agreement with the chain-transfer constant (0.6).

A variety of carbon acids has been shown to be effective as chain-transfer agents in GTP of MMA. Of the compounds studied, α-phenylpropionitrile and esters of phenylacetic acid are the most useful chain-transfer agents since they transfer efficiently and do not interfere with the activity of the anion catalysts used in the GTP process. The catalysts which are useful for GTP[4] also catalyze the chain-transfer process. Although our studies do not provide any direct evidence on the mechanism of silicon–proton exchange in the chain-transfer process, this process appears to be related to the tetrabutylammonium fluoride catalyzed silylation of aldehydes and ketones with ethyl (trimethylsilyl)acetate reported by Kuwajima and coworkers.[11] The mechanism proposed[11b] for this process involves the reaction of fluoride with ethyl (trimethylsilyl)acetate to form fluorotrimethylsilane and ester enolate which deprotonates the carbon acid. The resulting carbanion is then silylated by the fluorotrimethylsilane. We have no evidence to indicate whether, in the GTP chain-transfer process, a free enolate is an intermediate or whether an anion-activated silylenolate is the intermediate. Since the latter species has been proposed to be the reactive intermediate in the carbon–carbon bond-forming step of GTP[2,12] it seems reasonable that such an intermediate would have sufficient reactivity to undergo silicon–proton exchange with a carbon acid in the chain-transfer process. Although indene and phenylacetonitrile are chain-transfer agents in GTP exhibiting large chain-transfer constants, they both lead to slow polymerizations of MMA probably as a result of coordination with catalyst, and indene, in addition, leads to poor conversion to polymer. Thus, the most attractive chain-transfer agents are α-phenylpropionitrile and the α-arylacetates. Although the literature does not provide pK_a values for all of the carbon acids that have been evaluated as GTP chain-transfer agents in this study, all of the compounds that have good or moderate activity as chain transfer agents probably have pK_a (in DMSO) values of 25 or less.[13] Aliphatic esters, such as isobutyrates, which are estimated to have pK_a's in excess of 25,[13a] are not chain-transfer agents in GTP. Other, more acidic compounds with pK_a values below about 18, such as malonic esters, malononitrile, a diphenylacetonitrile, seem to produce termination of GTP for reasons not completely understood.

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"Immortal" Polymerization of ε-Caprolactone Initiated by Aluminum Porphyrin in the Presence of Alcohol

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ABSTRACT: The (5,10,15,20-tetraphenylporphinato)aluminum alkoxide–alcohol system is an excellent initiator for the polymerization of ε-caprolactone to give the corresponding polyester having a narrow molecular weight distribution, without the formation of cyclic oligomers. The number of polymer molecules produced exceeded that of aluminum porphyrin molecules, and the reaction thus has the character of "immortal" polymerization. ε-Caprolactone–ethylene oxide block copolymer with controlled chain lengths can also be synthesized.

Introduction

Polycaprolactone is widely used for the production of polyurethanes, and the synthesis of polycaprolactone with well-controlled molecular weight is very important in order to give a desired function to polyurethanes.

The polymerization of ε-caprolactone can be brought about with various initiators,[1,2] but examples of living polymerization have been very limited. Teyssié and coworkers reported the living polymerization of ε-caprolactone catalyzed by soluble bimetallic μ-oxoalkoxide, to

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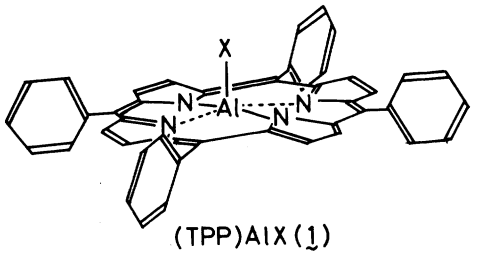
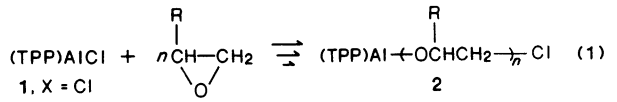
give a polymer with a narrow molecular weight distribution.[3] In this case, however, reequilibration and degradation reactions take place competitively. At 100% conversion, the molecular weight of the polymer reaches an equilibrium characterized by a trimodal distribution. Yamashita and co-workers showed that the anionic polymerization of ϵ-caprolactone with potassium or lithium *tert*-butoxide results in a living ring–chain equilibrium system, the cyclic oligomers being produced by back-biting degradation from the initially formed linear polymers.[4] Thus, it has been difficult to synthesize polycaprolactone with a narrow molecular weight distribution.

Recently, we found aluminum porphyrin, such as (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1, X = Cl), to be an excellent initiator for the

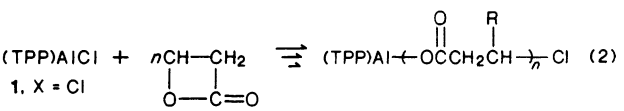


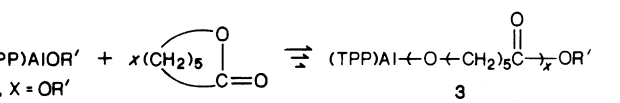
(TPP)AlX (1)

ring-opening polymerization of epoxides to give polyethers of controlled molecular weight with narrow distribution.[5] In this case, the growing species of polymerization is the (porphinato)aluminum alkoxide **2**, formed by the insertion of epoxide into the Al–Cl bond of the initiator (eq 1).[6]



Similarly, the ring-opening polymerization of a β-lactone with (TPP)AlCl proceeds by a "living" process,[7] where the growing species is a (porphinato)aluminum carboxylate, the product of ring-opening of the β-lactone at the alkyl–oxygen bond (eq 2).[8] In contrast to β-lactone, ϵ-caprolactone does not react with (porphinato)aluminum chloride or (porphinato)aluminum carboxylate, but the polymerization is initiated by (porphinato)aluminum alkoxide (1, X = OR'), which regenerates the alkoxide **3**, the product of the ring-opening at the acyl–oxygen bond (eq 3).[9]





(3)

In the course of studies on the reactivity of the growing species in these polymerizations, we have very recently found the "immortal" polymerization of epoxide,[10] where the growing species is not "killed" even in the presence of a protic compound such as alcohol. The aluminum porphyrin–alcohol system gives a polymer of narrow molecular weight distribution with the number of polymer molecules exceeding that of aluminum porphyrin molecules.

These interesting findings prompted us to examine the possibility of applying this excellent system to the polymerization of ϵ-caprolactone, in order to synthesize polycaprolactone with well-controlled molecular weight and without the formation of the cyclic oligomers.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[11] Diethylaluminum chloride (Et_2AlCl) and triethylaluminum (Et_3Al) were distilled under reduced pressure in a nitrogen atmosphere. Dichloromethane and chloroform were washed with concentrated sulfuric acid, neutralized with aqueous solution of sodium bicarbonate, dried over calcium chloride, and distilled over calcium hydride in a nitrogen atmosphere. ϵ-Caprolactone was dried over calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. Epoxyethane (ethylene oxide), stirred with a mixture of potassium hydroxide and calcium hydride at room temperature, was degassed to remove air and then collected in a trap cooled at the liquid nitrogen temperature (trap-to-trap method). Methanol was dried over calcium sulfate and distilled over magnesium treated with iodine under nitrogen atmosphere. Ethylene glycol, dried over potassium hydroxide, was distilled under reduced pressure in a nitrogen atmosphere over potassium hydroxide.

Preparation of (Porphinato)aluminum Alkoxide from (TPP)AlCl and Epoxide. (TPP)AlCl (1, X = Cl) was prepared by the reaction of Et_2AlCl with $TPPH_2$ as described previously.[5b] $TPPH_2$ (1 mmol) was placed in a Pyrex tear-drop-type flask connected with a three-way stop cock and purged with dry nitrogen. Dichloromethane (CH_2Cl_2, 20 mL) was introduced into this flask to dissolve $TPPH_2$. To this solution was added Et_2AlCl (about 0.15 mL (1.2 mmol), in 20% excess to $TPPH_2$), and the reaction mixture was allowed to stand for about an hour with magnetic stirring under nitrogen atmosphere at room temperature. From the above reaction mixture, volatile materials were removed under reduced pressure to give (TPP)AlCl as a purple solid with a metallic luster. CH_2Cl_2 was introduced again to dissolve the (TPP)AlCl, and 1,2-epoxypropane (propylene oxide) (2 mmol) was added to this solution. After the mixture was stirred for 2 days at room temperature, volatile materials were removed under reduced pressure to leave $(TPP)Al(PO)_2Cl$ (**2**, R = CH_3, n = 2), which was used as the initiator for polymerization.

Preparation of (Porphinato)aluminum Alkoxide from (TPP)AlEt and Alcohol. (Tetraphenylporphinato)aluminum ethyl ((TPP)AlEt, 1, X = C_2H_5) was prepared by the equimolar reaction of Et_3Al with $TPPH_2$ as described previously.[12] A tear-drop-type flask fitted with a three-way stop cock containing $TPPH_2$ (1 mmol) was purged with dry nitrogen, CH_2Cl_2 (20 mL) was introduced into the flask, and Et_3Al (0.14 mL, 1 mmol) was added to the solution with stirring. After the reaction mixture was stirred at room temperature for about an hour, the volatile materials were removed under reduced pressure, and CH_2Cl_2 (20 mL) was introduced again into the flask to dissolve the product, (TPP)AlEt.

(Tetraphenylporphinato)aluminum methoxide (1, X = OMe, (TPP)AlOMe) was prepared by the reaction of (TPP)AlEt with methanol. To a CH_2Cl_2 solution of (TPP)AlEt (1 mmol) was added methanol (10 mL) at room temperature, and the reaction mixture was allowed to stand for 3 days with magnetic stirring. After completion of the reaction, the color of the solution turned to reddish purple from greenish purple characteristic of (TPP)AlEt. The solvent and unreacted methanol were removed under reduced pressure to give (TPP)AlOMe as a purple solid.

The reaction of ethylene glycol with (TPP)AlEt was carried out by stirring the mixture in CH_2Cl_2 for 3 days at room temperature. After completion of the reaction, the color of the solution turned to reddish purple from greenish purple, similarly to the above. The solvent was removed under reduced pressure at room temperature, and the residue was used as the initiator system.

Polymerization. When the initiator was $(TPP)Al(PO)_2Cl$ (**2**, R = CH_3, n = 2) or (TPP)AlOMe (1, X = OMe), methanol was introduced by syringe into the flask containing the initiator, followed by ϵ-caprolactone. The mixture was kept at a constant temperature with magnetic stirring. After a prescribed time, a small amount of the reaction mixture was removed from the flask by syringe in a nitrogen stream and was dissolved in deuteriated chloroform ($CDCl_3$) or tetrahydrofuran. The conversion of

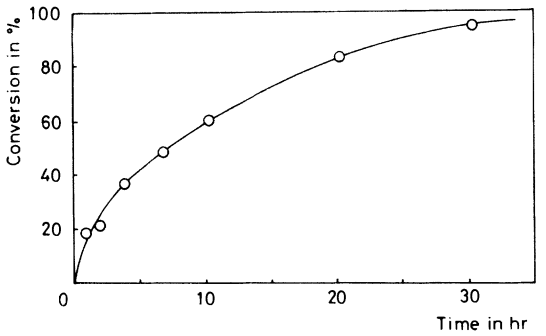


Figure 1. Time–conversion curve for the polymerization of ϵ-caprolactone (CL) with the (TPP)Al(PO)$_2$Cl (**2**, R = CH_3, n = 2)–MeOH system at room temperature in CH_2Cl_2. $[CL]_0/[MeOH]_0/[(TPP)Al(PO)_2Cl]_0$ = 200/9/1; $[(TPP)Al(PO)_2Cl]_0$ = 16.7 mmol·L^{-1}.

ϵ-caprolactone was calculated from the intensities of the signals due to the $-OCO(CH_2)_5-$ unit and ϵ-caprolactone remained unreacted in the ^{1}H NMR spectrum of the reaction mixture. The insoluble fraction in tetrahydrofuran (initiator residue) was filtered off by using a Teflon filter with pore size of 0.45 μm, and the solution was subjected to GPC analysis in order to determine the molecular weight and molecular weight distribution. In case of polymerization in the presence of ethylene glycol, the monomer was directly introduced into the initiator system (the reaction product from (TPP)AlEt and an excess of ethylene glycol) by syringe.

Isolation of Polycaprolactone. For example, to the chloroform solution (5 mL) containing 1 g of the polymerization mixture at 100% conversion ($\bar{M}_n$ = 7000, $\bar{M}_w/\bar{M}_n$ = 1.19) was added 500 mL of methanol, followed by 10 mL of 10% methanolic hydrochloric acid. The resulting precipitate was washed with a large amount of methanol until the filtrate became colorless. The residue was dissolved in chloroform, and the solution was evaporated to dryness to leave polycaprolactone as a white powder in almost quantitative recovery. No change was observed for the molecular weight ($\bar{M}_n$) and the distribution ($\bar{M}_w/\bar{M}_n$) during these treatments.

Measurements. ^{1}H and ^{13}C NMR spectra were measured in deuteriated chloroform by using a Hitachi R-40 spectrometer and a JEOL PS 100 spectrometer operating at 90 and 25.03 MHz, respectively. The chemical shift was determined with respect to tetramethylsilane (δ 0) for ^{1} NMR and to $CDCl_3$ (δ 77.102) for ^{13}C NMR. Gel permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-802A gel permeation chromatograph equipped with a differential refractometer detector using tetrahydrofuran as eluent: flow rate, 1.0 mL·min^{-1}; columns, 60 cm long with pore size 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). The molecular weight and the molecular weight distribution were estimated on the basis of the calibration curve obtained by using standard poly(ethylene oxides) for the higher molecular weight region and standard poly(propylene glycols) for the lower molecular weight region. Standard poly(ethylene oxides) were obtained from Toyo Soda Manufacturing Co., Lt.: $\bar{M}_n$ = 22000 ($\bar{M}_w/\bar{M}_n$ = 1.14); $\bar{M}_n$ = 39000 ($\bar{M}_w/\bar{M}_n$ = 1.03); $\bar{M}_n$ = 72000 ($\bar{M}_w/\bar{M}_n$ = 1.02). Standard poly(propylene glycols) were obtained from Lion Fat & Oil Co., Ltd.: $\bar{M}_n$ = 1000 and 2000 ($\bar{M}_w/\bar{M}_n \simeq$ 1).

Block Copolymerization. The prepolymer of ethylene oxide was prepared by the polymerization of ethylene oxide with (TPP)AlCl or with the reaction product from (TPP)AlEt and an excess of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A). Ethylene oxide was introduced to the initiator system by a trap-to-trap method.[5b] After a definite time, unreacted ethylene oxide and solvent was removed under reduced pressure, and ϵ-caprolactone was added to the prepolymer thus formed. Subsequent procedures were the same as described above for the homopolymerization.

Results and Discussion

Polymerization of ϵ-Caprolactone with the (TPP)-Al(PO)$_2$Cl (2, R = CH_3, n = 2)–MeOH System. Since

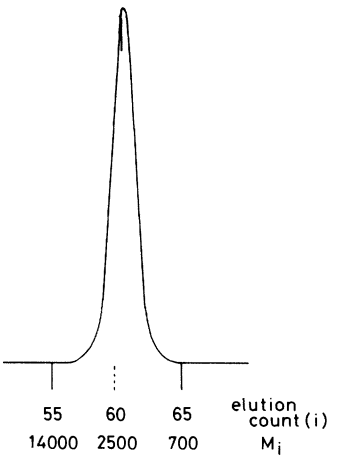


Figure 2. GPC curve of the reaction mixture in the polymerization of ϵ-caprolactone (CL) with the (TPP)Al(PO)$_2$Cl (**2**, R = CH_3, n = 2)–MeOH system; for reaction conditions, see Figure 1.

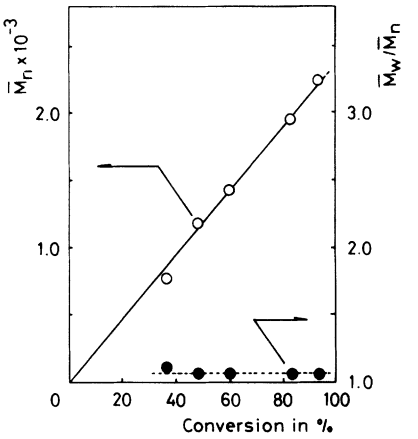


Figure 3. Polymerization of ϵ-caprolactone (CL) with the (TPP)Al(PO)$_2$Cl (**2**, R = CH_3, n = 2)–MeOH system. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and conversion; for reaction conditions, see Figure 1.

(porphinato)aluminum chloride ((TPP)AlCl, **1**, X = Cl), though effective for the polymerization of epoxide and β-lactone, does not react with ϵ-caprolactone, (TPP)AlCl was converted to an alkoxide by the reaction with 2 M equiv of 1,2-epoxypropane (propylene oxide, PO) (eq 1).

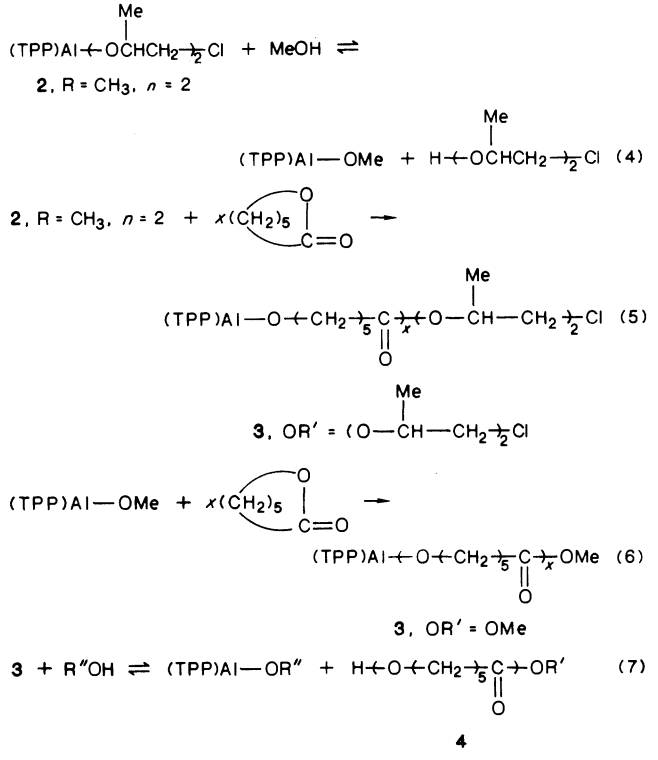
By using the living oligomer (TPP)Al(PO)$_2$Cl (**2**, n = 2) thus obtained as initiator, the polymerization of ϵ-caprolactone (CL) in the presence of methanol was examined. The time–conversion curve for the polymerization with the (TPP)Al(PO)$_2$Cl–methanol system is shown in Figure 1, where the initial molar ratios of ϵ-caprolactone and methanol to (TPP)Al(PO)$_2$Cl were 200 and 9, respectively. The polymerization gradually proceeded at room temperature until the added monomer was completely consumed. The gel permeation chromatogram (GPC) of the polymer obtained at 100% conversion showed the characteristics of narrow molecular weight distribution as indicated by the ratio of the weight-average molecular weight to the number-average molecular weight close to one ($\bar{M}_w/\bar{M}_n$ = 1.08, $\bar{M}_n$ = 2300) (Figure 2). The number-average molecular weight ($\bar{M}_n$) of the polymer increased linearly with conversion, keeping the molecular weight distribution narrow ($\bar{M}_w/\bar{M}_n$ = 1.06–1.12) (Figure 3). The concomitant formation of oligomer was excluded by the absence of the corresponding peak in the lower molecular weight region of the GPC chromatogram of the reaction mixture throughout the polymerization.

Table I
Polymerization of ϵ-Caprolactone (CL) with the (TPP)Al(PO)$_2$Cl (2, R = CH$_3$, n = 2)-MeOH System[a]

run	[MeOH]$_0$/[Al]$_0$	[Cl]$_0$/[Al]$_0$	time, h	conv, %	$\bar{M}_n$[b]	$\bar{M}_w$[b]/$\bar{M}_n$	N_P[c]/N_{Al}
1[d]	0	200	4	71	23000	1.49	0.7
2	4	200	3	65	3500	1.07	4.3
3[d]	4	1000	3	70	14600	1.21	5.5
4	9	200	49	82	1800	1.12	10.4
5[d]	9	200	220	100	2300	1.08	10.1
6[e]	9	600	4	94	7400	1.13	8.7
7	19	200	670	78	940	1.10	19.6
8[f]	49	1000	410	47	1000	1.08	54.3

[a] At room temperature without solvent. [b] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were estimated by GPC. [c] Ratio of the number of polymer molecules (N_p) to the number of aluminum atoms (N_{Al}). [d] In CH_2Cl_2. [e] Addition of 400 equiv of monomer to run 5 after 100% conversion. [f] At 50 °C.

In the presence of methanol, a polymer with narrow molecular weight distribution was obtained at any molar ratio of methanol to initiator and that of monomer to initiator (runs 2–8 in Table I). Furthermore, the number of polymer molecules (N_p) is almost equal to the sum of the numbers of the molecules of initiator (N_{Al}) and methanol. This indicates that the polymer chains grow not only from (TPP)Al(PO)$_2$Cl but also from the added methanol. In this system, (TPP)Al(PO)$_2$Cl (2, R = CH$_3$, n = 2), a (porphinato)aluminum alkoxide, exchanges with methanol rapidly and reversibly[10] (eq 4). (TPP)AlOMe (1, X = OMe) thus formed also initiates the polymerization of ϵ-caprolactone (eq 6), similarly to 2 (R = CH$_3$, n = 2) (eq 5). The growing species of the polymerization of ϵ-caprolactone is a (porphinato)aluminum alkoxide (eq 3, 5, and 6), and it exchanges rapidly and reversibly with methanol and any other alcohols such as 4 in the system (eq 7). Narrow molecular weight distribution of the



product indicates that the exchange reactions are much faster than the propagation reaction.

When 400 M equiv of epoxyethane with respect to aluminum porphyrin was added to the system at 100% conversion of the polymerization of ϵ-caprolactone (CL) by the (TPP)Al(PO)$_2$Cl–methanol (MeOH) system ([CL]$_0$/[(TPP)Al(PO)$_2$Cl]$_0$/[MeOH]$_0$ = 200/1/9), the polymerization of epoxyethane ensued at room temperature up to 50% conversion in 8 days. The number-average molecular weight ($\bar{M}_n$) of the polymer increased from 2390 to 2740, although the ratios $\bar{M}_w/\bar{M}_n$ and N_p/N_{Al} remaind almost unchanged from 1.12 to 1.17 and from 9.6 to 11.5, respectively. This observation demonstrates the formation of a block copolymer of ϵ-caprolactone and epoxyethane with quantitative efficiency.

Thus, the polymerization of ϵ-caprolactone with the (TPP)Al(PO)$_2$Cl–methanol system is of an "immortal" nature, similarly to the polymerization of epoxide.

The Polymerization of ϵ-Caprolactone by the (TPP)AlOMe (1, X = OMe)–MeOH System. The polymerization of ϵ-caprolactone was examined with (TPP)AlOMe prepared from (TPP)AlEt and methanol, in order to obtain the polymer with homogeneous end groups, since the end groups of the polymer synthesized by the (TPP)Al(PO)$_2$Cl–MeOH system are considered to be either chlorine or methyl ester (eq 5 and 6).

The polymerization of ϵ-caprolactone initiated by (TPP)AlOMe proceeded more slowly than that initiated by (TPP)Al(PO)$_2$Cl, but the polymer obtained was characterized by a narrow molecular weight distribution; for example, after 13 days at 50 °C without solvent, conversion was 97%, $\bar{M}_n$ = 2100, $\bar{M}_w/\bar{M}_n$ = 1.12, where the initial molar ratios of ϵ-caprolactone and methanol to (TPP)AlOMe were 200 and 9, respectively. The number of polymer molecules was almost equal to the sum of the numbers of the molecules of initiator and methanol (N_p/N_{Al} = 10.7). The ^{13}C NMR spectrum of this mixture showed a signal due to the CH$_3$O– terminal at δ 62.2. The number-average degree of polymerization, 20.0, as estimated from the intensity ratio of this signal and that due to the methylene carbon attached to the oxygen atom in the repeating unit (–CO$_2$C–, δ 64.1), was in good agreement with the observed value by GPC, 18.4. Thus, the polymerization of ϵ-caprolactone with the (TPP)AlOCH$_3$–MeOH system also proceeds with immortal nature from all the molecules of (TPP)AlOCH$_3$ and MeOH.

Polymerization of ϵ-Caprolactone with the (TPP)AlEt (1, X = Et)–Ethylene Glycol System. The synthesis of bifunctional polycaprolactone with narrow molecular weight distribution was attempted by the immortal polymerization of ϵ-caprolactone using ethylene glycol (EG) as an alcohol. In practice, (TPP)AlEt was reacted with an excess, prescribed amount of ethylene glycol, and the product was added to the monomer to bring about the polymerization.

The relationships between conversion and $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ are shown in Figure 4, where the initial molar ratios of ϵ-caprolactone and ethylene glycol to (TPP)AlEt were 200 and 10, respectively, at 50 °C without solvent. Similarly to the polymerization initiated by (TP)Al(PO)$_2$Cl or (TPP)AlOMe in the presence of methanol, the number-average molecular weight ($\bar{M}_n$) increased linearly with conversion, keeping the molecular weight distribution narrow.

Table II
Polymerization of ϵ-Caprolactone (CL) with the (TPP)AlEt (1, X = Et)-Ethylene Glycol (EG) System[a]

run	$[EG]_0/[Al]_0$	$[CL]_0/[Al]_0$	time, days	conv, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	N_p/N_{Al}[c]
1	1	200	21	49	10400	1.18	1.1
2	5	200	14	92	4200	1.11	5.1
3	10	200	24	100	2600	1.12	9.1
4[d]	10	200	21	100	2200	1.19	10.6
5	20	200	14	91	1100	1.10	20.8

[a] At 50 °C without solvent. [b] $\bar{M}_w/\bar{M}_n$ were estimated by GPC. [c] Ratio of the number of polymer molecules (N_p) to the number of aluminum atoms (N_{Al}). [d] At 100 °C.

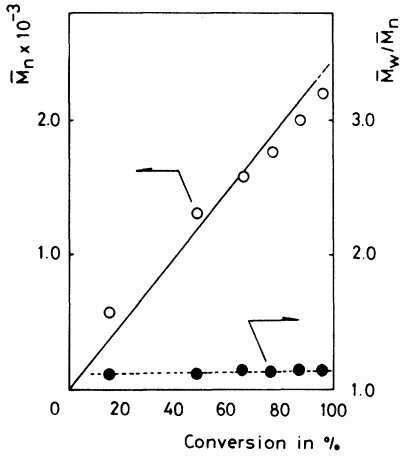


Figure 4. Polymerization of ϵ-caprolactone (CL) with the (TPP)AlEt (1, X = Et)–ethylene glycol (EG) system. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and conversion. $[CL]_0/[EG]_0/[(TPP)AlEt]_0$ = 200/10/1, at 50 °C without solvent.

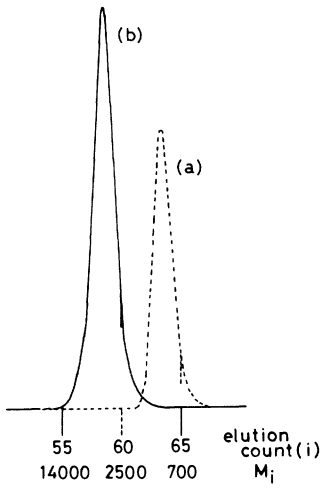
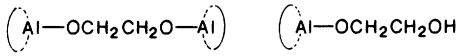


Figure 5. GPC at a ϵ-caprolactone–ethylene oxide block copolymer and the corresponding prepolymer of ethylene oxide, with the (TPP)AlCl (1, X = Cl)–methanol system: (a) Prepolymer, $[EO]_0/[MeOH]_0/[(TPP)AlCl]_0$ = 200/9/1; at 100% conversion, $\bar{M}_n$ = 960; $\bar{M}_w/\bar{M}_n$ = 1.05. (b) Block copolymer, $[CL]_0/[(TPP)AlCl]_0$ = 200/1; at 100% conversion, $\bar{M}_n$ = 3800, $\bar{M}_w/\bar{M}_n$ = 1.20; $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as estimated by GPC.

The results of the polymerization at various molar ratios of ethylene glycol to (TPP)AlEt are summarized in Table II. The polymers obtained were of narrow molecular weight distribution at any molar ratio, at a higher temperature such as 100 °C as well (run 4). The calculated number of polymer molecules (N_p/N_{Al}), assuming that the polymer chains grow from both hydroxyl groups of ethylene glycol, was almost equal to the number of ethylene glycol molecules ($[EG]_0/[(TPP)AlEt]_0$).

The system from (TPP)AlEt and an excess of ethylene glycol is a mixture of two types of aluminum porphyrin and ethylene glycol, I and II. Rapid exchanges among I,



I II

II, and ethylene glycol take place, to result in the uniform growth of polymer chains from both ends of ethylene glycol.

Ethylene Oxide–ϵ-Caprolactone Block Copolymerization with the (TPP)AlCl (1, X = Cl)–Methanol System. Block copolymerization of ϵ-caprolactone with the prepolymer of ethylene oxide having an alkoxide living end was attempted in order to synthesize a block copolymer consisting of well-controlled polyester–polyether sequences.

As the first step of the copolymerization, the prepolymer was prepared by the immortal polymerization of ethylene oxide with the (TPP)AlCl–MeOH system[10] at room temperature without solvent, where the initial molar ratios of ethylene oxide and methanol to (TPP)AlCl were 200 and 9, respectively. After 24 h, the prepolymer was formed with narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.05, $\bar{M}_n$ = 960) at 100% conversion.

When ϵ-caprolactone was added to this prepolymer with the initial molar ratio to (TPP)AlCl of 200, the lactone reacted to 100% conversion after 4 days at 50 °C. The GPC elution curve of the reaction mixture obtained after the completion of the second stage of polymerization clearly shifted toward a higher molecular weight region, retaining the narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.20, $\bar{M}_n$ = 3800). Furthermore, neither the peak corresponding to the prepolymer of ethylene oxide nor that corresponding to the homopolymer (and oligomer) of ϵ-caprolactone was observed (Figure 5).

Thus, the immortal nature of the polymerization of ethylene oxide with the (TPP)AlCl–CH_3OH system is successfully followed by the polymerization of ϵ-caprolactone at the subsequent stage, to give the corresponding AB-type block copolymer with narrow molecular weight distribution.

Ethylene Oxide–ϵ-Caprolactone Block Copolymerization with the (TPP)AlEt (1, X = Et)–Bisphenol A System. Synthesis of a bifunctional ABA-type block copolymer from ϵ-caprolactone and ethylene oxide was attempted by using the (TPP)AlEt–bisphenol A system.

The reaction between (TPP)AlEt and a phenol gives a (porphinato)aluminum phenoxide,[13] which does not initiate the polymerization of ϵ-caprolactone but initiates the polymerization of epoxide to give a (porphinato)aluminum alkoxide as the growing species.[9]

As the first step of the block copolymerization, the prepolymer ($\bar{M}_n$ = 1400, $\bar{M}_w/\bar{M}_n$ = 1.05 (GPC)) was prepared by the immortal polymerization of ethylene oxide with the (TPP)AlEt–bisphenol A system, where the initial molar ratios of ethylene oxide and bisphenol A to (TPP)AlEt were 200 and 5, respectively; reaction time 24 h, conversion ≃100%. To this prepolymer, ϵ-caprolactone was introduced with the initial molar ratio to (TPP)AlEt

Table III
Block Copolymerization of ϵ-Caprolactone (CL) with the Living Prepolymer of Ethylene Oxide (EO) Initiated by the (TPP)AlEt (1, X = Et)-Bisphenol A (BPA) System[a]

run	$[BPA]_0/[Al]_0$	$[EO]_0/[Al]_0$	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$[CL]_0/[Al]_0$	time, days	conv, %	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	N_p[c]$/N_{Al}$
1	5	200	1400	1.05	200	23	64	4800	1.09	5.1
2	10	200	800	1.03	200	15	71	2500	1.07	11.0
3	20	200	430	1.05	200	9	70	930	1.08	31.5

[a] At 50 °C without solvent. [b] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as estimated by GPC. [c] Ratio of the number of copolymer molecules (N_p) to the number of aluminum atoms (N_{Al}).

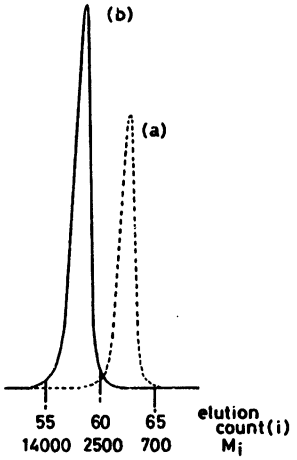


Figure 6. GPC of a ϵ-caprolactone–ethylene oxide block copolymer and the corresponding prepolymer of ethylene oxide, with the (TPP)AlEt (1, X = Et)–bisphenol A (BPA) system: (a) Prepolymer, $[EO]_0/[BPA]_0/[(TPP)AlEt]_0 = 200/5/1$; at 100% conversion, $\bar{M}_n = 1400$; $\bar{M}_w/\bar{M}_n = 1.05$. (b) Block copolymer, $[CL]_0/[(TPP)AlEt]_0 = 200$; at 74% conversion, $\bar{M}_n = 4800$; $\bar{M}_w/\bar{M}_n = 1.09$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as estimated by GPC.

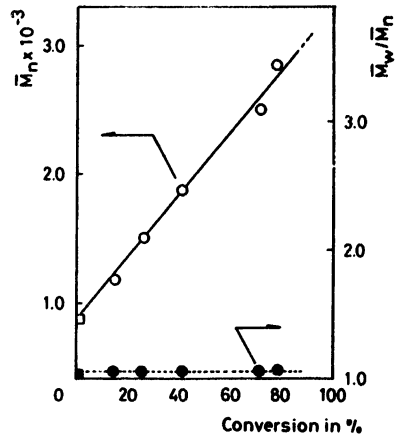


Figure 7. Block copolymerization of ϵ-caprolactone from the prepolymer of ethylene oxide with the (TPP)AlEt (1, X = Et)–bisphenol A (BPA) system. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) of the block copolymer and conversion. Prepolymer, $[EO]_0/[BPA]_0/[(TPP)AlEt]_0 = 200/10/1$; at 100% conversion, (□) $\bar{M}_n = 800$; (■) $\bar{M}_w/\bar{M}_n = 1.03$, $\bar{M}_n$ or $\bar{M}_w/\bar{M}_n$ as estimated by GPC. $[EO]_0/[BPA]_0/[(TPP)AlEt]_0 = 200/10/1$; $[CL]_0/[(TPP)AlEt]_0 = 200$, at 50 °C without solvent.

of 200. After 23 days, ϵ-caprolactone reacted to 64% conversion at 50 °C. The GPC chromatogram of the reaction mixture (Figure 6) showed the absence of the prepolymer and of the homopolymer or oligomer of ϵ-caprolactone, while a unimodal, sharp elution curve corresponding to the block copolymer was observed in the higher molecular weight region than that of the prepolymer ($\bar{M}_n = 4800$, $\bar{M}_w/\bar{M}_n = 1.09$). The results for other initial molar ratios of bisphenol A to (TPP)AlEt are summarized in Table III. The number of the polymer molecules (N_p/N_{Al}), calculated by assuming that the polymer chains grow from both hydroxyl groups of bisphenol A, was almost equal to the number of bisphenol A molecules ($[BPA]_0/[(TPP)AlEt]_0$).

The number-average molecular weight ($\bar{M}_n$) of the block copolymer increased linearly with the progress of the reaction, while $\bar{M}_w/\bar{M}_n$ remained almost constant (1.06–1.07) at any conversion, as shown in Figure 7. Thus, the chain lengths of polyether and polyester in the block copolymer of ethylene oxide and ϵ-caprolactone could be controlled respectively by the molar ratios of the first and the second monomers to bisphenol A.

Conclusion

The polymerization of ϵ-caprolactone initiated by (5,10,15,20-tetraphenylporphinato)aluminum alkoxide in the presence of alcohols, such as methanol and ethylene glycol, proceeds with an immortal nature to give poly(ϵ-caprolactone) with narrow molecular weight distribution and with the number of molecules more than that of catalyst molecules. The successive immortal polymerizations of ethylene oxide and ϵ-caprolactone give the corresponding block copolymer of well-defind block sequences with 100% efficiency. The concomitant formation of cyclic oligomer does not take place, indicating the essential difficulty in intra- and intermolecular attacks of the (porphinato)aluminum alkoxide to the ester group in the polymer chain because of the large, rigid porphyrin ring.

In the absence of alcohol, the molecular weight distribution of the product tended to be a little broader (for example, run 1 in Table I). GPC peaks were generally unimodal and narrow but exhibited a tail in the higher and lower molecular weight sides of the peak. Thus, the presence of alcohol is considered to affect the rates of initiation and/or propagation reactions, by the effect on the reactivities of aluminum porphyrin and/or the lactone, although details remain yet unknown.

Registry No. 1, 71102-37-9; 1 (X = C_2H_5), 63256-30-4; 1 (X = OMe), 66945-43-5; 2 (R = Me, $n = 2$), 99559-92-9; I, 110661-57-9; II, 110661-58-0; BPA, 80-05-7; MeOH, 67-56-1; ϵ-caprolactone, 502-44-3; poly(ϵ-caprolactone) (homopolymer), 24980-41-4; poly(ϵ-caprolactone) (SRU), 25248-42-4; (ϵ-caprolactone)(ethylene oxide) (block copolymer), 107596-21-4.

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Biosynthesis of Copolyesters in *Alcaligenes eutrophus* H16 from ^{13}C-Labeled Acetate and Propionate

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ABSTRACT: Copolyesters of 3-hydroxybutyrate (B) and 3-hydroxyvalerate (V) are isolated from *Alcaligenes eutrophus* H16 grown in nitrogen-free culture media containing the sodium salts of acetate and propionate. The content of V units in the copolyesters increases with increasing mole fraction of propionate to acetate in the culture medium. The copolyester is formed even when propionate is used as the sole carbon source, and the content of V units increases up to 45 mol % with increasing concentration of propionate in the medium. The biosynthetic pathway of the copolyester is investigated by using [1-^{13}C]acetate, [2-^{13}C]acetate, and [1-^{13}C]propionate as carbon sources. The use of ^{13}C-labeled acetate and propionate results in the formation of copolyesters specifically labeled with ^{13}C.

Introduction

Optically active poly(3-hydroxybutyrate) accumulates in a variety of bacteria and functions as a source of energy and carbon supply for the bacteria.[1] The biological function of poly(3-hydroxybutyrate) is similar to that of glycogen in mammals and starch in plants. Recently, the copolyester of 3-hydroxybutyrate (B) and 3-hydroxyvalerate (V) has been isolated from *Alcaligenes eutrophus* grown in a culture medium containing glucose and propionate.[2] This bacterial copolyester has attracted industrial attention as a possible candidate for large-scale biotechnological production, since the copolyester is environmentally degradable thermoplastic and has good mechanical properties, comparable to commercial thermoplastics such as isotactic polypropylene and poly(ethylene terephthalate).[2] The impact strength, flexural modulus, and melting temperature have been shown to be regulated by the content of V units in the copolyester.[2,3] It has been shown that the bacterial copolyester has a statistically random distribution of B and V units.[4,5] Marchessault et al.[5] found that the copolyester exhibits the unusual phenomenone of isodimorphism.

In this paper we report results on the biosynthesis of the copolyester in *Alcaligenes eutrophus* H16 from acetate and propionate. In addition, we determine the biosynthetic pathway of copolyester formation by using [1-^{13}C]acetate, [2-^{13}C]acetate, and [1-^{13}C]propionate as carbon sources.

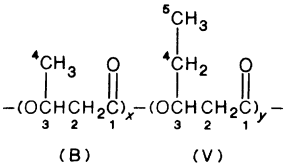
Experimental Section

Polyester Biosynthesis. Samples of the polyesters were isolated from *Alcaligenes eutrophus* H16 (ATCC 17699). The strain H16 was maintained on nutrient agar slants at 4 °C by monthly subculture. The bacteria were first grown at 30 °C in the nutrient-rich medium (100 cm^3) containing 10 g/dm^3 of yeast extract, 10 g/dm^3 of polypeptone, 5 g/dm^3 of meat extract, and 5 g/dm^3 of $(NH_4)_2SO_4$. The cells were harvested after 24 h, corresponding to the end of exponential growth, and washed with water. Under these culture conditions the accumulation of polyesters in the cells was not observed. To promote polyester synthesis, 0.20–0.15-g quantities of the washed cells were transferred into a nitrogen-free mineral medium[6] (100 cm^3) containing CH_3COONa and CH_3CH_2COONa. The cells were cultivated in this medium (pH 7.0) for 48 h at 30 °C, harvested by centrifugation, washed with acetone, and finally dried under vacuum at room temperature. Polyesters were extracted from the dried cells with hot chloroform in a Soxhlet apparatus and purified by reprecipitation with hexane.

NMR Analysis. The ^{1}H and ^{13}C NMR analyses of the polyester samples were carried out on a JEOL GX-500 spectrometer. The 500-MHz ^{1}H NMR spectra were recorded at 27 °C on a $CDCl_3$ solution of the polyester at a concentration of 0.01 g/cm^3 with a 45° pulse (3.5 μs), 6.0-s pulse repetition, 7000-Hz spectral width, 32K data points, and 100–400 accumulations. The proton-decoupled 125-MHz ^{13}C NMR spectra were recorded at 27 °C on a $CDCl_3$ solution of the polyester at a concentration of 0.02–0.05 g/cm^3 with a 45° pulse (10 μs), 5.0-s pulse repetition, 25 000-Hz spectral width, 64K data points, and 1000–5000 accumulations. Tetramethylsilane (Me_4Si, δ 0) was used as an internal chemical shift standard.

Results and Discussion

Biosynthesis of Copolyesters. Table I lists the results of the biosynthesis of polyesters from CH_3COONa and CH_3CH_2COONa by *A. eutrophus* H16. The ^{1}H NMR spectra of all copolyesters showed that the polymers contained the two monomeric units B and V as



The mole fractions of the two monomeric units, F_B and F_V, were determined from the ^{1}H NMR spectra, based on the intensity ratio of the doublet resonance at 1.274 ppm of the (B4) methyl protons to the triplet resonance at 0.894 ppm of the (V5) methyl protons.[4]

Poly(3-hydroxybutyrate) (PHB) was obtained when acetate was used as a carbon source, and the polymer content in dry cells increased with the concentration of acetate in the culture medium. Copolyesters of B and V units are produced in the presence of acetate and pro-

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