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"Immortal" Polymerization. Polymerization of Epoxide and β-Lactone with Aluminum Porphyrin in the Presence of Protic Compound

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ABSTRACT: Ring-opening polymerization of epoxides with aluminum porphyrin ((TPP)AlX (1); TPP represents 5,10,15,20-tetraphenylporphinato) as initiator gave polymers with narrow molecular weight distribution even in the presence of protic compounds such as hydrogen chloride, carboxylic acids, alcohols, and water. Similarly, the polymerization of β-lactones with (TPP)AlX could not be terminated by hydrogen chloride or carboxylic acids. In these polymerization reactions, the number of polymer molecules could be increased with the amount of protic compound added, retaining narrow molecular weight distribution. These results are much different from "living" polymerization, and a new concept of "immortal" polymerization is presented. Direct observations by NMR on the reactivity of aluminum porphyrins with protic compounds indicated an unusual reactivity of the aluminum atom–axial group bond (X: Cl, O_2CR, OH, OR) of aluminum porphyrin (1) as the origin of "immortality" of the polymerization.

Introduction

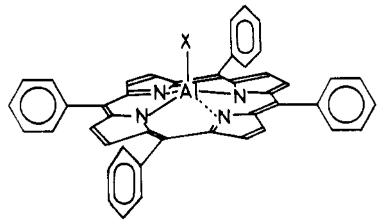
The formation of macromolecules with controlled molecular weight is of primary interest and importance, not only for the detailed design of polymeric materials but also in view of the uniform molecular weight of some biological macromolecules such as enzymes, proteins, and nucleic acids.

In addition and ring-opening polymerizations, the formation of polymers with narrow molecular weight distribution has been observed in "living" polymerization.[1,2] Living polymerization consists only of initiation and propagation reactions, with the absence of termination and chain-transfer reactions. When initiation and propagation reactions proceed uniformly with respect to all growing polymer molecules, the product has a narrow molecular weight distribution, and the number of polymer molecules is the same as that of initiator. Upon addition of the second monomer to the polymerization mixture of the first monomer after completion of the reaction, the polymerization ensues to give a block copolymer.

The living nature, however, does not ensure the immortality. For example, the polymerization of epoxyethane initiated with alkali metal alkoxide is of living nature.[1d] Upon addition of an acid such as hydrogen chloride, the reaction is killed, since alkali metal alkoxide as the growing species reacts with hydrogen chloride to give alcohol and unreactive alkali metal chloride such as sodium chloride.

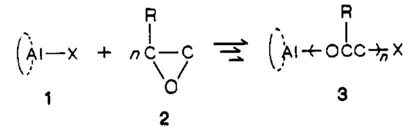
In the present article we will describe the novel concept of immortal polymerization.[3] Although the growing species is of nucleophilic nature, the reaction may not be killed even in the presence of a protic compounds such as alcohols, water, carboxylic acids, or hydrogen chloride, and the reaction gives polymer with a narrow molecular weight distribution, the number of the polymer molecules being more than that of initiator.

This was accomplished in the polymerization of epoxides or β-lactones initiated with aluminum porphyrin. We have already reported that aluminum porphyrins such as (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1 (X = Cl))

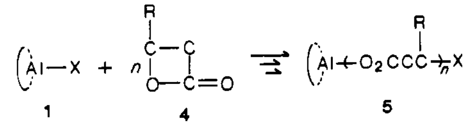


(TPP)AlX (**1**)

are excellent initiators for living polymerization of epoxides[4] (eq 1) and β-lactones (eq 2)[5] and for related co-



$$\text{Al}-\text{X} + n\,\text{C(R)}{-}\text{C}(\text{O}) \rightleftarrows \text{Al}{+}\text{OCC(R)}{+}_n\text{X} \quad (1)$$



$$\text{Al}-\text{X} + n\,\text{C(R)}{-}\text{C}{-}\text{O}{-}\text{C}{=}\text{O} \rightleftarrows \text{Al}{+}\text{O}_2\text{CCC(R)}{+}_n\text{X} \quad (2)$$

polymerizations[6,7] and that they give polymers with narrow

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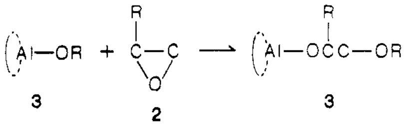
molecular weight distribution. The growing species in the polymerizations of epoxides and β-lactones are (porphinato)aluminum alkoxide[4b] (**3**) and carboxylate[5a] (**5**), respectively. Immortal polymerization is based on the unusual reactivity of these aluminum porphyrins.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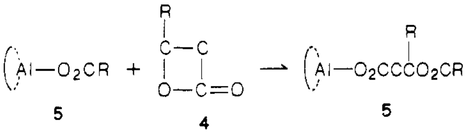
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Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[8] Dichloromethane was washed successively with sulfuric acid, water, and aqueous sodium bicarbonate, dried over calcium chloride, and distilled over calcium hydride under nitrogen atmosphere. Deuteriated chloroform was distilled over calcium hydride under nitrogen atmosphere. Benzene was pretreated similarly to the case of CH_2Cl_2, followed by distillation over sodium wire under nitrogen atmosphere. Dioxane was refluxed for 10 h with hydrochloric acid under bubbling nitrogen, shaken with potassium hydroxide, and then dried over a mixture of potassium hydroxide and calcium hydride, followed by distillation over sodium under nitrogen atmosphere. All the alcohols used were dried over calcium sulfate and distilled over magnesium treated with iodine under nitrogen atmosphere. Acetic acid was distilled in the presence of acetic anhydride under nitrogen atmosphere. 3,3-Dimethylbutanoic acid was distilled under reduced pressure in nitrogen atmosphere. Commercial 2,2-dimethylpropanoic acid, 2-chlorobutanoic acid, and poly(oxyethylene)diol (PEG; $\bar{M}_n = 3000$, $\bar{M}_w/\bar{M}_n = 1.04$) were used without further purification. Water was subjected to ion exchange with resin, followed by distillation under nitrogen atmosphere. Hydrogen chloride (HCl) was generated by adding concentrated sulfuric acid to ammonium chloride, followed by passing the mixture through the drying columns packed with calcium chloride, molecular sieve 5A, and phosphorus pentoxide and then trapping the mixture in dioxane (to dissolve it) under nitrogen atmosphere. The concentration was determined by alkaline titration in aqueous media to be 1 M. Epoxyethane (EO) was subjected repeatedly to thaw-to-flow cycles and distilled over a mixture of potassium hydroxide and calcium hydride. 1,2-Epoxypropane (PO), 1,2-epoxybutane (1BO), and 1-methoxy-2,3-epoxypropane were distilled over a mixture of potassium hydroxide and calcium hydride under nitrogen atmosphere. 1-Chloro-2,3-epoxypropane (epichlorohydrin, ECH) and β-butyrolactone (βBL) were distilled over calcium hydride under nitrogen atmosphere. Diethylaluminum chloride and triethylaluminum were distilled under reduced pressure under nitrogen atmosphere.

Preparation of Aluminum Porphyrins ((TPP)AlX (1)). (5,10,15,20-Tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1** (X = Cl)) was prepared by the reaction between $TPPH_2$ and 1.2 equiv of Et_2AlCl in CH_2Cl_2 at room temperature under nitrogen atmosphere, followed by evaporation of the volatile fractions under reduced pressure.[4] (TPP)AlEt (**1**, X = Et) was prepared by the equimolar reaction between $TPPH_2$ and Et_3Al in CH_2Cl_2 at room temperature under nitrogen atmosphere.[9] (TPP)AlO_2CR (**1**, X = O_2CR) was prepared by the reaction of (TPP)AlEt (**1**, X = Et) and a small excess of carboxylic acid in CH_2Cl_2 at room temperature under nitrogen atmosphere, followed by repeated azeotropic distillations with benzene to remove the excess carboxylic acid from the reaction mixture.[10] (TPP)AlOR (**1**, X = OR) was similarly prepared from (TPP)AlEt (**1**, X = Et) and a large excess of alcohol upon refluxing or with heating.[10] The living oligomer of 1,2-epoxypropane (**3** (R = CH_3, n = 5) and the living polymer of epoxyethane (**3** (R = H); $\bar{M}_n = 3200$, $\bar{M}_w/\bar{M}_n = 1.05$) were prepared, respectively, by the polymerization of the corresponding epoxide initiated with (TPP)AlCl (**1**, X = Cl) with an $[\text{epoxide}]_0/[\mathbf{1}]_0$ ratio of 5 and 120 at 100% conversion.[4] Similarly, the living oligomer (**5** (R = CH_3), n = 5) and the polymer (**5** (R = CH_3); $\bar{M}_n = 5900$, $\bar{M}_w/\bar{M}_n = 1.09$) of β-butyrolactone (βBL) were prepared with the ratio $[\beta\text{BL}]_0/[\mathbf{1}\ (\text{X} = \text{Cl})]_0$ equal to 5 (100% conversion) and 120 (77% conversion), respectively.[5]

Polymerization. Polymerizations of epoxides or β-lactones with aluminum porphyrin in the presence of protic compounds were carried out according to the following procedure:[3] To a 50-mL round-bottom flask equipped with a three-way stopcock containing (TPP)AlCl (**1**, X = Cl) was added a mixture of monomer and a protic compound by a hypodermic syringe in a nitrogen stream, and the reaction mixture was stirred magnetically at room temperature. After an appropriate time, the volatile fractions were removed under reduced pressure from the reaction system to leave the polymerized mixture, which was weighed to obtain the conversion and then subjected to gel permeation chromatography (GPC) and/or spectroscopic analyses. For the polymerization of 1,2-epoxypropane with (TPP)AlCl (**1**, X = Cl) using poly(oxyethylene)diol (PEG) as protic compound, (TPP)AlCl (1 mmol) was added as a CH_2Cl_2 solution (20 mL) to the flask in which PEG had been placed under nitrogen, and the reaction mixture was evaporated to dryness. Then, 3 mL of CH_2Cl_2 was added to dissolve the above mixture prior to the addition of 1,2-epoxypropane. Block copolymerization was carried out by the addition of the second monomer to the reaction mixture of the first stage of polymerization at 100% conversion.

Measurements. The ^1H NMR spectra were measured at room temperature (~25 °C) in a sealed tube under nitrogen atmosphere by using a Hitachi R-40 or JEOL JNM GX-400 spectrometer operating at 90 and 399.7 MHz, respectively. ^{13}C NMR spectra were measured in $CDCl_3$ without NOE by using a JEOL JNM PS-100 or GX-400 spectrophotometer operating at 25.03 and 100.5 MHz, respectively, with a pulse repetition time of 10 s. The chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) for ^1H NMR and with respect to $CDCl_3$ (δ 77.102) for ^{13}C NMR. Infrared spectra were recorded on a Hitachi 260-30 infrared spectrophotometer. For the estimation of number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) and molecular weight distributions of polymers, gel permeation chromatography was performed on a Toyo Soda Model HLC-802, a high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent with a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). The molecular weight calibration curve for polyethers was obtained by using standard poly(oxyethylenes) [$\bar{M}_n = 72\,000$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 39\,000$ ($\bar{M}_w/\bar{M}_n = 1.03$), $\bar{M}_n = 22\,000$ ($\bar{M}_w/\bar{M}_n = 1.14$)] from Toyo Soda Manufacturing Co., Ltd., and poly(propylene glycols) [$\bar{M}_n = 2000$ and 1000 ($\bar{M}_w/\bar{M}_n \sim 1$)] from Lion Fat & Oil Co., Ltd. For poly(β-butyrolactones), standard polystyrenes were used [$\bar{M}_n = 107\,000$ ($\bar{M}_w/\bar{M}_n = 1.01$), $\bar{M}_n = 16\,700$ ($\bar{M}_w/\bar{M}_n = 1.02$), $\bar{M}_n = 6200$ ($\bar{M}_w/\bar{M}_n = 1.04$), $\bar{M}_n = 2800$ ($\bar{M}_w/\bar{M}_n = 1.05$)] from Toyo Soda Manufacturing Co., Ltd.

Results and Discussion

Polymerization of Epoxides (2) or β-Lactones (4) with Aluminum Porphyrins (1) in the Presence of Hydrogen Chloride. In order to investigate the reactivity of (porphinato)aluminum alkoxide as the growing species of the epoxide polymerization, a living polymer of epoxyethane was prepared with (TPP)AlCl as initiator, and hydrogen chloride was added, followed by 1,2-epoxypropane. If the living polymer is killed by hydrogen chloride as a strong acid, no further reaction should take place upon addition of 1,2-epoxypropane. On the other hand, if hydrogen chloride does not participate in the reaction, the formation of epoxyethane–1,2-epoxypropane block copolymer should result. In either case the gel permeation chromatogram (GPC) of the reaction mixture should show a single unimodal peak. When dioxane containing 1.5 equiv of hydrogen chloride was added at room temperature by using a hypodermic syringe to the CH_2Cl_2 solution of the living polymer of epoxyethane (**3** (R = H); $\bar{M}_n = 3200$, $\bar{M}_w/\bar{M}_n = 1.05$), the color of the solution turned

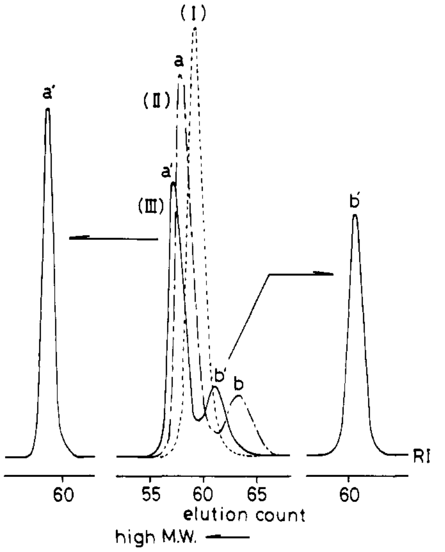
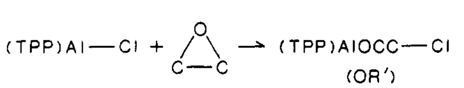


Figure 1. GPC profile of the polymerization of 1,2-epoxypropane (PO) initiated with the living polymer ((TPP)Al-(OCH(CH$_3$)-CH$_2$)$_n$-Cl, **3**) treated with hydrogen chloride (HCl), in CH$_2$Cl$_2$/dioxane (3/0.45 (mL)) at room temperature. [PO]$_0$/[Al]$_0$/[HCl]$_0$ = 36/0.3/0.45 (in mmol): (I) -(OCH(CH$_3$)CH$_2$)$_n$-Cl in the living polymer ($\bar{M}_n$ = 3200, $\bar{M}_w/\bar{M}_n$ = 1.05); (II) reaction mixture at 55% conversion; (II') reaction mixture at 65% conversion; (a') hexane-insoluble fraction ($\bar{M}_n$ = 5090, $\bar{M}_w/\bar{M}_n$ = 1.05); (b') hexane-soluble fraction ($\bar{M}_n$ = 1820, $\bar{M}_w/\bar{M}_n$ = 1.09).

from bright reddish purple to bluish purple, characteristic of (TPP)AlCl (**1**, X = Cl).[11] Upon addition of 120 equiv of 1,2-epoxypropane (**2**, R = CH$_3$) to the reaction mixture, the color turned back instantaneously to the original bright reddish purple characteristic of (porphinato)aluminum alkoxide. Of particular interest, two unimodal peaks a and b (Figure 1, elution curve II) were observed in the GPC of the reaction mixture; these peaks moved to the higher molecular weight region (a' and b') with the progress of the reaction at room temperature. On the other hand, the peak (I) due to the original poly(oxyethylene) disappeared.[12] The fractions corresponding to the two peaks could be separated by the difference of solubility in CHCl$_3$/hexane. The insoluble fraction corresponding to peak a' was identified by ^{1}H NMR[13] to be the block copolymer consisting of poly(oxyethylene) (80%) and poly(oxymethylethylene) (20%) ($\bar{M}_n$ = 5090, $\bar{M}_w/\bar{M}_n$ = 1.05), while the soluble fraction (peak b') was the homopolymer of 1,2-epoxypropane (homopoly(oxymethylethylene); $\bar{M}_n$ = 1820, $\bar{M}_w/\bar{M}_n$ = 1.09). The molecular weight estimated for the poly(oxymethylethylene) segment in the block copolymer ($\bar{M}_n$ (peak a') - $\bar{M}_n$ (peak I) = 1890) is substantially the same as that observed for the homopolymer (peak b'). The total number of the polymer molecules (N_p) as calculated[14] on the basis of the molecular weight of the isolated homopolymer was found to be in excellent agreement with the sum of the numbers of the molecules of the starting living poly(oxyethylene) (**3**) (N_{Al}) and of hydrogen chloride ($N_p = 2.51N_{Al}$). The homopolymer of 1,2-epoxypropane isolated was found by ^{13}C NMR to carry a chlorine terminal (δ 47.4, ClCH$_2$CH(CH$_3$)O).[4b] These observations indicate that the following sequence of reactions takes place, besides the repeated reactions of (TPP)AlOR with epoxide to form polyether (eq 3).

$$\text{(TPP)Al-OR} + \text{HCl} \ (\rightleftharpoons) \ \text{(TPP)Al-Cl} + \text{HOR} \quad (5)$$



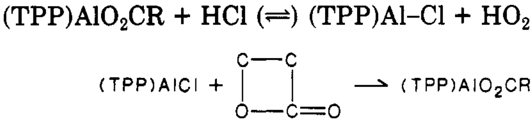
(6)

$$\text{(TPP)Al-OR}' + \text{HOR} \rightleftharpoons \text{(TPP)Al-OR} + \text{HOR}' \quad (7)$$

The reaction between the growing species (TPP)AlOR and hydrogen chloride gives (TPP)AlCl, which can initiate the polymerization of epoxide.[4] If reaction 5 is reversible, the "dead" polymer molecule ROH actually is not dead but can revive to the growing species by the backward reaction. Even if reaction 5 is irreversible, (TPP)AlOR' formed by reaction 6 exchanges with ROH, the dead polymer, which eventually revives to the growing species (eq 7). Thus, in the above experiments, the polymerization of 1,2-epoxypropane took place uniformly from all the molecules of the living poly(oxyethylene) (**3**, R = H) and hydrogen chloride.

A similar observation was made in the polymerization of β-butyrolactone (βBL) initiated with the reaction mixture between the living poly(β-butyrolactone)[12] (**5** (R = CH$_3$); $\bar{M}_n$ = 5900, $\bar{M}_w/\bar{M}_n$ = 1.09) and 1.5 equiv of hydrogen chloride (HCl) ([βBL]$_0$/[**5**]$_0$/[HCl]$_0$ = 15/0.3/0.45 (in mmol)) in CH$_2$Cl$_2$ (3 mL). The reaction proceeded to give the polymeric mixture with two unimodal elution peaks in GPC, corresponding to $\bar{M}_n$ = 7700 ($\bar{M}_w/\bar{M}_n$ = 1.12) and $\bar{M}_n$ = 2050 ($\bar{M}_w/\bar{M}_n$ = 1.14). If the living poly(β-butyrolactone) is killed by hydrogen chloride, no change in molecular weight will take place upon further addition of the monomer. On the other hand, a simple increase in molecular weight retaining the single GPC peak will result if hydrogen chloride does not participate in the reaction. Thus, the following reactions are considered to take place in the present system, besides the repeated reactions of (TPP)AlO$_2$CR with β-lactone to give polyester (eq 4).

$$\text{(TPP)AlO}_2\text{CR} + \text{HCl} \ (\rightleftharpoons) \ \text{(TPP)Al-Cl} + \text{HO}_2\text{CR} \quad (8)$$



(9)

$$\text{(TPP)AlO}_2\text{CR}' + \text{HO}_2\text{CR} \rightleftharpoons \text{(TPP)AlO}_2\text{CR} + \text{HO}_2\text{CR}' \quad (10)$$

By the virtue of these reactions, dead polymer molecule HO$_2$CR is not really dead but can revive to the growing species (TPP)AlO$_2$CR.

Thus, the polymerization of epoxides and β-lactones, respectively, by aluminum porphyrin may not be killed even by hydrogen chloride and may be regarded as having an "immortal" nature. When compared, for example, with the corresponding polymerization of epoxide initiated with the alkali-metal alkoxide, an unusually high reactivity, as the nucleophile of the aluminum-chloride bond of aluminum porphyrin (**1**, X = Cl), accounts for the origin of the immortality of this polymerization. In contrast, the polymerization with alkali-metal alkoxide is killed by hydrogen chloride, since a comparable reactivity can hardly be expected for alkali-metal chloride.

Exchange Reactions of the Axial Group (X) of Aluminum Porphyrins ((TPP)AlX, 1) with Protic Compounds. In order to obtain direct information on the reactions of aluminum porphyrins with protic compounds (eq 5, 7, 8, and 10), NMR spectral investigations were made by taking advantage of a strong magnetic shielding effect induced by a porphyrin ring upon the axial group.

An example of the reaction of a (porphinato)aluminum alkoxide with alcohol is shown for the equimolar mixture between (TPP)AlOCH$_2$CH$_3$ (**1**, X = OCH$_2$CH$_3$) and (CH$_3$)$_3$CCH$_2$OH in CDCl$_3$ at room temperature (~25 °C) (Figure 2). The appearance of two sets of signals assignable respectively to (TPP)AlOCH$_2$C(CH$_3$)$_3$ (c, δ -1.6 (CH$_2$); d, δ -1.4 (CH$_3$))[10] and CH$_3$CH$_2$OH (a', δ 3.2 (CH$_2$); b', δ 1.2 (CH$_3$)) was observed with a decrease in intensity of the signals due to (TPP)AlOCH$_2$CH$_3$ (a, δ -1.2 (CH$_2$); b, δ -2.1 (CH$_3$)). The ratio of the mole fractions of the CH$_3$CH$_2$O and (CH$_3$)$_3$CCH$_2$O groups on aluminum por-

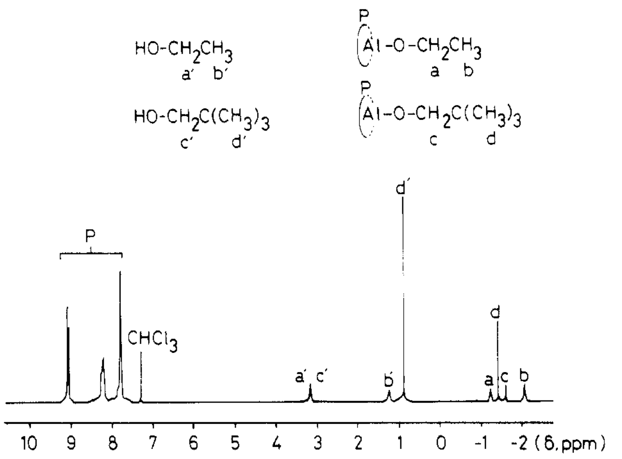


Figure 2. ^{1}H NMR spectrum (399.7 MHz) of the equimolar mixture of (TPP)AlOCH$_2$CH$_3$ (1, X = OCH$_2$CH$_3$) and (CH$_3$)$_3$CCH$_2$OH in CDCl$_3$ at room temperature after 6.9 min.

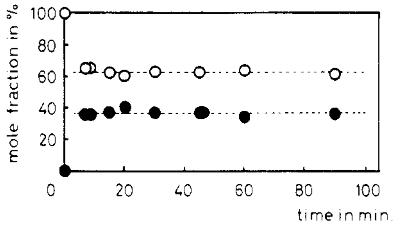


Figure 3. Relationship between the mole fractions of (TPP)AlOCH$_2$CH$_3$ (1, X = OCH$_2$CH$_3$; ○) and (TPP)AlOCH$_2$C(CH$_3$)$_3$ (1, X = OCH$_2$C(CH$_3$)$_3$; ●) and the time in the equimolar mixture of (TPP)AlOCH$_2$CH$_3$ and (CH$_3$)$_3$CCH$_2$OH in CDCl$_3$ at room temperature.

phyrin, as determined by the intensities of the signals P^1 and P^2 due respectively to the pyrrole β-protons of (TPP)AlOCH$_2$CH$_3$ and (TPP)AlOCH$_2$C(CH$_3$)$_3$, was 67/33 (%) after 6.9 min and remained unchanged throughout the observation for another 1.5 h (Figure 3), indicating that the exchange reaction between (TPP)AlOR and alcohol comes to equilibrium at a very early stage upon mixing.

On the contrary, the exchange reaction of (TPP)AlOR was found substantially irreversible when the protic compound was combined with carboxylic acid or hydrogen chloride. For example, when an equimolar amount of (CH$_3$)$_3$CCH$_2$CO$_2$H was added to (TPP)AlOCH$_2$CH$_3$, the signals due to the CH$_3$CH$_2$OAl group disappeared completely to give (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$ (1, X = O$_2$CCH$_2$C(CH$_3$)$_3$; c, δ -0.7 (CH$_2$); d, δ -0.8 (CH$_3$))[10] and CH$_3$CH$_2$OH (a' (CH$_2$), b' (CH$_3$)), while the signals due to (CH$_3$)$_3$CCH$_2$CO$_2$H' were not observed (δ 2.4 (CH$_2$), δ 1.05 (CH$_3$)) (Figure 4). On the other hand, in the ^{1}H NMR spectrum of (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$ (1, X = O$_2$CCH$_2$C(CH_3)$_3$ (δ -0.8)) in the presence of an equimolar amount of (CH$_3$)$_3$CCH$_2$OH, (TPP)AlOCH$_2$C(CH$_3$)$_3$ (1, X = OCH$_2$C(CH$_3$)$_3$ (δ -1.4)) was not detected under the same conditions. Thus, the exchange reaction between (porphinato)aluminum alkoxide (1, X = OR) and carboxylic acid is substantially irreversible.

The exchange reaction with hydrogen chloride was similarly examined by using (porphinato)aluminum alkoxide as the living oligomer of 1,2-epoxypropane (3, R = CH$_3$, n = 5) prepared with (TPP)AlCl (1, X = Cl) as initiator (eq 1). When the CDCl$_3$ solution of 3 is mixed with dioxane containing 1.5 equiv of hydrogen chloride, an instantaneous color change from the original bright reddish purple to the bluish purple was observed. The ^{1}H NMR spectrum of the reaction mixture showed a complete disappearence of the signal due to the methyl group at the alkoxy terminal of 3 (δ -1.9,[4b,15] AlOCH(CH_3)CH$_2$), together with an upfield shift of the signal due to the pyrrole β-proton of porphyrin ring from δ 9.1 (3) to δ 9.0 assignable to that of (TPP)AlCl (1, X = Cl). On the other hand, the addition of a large excess of CH$_3$OH to (TPP)AlCl did not cause any spectral change due to the formation of (TPP)AlOCH$_3$ (1, X = OCH_3 (δ -1.3)).[10] Thus, the exchange reaction between (TPP)AlOR and hydrogen chloride to give (TPP)AlCl and ROH takes place very rapidly and irreversibly.

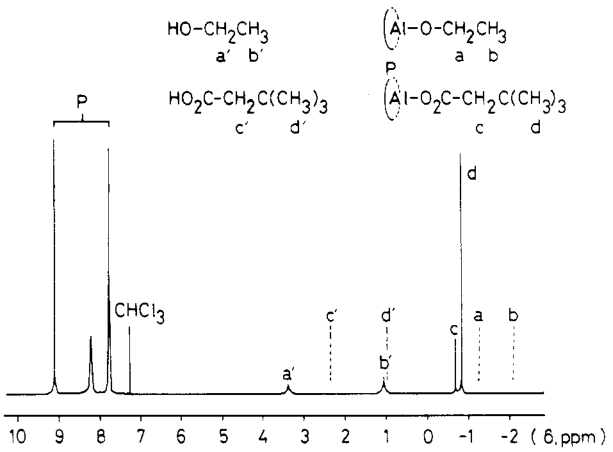


Figure 4. ^{1}H NMR (399.7 MHz) spectrum of the equimolar mixture of (TPP)AlOCH$_2$CH$_3$ (1, X = OCH$_2$CH$_3$) and (CH$_3$)$_3$CCH$_2$CO$_2$H in CDCl$_3$ at room temperature after 10.7 min.

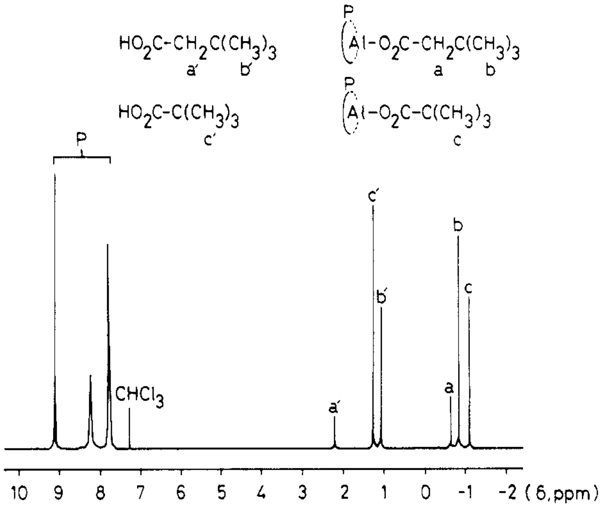


Figure 5. ^{1}H NMR spectrum (399.7 MHz) of the equimolar mixture of (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$ (1, X = O$_2$CCH$_2$C(CH$_3$)$_3$) and (CH$_3$)$_3$CCO$_2$H in CDCl$_3$ at room temperature after 9.3 min.

When an equimolar amount of (CH$_3$)$_3$CCO$_2$H (c', δ 1.3) was added to (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$ (1, X = O$_2$CCH$_2$C(CH$_3$)$_3$) in CDCl$_3$ at room temperature, the ^{1}H NMR spectrum of the reaction mixture (Figure 5) showed an appearence of a new signal c (δ -1.1) assignable to (TPP)AlO$_2$CC(CH_3)$_3$ and paired signals a' (CH$_2$) and b' (CH$_3$) assignable to (CH$_3$)$_3$CCH$_2$CO$_2$H, with a decrease in intensity of the signals a (CH$_2$) and b (CH$_3$) due to the original (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$.[10] The intensity ratio of the signals b (9H) and c (9H) after 9.3 min was observed to be 61/39 (%), which remained unchanged for another 1.5 h, indicating the occurrence of a rapid exchange reaction between (TPP)AlO$_2$CR and carboxylic acid. This exchange process is reversible; the exchange reaction between (TPP)AlO$_2$CC(CH$_3$)$_3$ and (CH$_3$)$_3$CCH$_2$CO$_2$H, which corresponds to the backward reaction, was found to take place and to give the mixture of (TPP)AlO$_2$CC(CH$_3$)$_3$ and (TPP)AlO$_2$CCH$_2$C(CH$_3$)$_3$ with the molar ratio comparable

Table I
Polymerization of Epoxides (2) with (TPP)AlCl (1, X = Cl) in the Presence of Protic Compounds (HY)[a]

run	epoxide (2) R	HY	$[2]_0/[1]_0$	$[HY]_0/[1]_0$	time, h	conv, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	N_p/N_{Al}[c]
1	H	CH_3OH	200	9	48	100	700	1.05	12.6
2			200	9	0.5	70	780	1.10	10.4
3	CH_3	CH_3OH	200	9	48	100	1300	1.08	8.9
4			500	24	48	100	1200	1.08	24.2
5	CH_3CH_2	CH_3OH	200	9	96	100	1200	1.10	12.0
6[d]	CH_3OCH_2	CH_3OH	185	9	168	60	610	1.07	16.0
7	$ClCH_2$	CH_3OH	200	4	50	100	2060	1.13	8.9
8			200	9	4	90	1050	1.08	15.9
9			200	9	48	100	1500	1.04	12.3
10			500	24	24	70	850	1.08	38.1
11			500	24	96	100	1400	1.06	33.0
12			1000	49	264	90	1200	1.06	69.4
13[d]			1000	49	21	100	1400	1.09	66.1
14	CH_3	$(CH_3)_3CCH_2CO_2H$	200	1	48	100	4100	1.09	2.8
15			200	4	312	100	2000	1.04	5.8
16			200	9	312	100	1400	1.04	8.3
17			500	17	408	90	1200	1.04	24.2

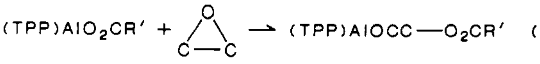
[a] At room temperature without solvent. [b] GPC. [c] Number of polymer molecules (N_p)/number of aluminum atoms (N_{Al}) = (MW of 2)($[2]_0/[1]_0$)(conv/100)$\bar{M}_n^{-1}$. [d] 70 °C.

to that in the forward reaction described above. On the other hand, in the reaction with hydrogen chloride a complete replacement of the axial carboxylate group by a chloride group on aluminum porphyrin was observed. An example is the reaction between the living oligomer of β-butyrolactone (5, R = CH_3, n = 5) with hydrogen chloride (1/1.5). The reaction mixture showed the complete disappearence of the doublet signal due to the methyl group at the terminal carboxylate group (δ -0.2,[5a] $AlO_2CCH_2C(CH_3)$), together with a shift of the signal due to the pyrrole β-proton of 5 (δ 9.1) up to δ 9.0, assignable to that of (TPP)AlCl (1, X = Cl). A rapid color change characteristic of the formation of (TPP)AlCl was also observed. On the other hand, in the ^1H NMR spectrum of (TPP)AlCl under similar conditions in the presence of a large excess of CH_3CO_2H $(TPP)AlO_2CCH_3$ (1, X = O_2CCH_3 (δ -1.4))[10] could not be detected. Thus, the exchange reaction of $(TPP)AlO_2CR$ with hydrogen chloride to give (TPP)AlCl and RCO_2H takes place very rapidly but irreversibly.

To summarize, the reactions between (TPP)AlOR and alcohol and between $(TPP)AlO_2CR$ and carboxylic acid (eq 7 and 10) are rapid and reversible. On the other hand, the reactions of (TPP)AlOR or $(TPP)AlO_2CR$ with hydrogen chloride (eq 5 and 8) are irreversible. Thus, reactions 6 and 9 are also important for the immortality of the polymerization of epoxides and β-lactones, respectively, in the prsence of hydrogen chloride as a strong acid.

Polymerization of Epoxides (2) or β-Lactones (4) with Aluminum Porphyrins (1) in the Presence of Carboxylic Acids. The above results of the spectral investigations suggest that the polymerization of epoxide with aluminum porphyrin will not be killed by carboxylic acid. Although reaction 11 is irreversible, $(TPP)AlO_2CR'$ can initiate the polymerization of epoxide (eq 12).[5]

$$(TPP)AlOR + HO_2CR' \rightarrow (TPP)AlO_2CR' + HOR \quad (11)$$



(12)

(Porphinato)aluminum alkoxide thus formed exchanges reversibly with the dead polymer HOR (eq 7), which revives to the growing species. If the reversible exchange reaction 7 is much faster than the reactions involving epoxide (eq 3 and 12), the molecular weight distribution of the product will remain narrow even in the presence of exchange reactions.

In fact, the polymerization of 1,2-epoxypropane with (TPP)AlCl in the presence of $(CH_3)_3CCH_2CO_2H$ proceeded to afford the polymer with narrow molecular weight distribution. The number of the polymer molecules increased with the amount of the carboxylic acid (Table I, runs 13–16).

In this reaction system, the polymerization is initiated by the reaction of (TPP)AlCl with the epoxide (eq 6), and reactions 11, 12, and 7 follow. Therefore, every polymer molecule is considered to carry a chlorine or a carboxylic ester group. In fact, the reaction mixture of Table I, run 15, for example, showed an infrared absorption at 1730 cm^{-1} characteristic of the ester linkage, while the absorption at 1705 cm^{-1} due to $(CH_3)_3CCH_2CO_2H$ was hardly detected. In conformity with this, the ^{13}C NMR spectrum showed a set of the signals assignable to the ester group $(CH_3)_3CCH_2CO_2$ at the terminal of the polymer (δ 28.6 (CH_3), δ 29.4 (CH_2), δ 46.6 (C), and δ 170.0 (CO)) in addition to a relatively weak signal due to the terminal chlorine (δ 47.4, $ClCH_2CH(CH_3)O$)[4b] originating from (TPP)AlCl. The number of the repeating oxymethylethylene units in the polymer chain, calculated on the basis of the intensities of the signals of these two terminals relative to the main chain group ($CH_2CH(CH_3)O$, δ 16.4), was 20 and was in excellent agreement with the GPC data (22) as well as with the ratio ($[epoxide]_0/[(TPP)AlCl]_0 + [HY]_0$) of 20. No reaction between 1,2-epoxypropane and $(CH_3)_3CCH_2CO_2H$ (20/1) to form ester was found to take place under similar conditions when (TPP)AlCl was absent.

The polymerization of β-lactone with the (porphinato)aluminum carboxylate–carboxylic acid system gave the polymer with narrow molecular weight distribution, with the number of the molecules (N_p) more than that of the aluminum porphyrin (N_{Al}) (Table II). The polymerization proceeds by the participation of reactions 4 and 10.

Polymerization of Epoxides (2) with Aluminum Porphyrins (1) in the Presence of Alcohols. Similarly, in the polymerization of epoxide by using the system of (TPP)AlCl (1, X = Cl) coupled with CH_3OH, a polymer of uniform molecular weight is formed with the number of the molecules (N_p) more than that of the initiator ((TPP)AlCl) (N_{Al}). The reaction may be applied to the polymerization of various epoxides (2) such as epoxyethane (R = H), 1,2-epoxypropane (R = CH_3), 1,2-epoxybutane (R = CH_2CH_3), and 1-chloro-2,3-epoxypropane (R = CH_2Cl) (Table I). In the present system, the polymerization proceeds by the participation of reactions 3, 6, and

Table II
Polymerization of β-Butyrolactone (4, R = CH_3) with $(TPP)AlO_2CCH_2C(Cl)CH_3$ (1, X = $O_2CCH_2C(Cl)CH_3$) in the Presence of $CH_3C(Cl)CH_2CO_2H$

run	$[4]_0/[1]_0$	$[CH_3(Cl)CH_2CO_2H]_0/[1]_0$	time, h	conv, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	N_p/N_{Al}[c]
1	200	1	120	100	8620	1.08	2.0
2	200	4	120	100	3890	1.10	4.4
3	200	9	120	93	1940	1.11	8.2
4	400	19	528	95	1810	1.13	18.1
5	800	39	480	46	930	1.16	34.0

[a] At room temperature without solvent. [b] GPC. [c] $0.86([4]_0/[1]_0)(\text{conv})(\bar{M}_n^{-1})$.

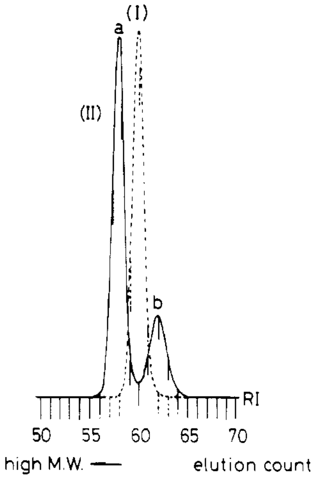


Figure 6. GPC profile of the polymerization of 1,2-epoxypropane (PO) initiated with (TPP)AlCl (1, X = Cl) in the presence of poly(oxyethylene)diol (PEG) in CH_2Cl_2 (3 mL) at room temperature. $[PO]_0/[(TPP)AlCl]_0/[PEG]_0$ = 103/1/1 (in mmol). At 91% conversion (3 days): (I) PEG, $\bar{M}_n$ = 3000, $\bar{M}_w/\bar{M}_n$ = 1.04; (II) reaction mixture; (a) $\bar{M}_n$ = 6000, $\bar{M}_w/\bar{M}_n$ = 1.04; (b) $\bar{M}_n$ = 1800, $\bar{M}_w/\bar{M}_n$ = 1.08.

7. The narrow molecular weight distribution of the product indicates the fact that the reversible exchange reaction 7 proceeds much faster than the propagation reaction (eq 3).

For example, the bulk polymerization of 1,2-epoxypropane (propylene oxide, PO) with (TPP)AlCl (1, X = Cl) as initiator in the presence of CH_3OH ($[PO]_0/[1]_0/[CH_3OH]_0$ = 100/1/9) proceeded very rapidly with heat evolution at room temperature up to 70% conversion in 0.5 h to give poly(oxymethylethylene) with narrow molecular weight distribution as indicated by the $\bar{M}_w/\bar{M}_n$ ratio of 1.10 ($\bar{M}_n$ = 780; run 2, Table I). Similarly, the polymerization of 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) proceeded readily at room temperature even in the presence of CH_3OH to give the polymer with narrow molecular weight distribution. With varying amounts of CH_3OH used with respect to (TPP)AlCl (runs 7–13), the number of the polymer molecules (N_p) could be increased while the narrow molecular weight distribution was retained ($\bar{M}_w/\bar{M}_n$ = 1.04–1.13). An elevated reaction temperature accelerated the polymerization without broadening the molecular weight distribution of polymer (run 13). The exchange reaction (eq 7) is accelerated to an extent higher than, or at least as much as, the chain growth (eq 3 and 6) with increasing temperature.

When the polymerization of 1,2-epoxypropane (PO) was attempted with an equimolar mixture of (TPP)AlCl (1, X = Cl) and poly(oxyethylene)diol (PEG, $\bar{M}_n$ = 3000, $\bar{M}_w/\bar{M}_n$ = 1.04; $[PO]_0/[1]_0/[PEG]_0$ = 103/1/1 (mmol)) in CH_2Cl_2 (3 mL), the reaction product exhibited two peaks in GPC (Figure 6). The corresponding fractions could be separated by the difference of solubility in hexane. The insoluble fraction was the ABA-type block copolymer consisting of poly(oxyethylene) (B, 59%)[13] and poly(oxymethylethylene) (A, 41%)[13] segments ($\bar{M}_n$ = 6000, $\bar{M}_w/\bar{M}_n$ = 1.04 (peak a)). The soluble fraction was the homopolymer of 1,2-epoxypropane carrying a chlorine atom at one of the terminals ($\bar{M}_n$ = 1800, $\bar{M}_w/\bar{M}_n$ = 1.08 (peak b); 91% conversion in 72 h). An excellent agreement between the molecular weight of this homopolymer and that estimated for the poly(oxymethylethylene) segment (A) in the block copolymer ($\bar{M}_n$ (peak a) − $\bar{M}_n$ (peak I)/2 = 1500) indicates the uniform chain growth from all the molecules of (TPP)AlCl (1, X = Cl) and both hydroxyl groups of poly(oxyethylene)diol.

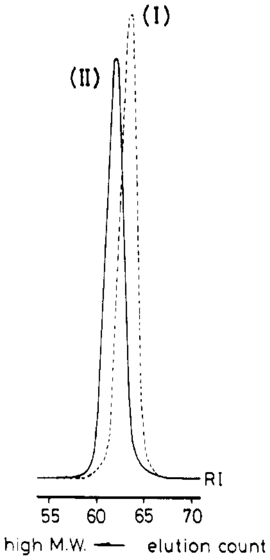


Figure 7. GPC profile of the polymerization of 1,2-epoxypropane (PO, 200 mmol) initiated with the reaction mixture between 1-chloro-2,3-epoxypropane (ECH), (TPP)AlCl (1, X = Cl), and CH_3OH. $[ECH]_0/[(TPP)AlCl]_0/[CH_3OH]_0$ = 200/9/1 (in mmol), 100% conversion. At 100% conversion of PO: (I) reaction mixture at the first stage ($\bar{M}_n$ = 1500, $\bar{M}_w/\bar{M}_n$ = 1.04); (II) reaction mixture at the second stage ($\bar{M}_n$ = 2100, $\bar{M}_w/\bar{M}_n$ = 1.06).

Successive Polymerization of Epoxides (2) with Aluminum Porphyrin (1)–Alcohol Systems. Formation of Block Copolymers. In the immortal polymerization of epoxides described above, the molecules of the polymer alive and dead (more relevantly, "dormant") exist together in a moment, but both of them can grow up uniformly to the polymer with higher molecular weight. In fact, when the polymerization of 1,2-epoxypropane (PO) with the (TPP)AlCl–CH_3OH system ($[PO]_0/[(TPP)AlCl]_0/[CH_3OH]_0$ = 100/1/4.5, 100% conversion) was followed by the addition of another 100 equiv of 1,2-epoxypropane, the molecular weight of the polymer at the first stage ($\bar{M}_n$ = 1300) increased twofold ($\bar{M}_n$ = 2600) at the end of the second stage, retaining a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.09–1.05). The number of the molecules of polymer remained constant at 4.4 with respect to that of (TPP)AlCl. In the polymerization of 1,2-epoxypropane (PO, 200 equiv) initiated with the reaction mixture of the polymerization of 1-chloro-2,3-epoxypropane (ECH) by the (TPP)AlCl–CH_3OH system

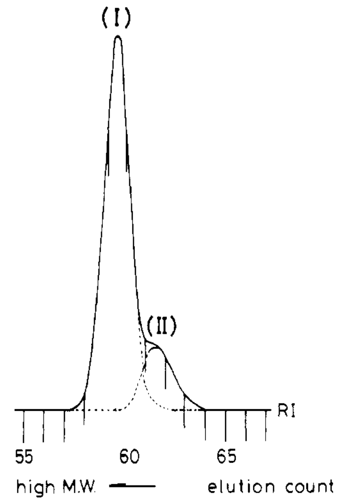


Figure 8. GPC profile of the polymerization of 1,2-epoxypropane (PO) initiated with (TPP)AlCl (1, X = Cl) in the presence of water (H_2O) at 35 °C. $[PO]_0/[(TPP)AlCl]_0/[H_2O]_0 = 400/1/4.5$ (in mmol). At 100% conversion (48 h): (I) $\bar{M}_n = 4500$ ($\bar{M}_w/\bar{M}_n = 1.05$); (II) $\bar{M}_n = 2400$ ($\bar{M}_w/\bar{M}_n = 1.07$).

($[ECH]_0/[(TPP)AlCl]_0/[CH_3OH]_0 = 200/1/9$, 100% conversion), the GPC profile of the product (Figure 7) showed a clear shift of the peak (I) corresponding to the prepolymer of 1-chloro-2,3-epoxypropane ($\bar{M}_n = 1500$, $\bar{M}_w/\bar{M}_n = 1.04$) toward the higher molecular weight region to the peak (II) ($\bar{M}_n = 2100$, $\bar{M}_w/\bar{M}_n = 1.06$) at 70% conversion. An excellent agreement was observed between the composition of the polymeric product determined by ^1H NMR[13] ($f_{ECH}/f_{PO} = 63/37$) and that estimated from the molecular weights corresponding to the peaks (I) and (II) (65/35). The composition was also in agreement with the molar ratio of the two epoxides reacted (59/41). These facts indicate the formation of a block copolymer consisting of poly(oxy(chloromethyl)ethylene) and poly(oxymethylethylene) segments of narrow molecular weight distribution with an efficiency of 100%. In conformity with this, the number of the molecules of polymer with respect to that of (TPP)AlCl (N_p/N_{Al}) remained almost unchanged between the first- and the second-stages of polymerizations (12.3 → 12.7). Similarly, the ABA type of block copolymer consisting of poly(oxymethylethylene) (A, $\bar{M}_n = 1300$; A′, $\bar{M}_n = 450$) and poly(oxyethylene) (B, $\bar{M}_n = 1050$) segments with narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.06$) could be synthesized with a ratio N_p/N_{Al} of 9.9 by the successive polymerizations of 200 equiv of 1,2-epoxypropane (100%), epoxyethane (100%), and 1,2-epoxypropane (63%), with the (TPP)AlCl–CH_3OH (1 equiv/9 equiv) system. Successful formation of block copolymers in the present system represents the essential difference between immortal polymerization and living polymerization, since it is necessary in the latter case to keep all the molecules of the prepolymer uniformly alive for successful block copolymerization.

Polymerization of Epoxide (2) with Aluminum Porphyrin (1) in the Presence of Water. Of particular interest is the fact that the immortality of polymerization was retained even when water was present in the polymerization of epoxide with aluminum porphyrin. An example is shown for the polymerization of 1,2-epoxypropane (PO) with (TPP)AlCl (1, X = Cl) in the presence of water at 35 °C ($[PO]_0/[(TPP)AlCl]_0/[H_2O]_0 = 400/1/4.5$). The GPC profile of the reaction mixture, obtained at 100% conversion after 48 h, showed two unimodal elution peaks (I and II; Figure 8). The molecular weight of peak I ($\bar{M}_n = 4500$, $\bar{M}_w/\bar{M}_n = 1.05$) was almost twice as much as that of peak II ($\bar{M}_n = 2400$, $\bar{M}_w/\bar{M}_n = 1.07$), indicating that the former corresponds to the poly(oxymethylethylene)diol which has grown from the molecules of water in two directions, while the latter has a hydroxyl end and a chlorine end from (TPP)AlCl.

Table III
Chain-Transfer Constants in the Polymerization of Epoxides and a β-Lactone with Aluminum Porphyrin in the Presence of Protic Compounds

monomer	protic compd (transfer agent)	chain-transfer constant (k_{tr}/k_p)
1,2-epoxypropane	CH_3OH	9.8
	$(CH_3)_3CCH_2CO_2H$	10.1
1-chloro-2,3-epoxypropane	CH_3OH	9.4
β-butyrolactone	$CH_3CH(Cl)CH_2CO_2H$	7.6

Conclusion

The unique behaviors observed in the polymerization of epoxides and β-lactones with aluminum porphyrin have led to a novel concept of immortal polymerization, where the polymer with narrow molecular weight distribution is formed even in the presence of protic compounds although nucleophilic growing species are involved. Immortal polymerization is essentially free of termination reactions but involves chain-transfer reactions (exchange reactions, eq 7 and 10). This is in clear contrast with living polymerization, where the absence of any such side reactions is rigorously required. Narrow molecular weight distribution of the polymers in the immortal polymerization indicates that the chain-transfer processes involved are reversible and take place much more rapidly than chain growth.

The quantitative treatment of chain-transfer reactions is usually made by obtaining the chain-transfer constant (the ratio of the rate constants of chain-transfer and propagation reactions, k_{tr}/k_p) by using eq 13, which is based on the assumption of the stationary state as for the concentration of the growing species:[16]

$$\bar{P}_n^{-1} = \bar{P}_{n0}^{-1} + (k_{tr}/k_p)[T][M]^{-1} \qquad (13)$$

where $\bar{P}_n$ and $\bar{P}_{n0}$ are the degrees of polymerization of the polymers obtained with and without chain-transfer agent, respectively, and [T] and [M] are the concentrations of chain-transfer agent and monomer, respectively.

In the present system, the stationary state is established since the concentration of the growing species is kept constant and equal to that of aluminum porphyrin throughout the reaction. When this treatment is applied to the data presented in Tables I and II, and those described in the preliminary communication,[3] chain-transfer constants were estimated as listed in Table III. Thus, the chain-transfer reactions are about 8–10 times faster than the propagation reactions.

Even a strong acid such as hydrogen chloride cannot kill the immortal polymerization of epoxide or β-lactone, although it reacts with the growing species **3** or **5** irreversibly, since the resulting (porphinato)aluminum chloride (**1**, X = Cl) is highly reactive as a nucleophile toward the monomer to regenerate the corresponding growing species instantaneously. Thus, the immortality of polymerization is due to the unusual reactivity of the aluminum atom–axial ligand bond (Al–X) of aluminum porphyrin. Immortal polymerizations of epoxides and β-lactones with aluminum porphyrins as initiator provide a novel method for the syntheses of homo and block copolymers with narrow molecular weight distribution. The advantage of immortal polymerization over living polymerization is that the number of the molecules of polymer is not limited by the amount of initiator but can be increased at will by the amount of protic compound added.

Registry No. 1 (X = OCH_2CH_3), 98539-97-0; 1 (X = $OCH_2C(CH_3)_3$), 113474-64-9; 1 (X = Cl), 71102-37-9; 1 (X = $O_2CCH_2CHClCH_3$), 113474-65-0; **2** (R = H), 25322-68-3; **2** (R = CH_3), 25322-69-4; **2** (R = CH_2CH_3) (homopolymer), 24969-07-1; **2** (R = CH_2CH_3) (SRU), 108421-58-5; **2** (R = CH_2OCH_3) (homopolymer), 28325-89-5; **2** (R = CH_2OCH_3) (SRU), 113474-57-0; **2** (R = CH_2Cl) (homopolymer), 24969-06-0; **2** (R = CH_2Cl) (SRU), 61710-61-0; **4** (R = CH_3) (homopolymer), 38566-36-8; **4** (R = CH_3) (SRU), 26099-72-9.

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(11) (TPP)AlCl shows dark reddish purple in $CDCl_3$ but bluish purple in $CDCl_3$/dioxane.

(12) No change such as broadening was observed for the GPC curve of the prepolymer upon treatment of **3** or **5** with HCl.

(13) For $-(OCH_2CH_2)_x-$: δ 3.7 (CH_2). For $-(OCH(CH_3)CH_2)_x-$: δ 1.15 (CH_3), δ 3.6 (CH and CH_2). For $-(OCH(CH_2Cl)CH_2)_x-$: δ 3.7 (CH_2Cl), δ 3.6 (CH and CH_2) in $CDCl_3$ at room temperature.

(14) N_p/N_{Al} = (MW of **2**) $([\mathbf{2}]_0/[\mathbf{1}]_0)$ (conv/100)$\bar{M}_n^{-1}$.

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Chain Transfer by 2-Iodopropane and Propionic Acid Chloride in the Polymerization of Tetrahydrofuran

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ABSTRACT: The polymerization of tetrahydrofuran was initiated by the addition of silver hexafluoroantimonate and an excess of 2-iodopropane or propionic acid chloride. Rapid chain transfer to the acid chloride was observed. Chain transfer to 2-iodopropane was slow and occurred with the incorporation of the 2-propyl group at the end of the chain. A mechanism is proposed which involves an iodonium ion intermediate.

Introduction

The ring-opening polymerization of cyclic ethers, initiated by the carbenium or oxocarbenium ion generated by the reaction of an alkyl or acyl halide with silver hexafluoroantimonate, has been extensively studied by this laboratory[1] and in others.[2] This system allows rapid and quantitative initiation with the proper choice of the alkyl or acyl halide. In previous experiments the ratio of halide to silver salt was intentionally kept below unity. Therefore the initiator concentration was determined by the halide concentration as the limiting reagent. This was preferred as the silver salt is much more difficult to purify than the halide. We now wish to report our results on the use of an excess of the halide on the polymerization of tetrahydrofuran.

Experimental Section

Silver hexafluoroantimonate was recrystallized in dry diethyl ether under high vacuum. The fine white needles which resulted were transferred under vacuum into a tared flask equipped with a Rotoflo stopcock and pumped on for 24 h. A few crystals were removed under dry nitrogen and the flask was weighed. The elemental analysis of the crystals was consistent with the formula $AgSbF_6 \cdot C_4H_{10}O$. A standard solution was prepared by distilling THF onto the silver salt and off of the salt twice under vacuum to remove the residual diethyl ether, followed by dilution to the mark with THF.

Polymerizations were carried out under vacuum as described elsewhere.[1] Tetrahydrofuran was distilled twice from sodium metal and stored under vacuum in the presence of sodium-potassium alloy. Propionic acid chloride and 2-iodopropane were distilled from calcium hydride and stored under vacuum in the dark.

Samples for NMR spectroscopy were prepared by the reaction of $AgSbF_6$ with 2-iodopropane in THF-d_8 at −78 °C under vacuum in a round-bottom flask. The polymerization mixture was decanted from the silver iodide into the NMR sample tube under vacuum and the tube sealed just prior to placing the tube in the probe.

Results and Discussion

Propionic Acid Chloride. The polymerization of THF was initiated in bulk by 0.141 M propionic acid chloride and 2.1×10^{-3} M $AgSbF_6$ and followed by dilatometry at 24.5 °C. Aliquots were removed at 90, 290, 570, and 7200 min and quenched with sodium phenoxide. The first-order plot for the consumption of the monomer was linear and went through the origin yielding a rate constant of 3.0×10^{-2} L mol^{-1} s^{-1}. This is identical with that determined by using the silver salt in excess of the halide. The GPC data on the aliquots from this run were in sharp contrast to those with the silver salt in excess, with the acid halide at 2.1×10^{-3} M. The initial aliquot had a broad molecular weight distribution with a low molecular weight tail (Figure

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