate and distilled over magnesium in nitrogen atmosphere. 3,3-Dimethylbutanoic acid (*tert*-butylacetic acid) was distilled under reduced pressure in nitrogen atmosphere. Commercial 2,2-dimethylpropanoic acid (trimethylacetic acid) was used without further purification. β-Butyrolactone was dried over calcium hydride and then distilled under reduced pressure in nitrogen atmosphere. 1,2-Epoxypropane (propylene oxide, PO) was distilled after refluxing over a mixture of calcium hydride and potassium hydroxide.

Preparation of Aluminum Porphyrin ((TPP)AlX, (EtioP)AlX, and (*p*-ClTPP)AlX). (Tetraphenylporphinato)ethylaluminum (TPPAlEt, **1b**), (etioporphinato)ethylaluminum ((EtioP)AlEt, **2b**), and (tetrakis(*p*-chlorophenyl)porphinato)ethylaluminum ((*p*-ClTPP)AlEt, **3b**) were prepared by the



	(TPP)AlX	(EtioP)AlX	((p-Cl)TPP)AlX
-Cl	1a	2a	–
$-CH_2CH_3$	1b	2b	3b
$-OCH_3$	1c	2c	–
$-OCH_2CH_3$	1d	2d	–
$-OCOC(CH_3)_3$	1e	–	3e
$-OCOCH_2C(CH_3)_3$	1f	–	3f

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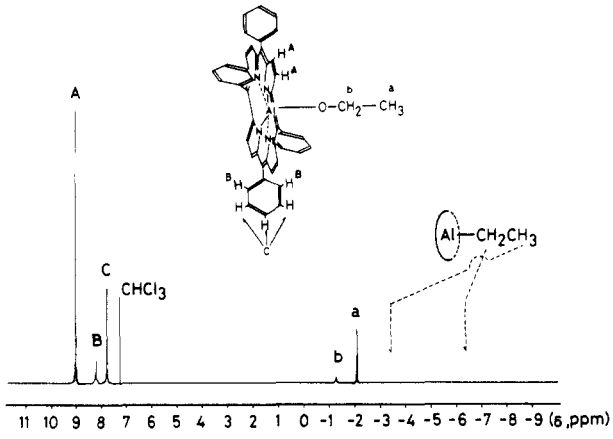

Figure 1. ^1H NMR spectrum of the product of the reaction between (TPP)AlEt (**1b**) and ethanol in $CDCl_3$.

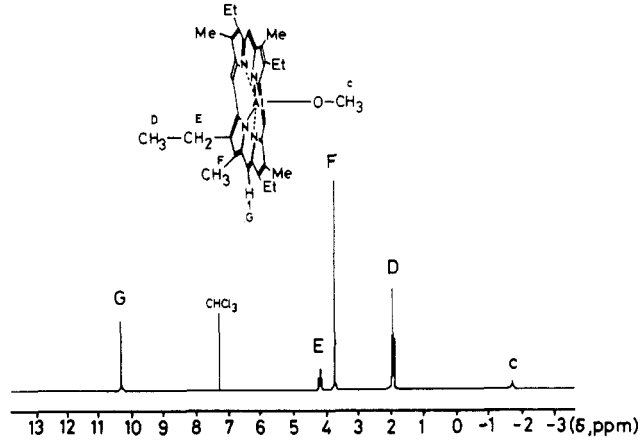

Figure 2. ^1H NMR spectrum of the product of the reaction between (EtioP)AlEt (**2b**) and methanol in $CDCl_3$.

equimolar reaction between Et_3Al and the corresponding porphine in CH_2Cl_2 at room temperature in nitrogen atmosphere.[8] (Tetraphenylporphinato)aluminum carboxylate ((TPP)AlOCOR, **1e**, **1f**) or (tetrakis(*p*-chlorophenyl)porphinato)aluminum carboxylate ((*p*-ClTPP)AlOCOR, **3e**, **3f**) was prepared by the reaction of **1b** or **3b** with a small excess of carboxylic acid in CH_2Cl_2 at room temperature in nitrogen atmosphere.[9] (Tetraphenylporphinato)aluminum alkoxide ((TPP)AlOR, **1c**, **1d**) or (etioporphinato)aluminum alkoxide ((EtioP)AlOR, **2c**, **2d**) was prepared by the reaction of **1b** or **2b** with the corresponding alcohol in nitrogen atmosphere. For example, the procedure of preparation of (tetraphenylporphinato)aluminum methoxide, (TPP)-$AlOCH_3$ (**1c**), is as follows:[10] (TPP)AlEt (**1b**) (1 mmol) was prepared in CH_2Cl_2 (20 mL) in a 50-mL teardrop type flask equipped with a reflux condenser. After the CH_2Cl_2 was removed under reduced pressure, methanol (20 mL, 0.50 mol) was introduced into the flask by a syringe and the mixture was refluxed overnight. Unreacted methanol was removed from the reaction mixture under reduced pressure to leave a purple solid, which was dissolved in $CDCl_3$ and subjected to ^1H NMR spectroscopy. The ^1H NMR spectrum of the product of the reaction between (TPP)AlEt (**1b**) and ethanol is shown in Figure 1, where the signals due to methyl and methylene protons of ethoxide groups bound to aluminum porphyrin are observed at δ −2.1 (a) and −1.3 (b), respectively, with the absence of the signals due to the ethyl group of **1b** (δ −3.4, methyl; −6.4, methylene).[8] The intensity ratio of the signals of the ethoxide group (a, 3 H; b, 2 H) to the porphyrin group (A, 8 H; B, 8 H; C, 12 H) confirms the formation of (TPP)$AlOCH_2CH_3$ (**1d**). Figure 2 shows the ^1H NMR spectrum of the product of the reaction between (EtioP)$AlCH_2CH_3$ (**2b**) and methanol. The appearance of a singlet signal at δ −1.8 (c) indicates the formation of the methoxide group bound to (etioporphinato)aluminum. Similarly, the formation of (TPP)$AlOCH_3$ (**1c**) from **1b** and methanol and of (EtioP)$AlOCH_2CH_3$ (**2d**) from **2b** and ethanol were also confirmed by ^1H NMR. These characteristic signals at unusually high magnetic field due to the strong shielding effect of the porphyrin ring, because they are not overlapped by other usual signals, make it easy to follow the reaction of the axial alkoxide group bound to aluminum porphyrin.

Mixture of Two Types of Aluminum Porphyrin with Different Axial Ligands. (TPP)$AlOCH_2CH_3$ (**1d**) and (EtioP)$AlOCH_3$ (**2c**) were mixed as follows: To a 50-mL flask equipped with a three-way cock containing **1d** (0.5 mmol) was added a $CDCl_3$ solution (20 mL) of **2c** (0.5 mmol) at room temperature with stirring. A portion of the above reaction mixture was transferred into a glass tube (o.d. = 5 mm) by a syringe, sealed in nitrogen, and the ^1H NMR spectrum measured. (TPP)$AlOCOC(CH_3)_3$ (**1e**) and (*p*-ClTPP)$AlOCOCH_2C(CH_3)_3$ (**3f**) were mixed by pouring the respective $CDCl_3$ solutions (about 1 mmol of porphyrin/20 mL of $CDCl_3$) into a glass tube (o.d. = 5 mm) at room temperature.

Polymerization of 1,2-Epoxypropane or β-Butyrolactone with (TPP)AlCl (1a), (EtioP)AlCl (2a), or the Equimolar Mixture of 1a and 2a. Detailed procedures of the polymerization of 1,2-epoxypropane or β-butyrolactone by aluminum porphyrin and the determination of molecular weight and molecular weight distribution of the products were described in previous papers.[1,2] Polymerization using the equimolar mixture of **1a** and **2a** was carried out as follows: To a 50-mL flask connected with a three-way cock were added the solutions of **1a** and **2a** (5 mL, respectively; 1 mmol of porphyrin/20 mL of CH_2Cl_2) at room temperature in nitrogen atmosphere, followed by the introduction of 1,2-epoxypropane (100 mmol) or β-butyrolactone (50 mmol). After an appropriate time, the volatile fraction was removed under reduced pressure to leave the polymerization product. For vapor pressure osmometry of poly(1,2-epoxypropane), the product purified according to the following procedure was employed: The reaction mixture after the removal of volatile fractions was dissolved in hexane (30 mL), and insoluble fractions, the catalyst residue, were filtered off from the solution. A pale purple viscous liquid obtained by evaporating the filtrate was dissolved in acetone (30 mL), followed by shaking with ion-exchange resin Dowex 500W X-4 (1.5 g) for a few minutes. After the ion-exchange resin was filtered off, the filtrate was subjected to evaporation to give the polymer as a slightly yellow viscous liquid. Repeating the treatment with ion-exchange resin once more and evaporating the benzene solution of the residue under reduced pressure at 60–80 °C for half a day gave poly(1,2-epoxypropane) as an almost colorless viscous liquid.

Measurements. The ^1H NMR spectrum of the reaction system in $CDCl_3$ was measured in a sealed tube in nitrogen atmosphere by using a JEOL Type JNM GX-400 spectrophotometer operating at 399.7 MHz, and the chemical shift was determined with respect to $CHCl_3$ (δ 7.28). The molecular weight and molecular weight distribution of the product in the polymerization were determined by gel permeation chromatogram (GPC) on a Toyo Soda Model HLC-802A high-speed liquid chromatograph equipped with a differential refractometer detector, using polystyrene as standard for the product from β-butyrolactone and using poly(1,2-epoxyethane) (poly(ethylene oxide), PEO) and poly(propylene glycol) (PPG) for the product from 1,2-epoxypropane. Vapor pressure osmometry in benzene was performed on a Corona Model 117 vapor pressure osmometer by using polystyrene as standard.

Results and Discussion

NMR Studies of the Mixture of (TPP)$AlOCH_2CH_3$ (1d) and (EtioP)$AlOCH_3$ (2c). Exchange of Alkoxide Groups on Aluminum Porphyrin. In order to investigate the behavior of aluminum alkoxide bonds in aluminum porphyrin, the NMR spectrum of a mixture of two types of aluminum porphyrin having different alkoxide groups was examined. If no exchange of alkoxide groups occurs between the molecules of aluminum porphyrin, only two kinds of alkoxide group corresponding to the starting aluminum porphyrins must be observed. Figure 3 shows the ^1H NMR spectrum of the equimolar mixture of (TPP)$AlOCH_2CH_3$ (**1d**) and (EtioP)$AlOCH_3$ (**2c**) in $CDCl_3$ and its high magnetic field region, where the signals due to alkoxide groups are observed. In addition to the signals

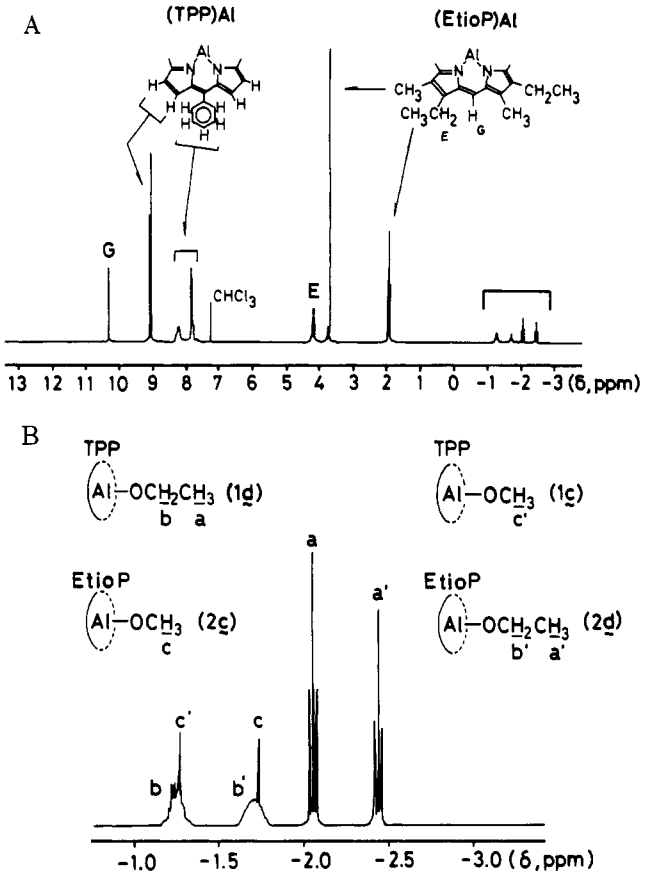

Figure 3. (A) ^1H NMR spectrum of the equimolar mixture of (TPP)AlOCH$_2$CH$_3$ (**1d**) and (EtioP)AlOCH$_3$ (**2c**) in CDCl$_3$ at room temperature after 30 min. (B) High magnetic field region.

due to the ethoxide group of (TPP)AlOCH$_2$CH$_3$ (**1d**) (a and b) and the signal due to the methoxide group of (EtioP)AlOCH$_3$ (**2c**) (c), it is rather unexpected and interesting to observe that new signals appear at δ −2.4 (a′) and −1.7 (b′), assignable respectively to the methyl and methylene protons of the ethoxide group on (etioporphinato)aluminum (**2d**) and at δ −1.3 (c′) due to the methoxide group on (tetraphenylporphinato)aluminum (**1c**). These signals are in agreement with the signals of respective aluminum porphyrin separately prepared. Thus, the alkoxide group bound to aluminum porphyrin was confirmed to exchange between the molecules of (porphinato)aluminum alkoxide even at room temperature.

$$\underset{\mathbf{1d}}{\text{(TPP)AlOCH}_2\text{CH}_3} + \underset{\mathbf{2c}}{\text{(EtioP)AlOCH}_3} \rightleftharpoons \underset{\mathbf{1c}}{\text{(TPP)AlOCH}_3} + \underset{\mathbf{2d}}{\text{(EtioP)AlOCH}_2\text{CH}_3}$$

Mole fractions of the four aluminum porphyrins can be estimated by the intensity of the signals. As shown in Figure 4, mole fractions of (EtioP)AlOCH$_3$ (**2c**) employed in the mixing and (EtioP)AlOCH$_2$CH$_3$ (**2d**) formed by the exchange of the alkoxide group became about 25%, respectively, in 30 min. The same phenomenon was observed for the mole fractions of (TPP)AlOCH$_3$ (**1c**) and (TPP)AlOCH$_2$CH$_3$ (**1d**). Thus, fairly rapid exchange of alkoxide groups bound to aluminum porphyrin was confirmed to take place.

NMR Studies of the Mixture of (TPP)AlOCOC(CH$_3$)$_3$ (1e) and (*p*-ClTPP)AlOCOCH$_2$C(CH$_3$)$_3$ (3f). Exchange of Carboxylate Groups on Aluminum Porphyrin. Two types of aluminum porphyrin with different carboxylate groups were mixed, and the NMR

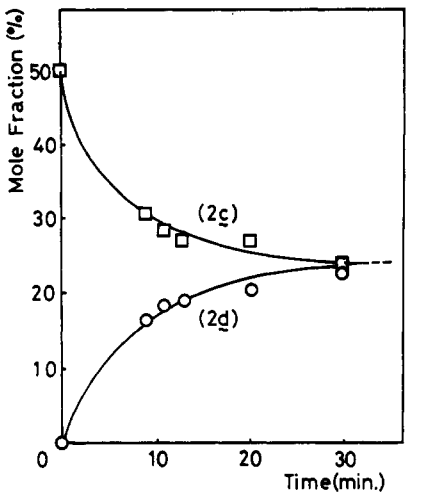

Figure 4. Relationship between the mole fractions of (EtioP)AlOCH$_3$ (**2c**) and (EtioP)AlOCH$_2$CH$_3$ (**2d**) and the reation time in the equimolar mixture of (TPP)AlOCH$_2$CH$_3$ (**1d**) and (EtioP)AlOCH$_3$ (**2c**) in CDCl$_3$ at room temperature.

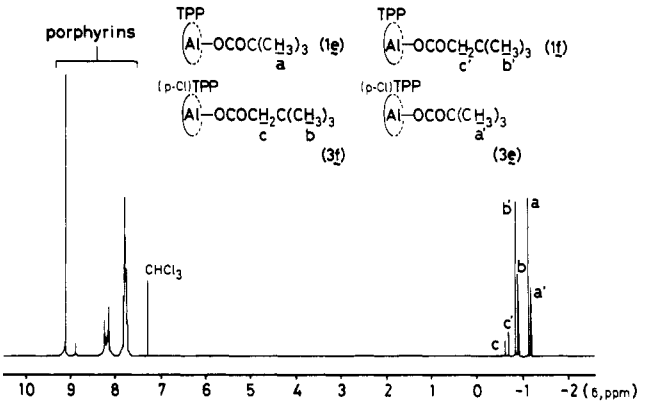

Figure 5. ^1H NMR spectrum of the reaction mixture of (TPP)AlOCOC(CH$_3$)$_3$ (**1e**) and (*p*-ClTPP)AlOCOCH$_2$C(CH$_3$)$_3$ (**3f**) in CDCl$_3$ at room temperature.

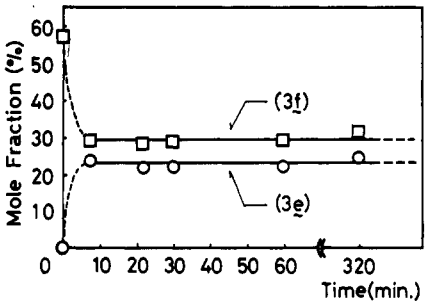

Figure 6. Relationship between the mole fractions of (*p*-ClTPP)AlOCOC(CH$_3$)$_3$ (**3e**) and (*p*-ClTPP)AlOCOCH$_2$C(CH$_3$)$_3$ (**3f**) and the reaction time in the mixture of (TPP)AlOCOC(CH$_3$)$_3$ (**1e**) and (*p*-ClTPP)AlOCOCH$_2$C(CH$_3$)$_3$ (**3f**) (0.8:1) in CDCl$_3$ at room temperature.

spectrum was examined. The ^1H NMR spectrum of the mixture of (TPP)AlOCOC(CH$_3$)$_3$ (**1e**) and (*p*-ClTPP)AlOCOCH$_2$C(CH$_3$)$_3$ (**3f**) (mole ratio of **1e** to **3f**, 0.8) is shown in Figure 5, where the signals due to carboxylate groups are observed at unusually high magnetic field, influenced by the large magnetic effect of the porphyrin ring. In addition to the signals due to **3f** (b, δ −0.9, methyl; c, δ −0.6, methylene) and **1e** (a, δ −1.1, methyl), new signals are observed assignable to the carboxylate groups of (TPP)AlOCOCH$_2$C(CH$_3$)$_3$ (**1f**) (b′, δ −0.8, methyl; c′, δ −0.7, methylene) and (*p*-ClTPP)AlOCOC(CH$_3$)$_3$ (**3e**) (a′, δ −1.2,

Table I
Polymerization of 1,2-Epoxypropane (Propylene Oxide, PO)[a]

run	catalyst	$[PO]_0/[cat]_0$	conversion, %	M_n[b]	M_w/M_n[c]	N_p/Al[d]
I	(TPP)AlCl	193	100	9000	1.12	1.2
II	(EtioP)AlCl	191	28	2700	1.09	1.1
III	(TPP)AlCl + (EtioP)AlCl (1/1)	199	67	7900 (6300)[e]	1.20	1.0 (1.2)[e]

[a] $[Cat]_0$ = 29.4 mM, in CH_2Cl_2 under N_2 at room temperature for 4 days. [b] Number-average molecular weight, estimated by GPC calibrated with PEO and PPG. [c] Ratio of weight-average molecular weight to number-average molecular weight, estimated by GPC. [d] Ratio of the number of polymer molecules to the number of aluminum atoms. [e] Estimated by VPO.

Table II
Polymerization of β-Butyrolactone (βBL)[a]

run	catalyst	$[\beta BL]_0/[cat]_0$	conversion, %	M_n[b]	M_w/M_n[c]	N_p/Al[d]
I	(TPP)AlCl	102	87	6700	1.05	1.1
II	(EtioP)AlCl	97	15	1500	1.10	0.8
III	(TPP)AlCl + (EtioP)AlCl (1/1)	98	39	3700	1.07	0.9

[a] $[cat]_0$ = 34.5 mM, in CH_2Cl_2 under N_2 at room temperature for 29 days. [b] Number-average molecular weight, estimated by GPC calibrated with polystyrene. [c] Ratio of weight-average molecular weight to number-average molecular weight, estimated by GPC. [d] Ratio of the number of polymer molecules to the number of aluminum atoms.

methyl), which are formed by the exchange of carboxylate groups between **3f** and **1e**. As shown in Figure 6, mole fractions of **3f** employed in mixing and of newly formed **3e** became constant in less than 10 min, which indicates that fairly rapid exchange of carboxylate groups takes place between the molecules of (porphinato)aluminum carboxylate.

$$\underset{\textbf{1e}}{(TPP)AlOCOC(CH_3)_3} + \underset{\textbf{3f}}{(p\text{-ClTPP})AlOCOCH_2C(CH_3)_3} \rightleftharpoons \underset{\textbf{1f}}{(TPP)AlOCOCH_2C(CH_3)_3} + \underset{\textbf{3e}}{(p\text{-ClTPP})AlOCOC(CH_3)_3}$$

The same observation was made also for the change in mole fractions of **1e** and **1f** with time.

Polymerization of Epoxide with an Equimolar Mixture of (TPP)AlCl (1a) and (EtioP)AlCl (2a). As mentioned in the Introduction, the aluminum–alkoxide bond of aluminum porphyrin undergoes successive insertion of epoxide to regenerate the aluminum–alkoxide bond resulting in the growth of polyether chain (eq 2). The rate of insertion of epoxide into aluminum–alkoxide bonds (the rate of chain growth) is much dependent on the structure of the porphyrin. For example, the polymerization of 1,2-epoxypropane with (TPP)AlCl (**1a**) proceeds much faster than that by (EtioP)AlCl (**2a**), giving products with different chain lengths (molecular weight, M_n) at the same reaction time (Table I). The polymerization of epoxide initiated by aluminum porphyrin is characterized by the uniformity (narrow distribution) in the molecular weight (M_n) or the degree of polymerization of the product, as represented by the ratio of weight-average and number-average molecular weights (M_w/M_n) close to unity.

When the polymerization is carried out with the equimolar mixture of (TPP)AlCl (**1a**) and (EtioP)AlCl (**2a**), and if the reactions on **1a** and **2a** proceed separately, the product should be a mixture of the polymers having two different molecular weights (chain lengths) with narrow distribution, which should give a bimodal curve in the gel permeation chromatogram (GPC) of the product. Quite unexpectedly, poly(1,2-epoxypropane) (poly(propylene oxide)) obtained by polymerization with the equimolar mixture of **1a** and **2a** exhibited a narrow, unimodal distribution curve in GPC (Figure 7). This fact should be related to the fact that two different reactions, the exchange of alkoxide groups between the molecules of porphyrin as described in the previous section and the insertion of epoxide into the aluminum–alkoxide bond, are occurring concurrently on the aluminum atom located in the porphyrin ring.

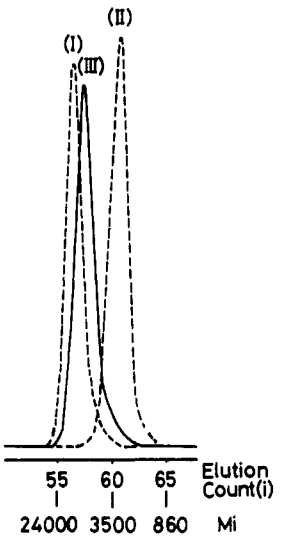

Figure 7. GPC curves of the polymerization product from 1,2-epoxypropane: (I) with (TPP)AlCl (**1a**), (II) with (EtioP)AlCl (**2a**), (III) with the equimolar mixture of **1a** and **2a**. See Table I.

The findings described above reveal the relationship between the exchange of alkoxide groups on aluminum porphyrin and the insertion of epoxide into aluminum–alkoxide bonds. The unimodal GPC curve shown in Figure 7 clearly indicates that exchange of alkoxide groups between the molecules of aluminum porphyrin takes place much faster than the insertion reaction of epoxide into the aluminum–alkoxide bond, and the reaction appears to proceed on a single aluminum porphyrin species.

Polymerization of β-Lactone with an Equimolar Mixture of (TPP)AlCl (1a) and (EtioP)AlCl (2a). (Porphinato)aluminum carboxylate undergoes repeated insertion of β-lactone into the aluminum–carboxylate bond, resulting in the growth of polyester chain (eq 3). (TPP)AlCl (**1a**) and (EtioP)AlCl (**2a**) afford poly(β-butyrolactone) with narrow distribution as to the chain length (molecular weight), but polymerization with **1a** proceeds much faster than that with **2a** to give products with different chain lengths (molecular weight) at the same reaction time (Table II). Polymerization of β-butyrolactone with the equimolar mixture of (TPP)AlCl (**1a**) and

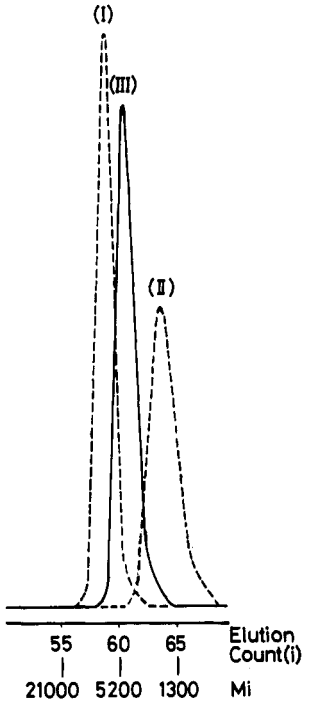

Figure 8. GPC curves of the polymerization product from β-butyrolactone: (I) with (TPP)AlCl (**1a**), (II) with (EtioP)AlCl (**2a**), (III) with the equimolar mixture of **1a** and **2a**. See Table II.

(EtioP)AlCl (**2a**) was also examined in order to investigate the relationship between the exchange of aluminum–carboxylate groups and the insertion reaction of β-butyrolactone to the aluminum–carboxylate bond. If no exchange reaction occurs with the axial carboxylate groups, the polymer is considered to grow on respective aluminum porphyrin, resulting in a bimodal distribution of the chain length (molecular weight). As shown by a single narrow peak in the GPC curve illustrated in Figure 8 (III), the product had a narrow and unimodal distribution of the chain length (molecular weight). It is clear that the exchange of carboxylate groups on (porphinato)aluminum occurs much faster than the insertion of β-lactone into aluminum–carboxylate bonds.

Conclusion

Exchange of alkoxide or carboxylate groups on aluminum porphyrin was directly confirmed by ^{1}H NMR spectroscopy by using combinations of two types of aluminum porphyrin with different alkoxide or carboxylate groups. A much faster rate for the exchange of alkoxide or carboxylate groups compared with the insertion of epoxide or β-lactone into aluminum–alkoxide or –carboxylate bonds was also confirmed by taking advantage of the narrow molecular weight distribution of the polymer formed as the product of successive insertions. These interesting findings will develop novel aspects in the elucidation of the mechanism of the polymerization reaction.

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Binding to Polymer-Bound Crown Ethers and Linear Polyethers. Cooperative and Environmental Effects

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ABSTRACT: Binding of sodium and potassium picrate to polystyrene- and polymethacrylate-bound benzo-15-crown-5, benzo-18-crown-6, and linear polyethers was studied in toluene, dioxane, and tetrahydrofuran, and the results were compared with those obtained for the monomeric ligand analogues. The measurements were carried out spectrophotometrically by letting the soluble ligand, L, compete for the salt A^-M^+ with a crown ether or polyether ligand immobilized on a solvent-swollen network N according to the reaction $A^-M^+N + L \rightleftarrows (K)\ A^-M^+L + N$. Formation constants, K_L, of the ion pair–ligand complexes A^-M^+L in dioxane and THF were calculated from the equilibrium constant, K, of the competition reaction and the known binding constants, K_N, of the picrate salts to the network polymers. Comparison of K_L or K values of the polymeric ligands and their corresponding monomeric analogues clearly shows polymeric effects. Cooperative effects in ion binding can be observed when crown ether or linear polyether ligands are closely spaced along the polymer chain. The interionic ion pair distance of the poly(crown ether)-bound ion pairs depends on the crown content of the polymer. Comonomer units such as styrene, methyl methacrylate, or glycidyl methacrylate did not greatly affect the binding of picrate salt to the polymeric ligand, but incorporation of monomers with long polyethylene oxide side chains significantly enhances the binding to polymer-bound crown ether, possibly as a result of the more polar environment of the ethylene oxide unit surrounding the crown-bound ion pair.

Introduction

Earlier reports on the binding of ionic solutes to polymers with pendant crown ether ligands indicated a dependence of the binding constants on the presence of neighboring ligands or comonomer substituents.[1-8] Cooperation of two crown ether ligands in the formation of

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