to Drs. K. Adachi and H. Ohnuma of this department for their kind discussions.

Registry No. Poly(vinylidene fluoride) (homopolymer), 24937-79-9.

References and Notes

(1) Sasabe, H.; Saito, S.; Asahina, M.; Kakutani, H. *J. Polym. Sci., Part A-2* **1969**, *7*, 1405.
(2) Kakutani, H. *J. Polym. Sci., Part A-2* **1970**, *8*, 1177.
(3) Yano, S. *J. Polym. Sci., Part A-2* **1970**, *8*, 1057.
(4) Nakagawa, K.; Ishida, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 1503.
(5) McBrierty, V. J.; Douglass, D. C.; Weber, T. A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1271.
(6) Miyamoto, Y.; Miyaji, H.; Asai, K. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 597.
(7) Clark, J. D.; Taylor, P. L.; Hopfinger, A. J. *J. Appl. Phys.* **1981**, *52*, 5903.
(8) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules*, in press.
(9) Farmer, B. L.; Hopfinger, A. J.; Lando, J. B. *J. Appl. Phys.* **1972**, *43*, 4293.
(10) Takahashi, Y.; Matsubara, Y.; Tadokoro, H. *Macromolecules* **1982**, *15*, 334.
(11) Takahashi, Y.; Tadokoro, H. *Macromolecules*, in press.

Living Polymerization of β-Lactone Catalyzed by (Tetraphenylporphinato)aluminum Chloride. Structure of the Living End

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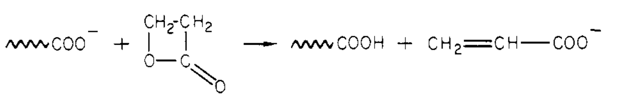
ABSTRACT: ($\alpha,\beta,\gamma,\delta$-Tetraphenylporphinato)aluminum chloride, obtained by equimolar reaction between diethylaluminum chloride and $\alpha,\beta,\gamma,\delta$-tetraphenylporphine, is a good catalyst for the living polymerization of β-propiolactone and β-butyrolactone, to give the corresponding polyesters with narrow molecular weight distribution. By ^{13}C- and ^{1}H-NMR spectrometry, the structure of the living end of the polymer of β-lactone is concluded to be a (porphinato)aluminum carboxylate. The equimolar reaction product between (tetraphenylporphinato)aluminum ethyl and carboxylic acid exhibits a high catalytic activity for the polymerization of β-lactone to form polyester with narrow molecular weight distribution.

Introduction

Although the synthesis of polymers of well-controlled molecular weight is of primary importance from both fundamental and practical standpoints, examples up to now have been rather limited. In the polymerization of β-lactone, the proton abstraction reaction from the methylene or methine group adjacent to the carbonyl group of the monomer by propagating species often occurs, resulting in chain transfer, e.g., as shown in Scheme I. The polymerization of α,α-disubstituted-β-lactone has been claimed to be of a living nature on the basis of, e.g., the linear relationship between the molecular weight of the polymer and the conversion of polymerization.[1] More recently, simlar behavior has been observed in the polymerization of unsubstituted β-propiolactone catalyzed by alkaline metal acetates coupled with crown ether.[2] However, no direct information as to the molecular weight distribution of the polymers has been described.

We have already reported that ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)aluminum chloride (TPPAlCl), an equimolar reaction product of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (TPPH$_2$) with diethylaluminum chloride (Et$_2$AlCl), is an excellent catalyst for the living polymerization of epoxides to give polyethers[3] and their block copolymers[4] with narrow molecular weight distribution. In this polymerization, the propagating end of the living polymer was confirmed to be a (porphinato)aluminum alkoxide (Scheme II).[5] More recently, TPPAlCl was found to show a high catalytic activity for the polymerization of β-lactones such as β-propiolactone and β-butyrolactone. The polymerization exhibits a living nature, giving the corresponding polyester having a well-controlled molecular weight with narrow distribution.[6]

Scheme I



Scheme II

In this paper, we report the investigation of the structure of the propagating end of β-lactone in the polymerization catalyzed by TPPAlCl in detail, taking advantage of the fact that the propagating end group attached to aluminum may be conveniently observed by NMR analysis because of the signals at high magnetic field due to the large magnetic effect of the porphyrin ring.

Experimental Section

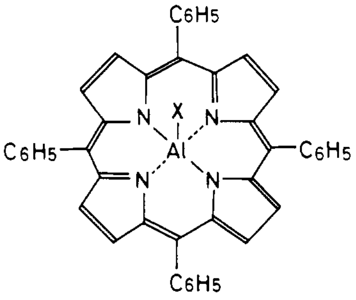
Materials. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine (TPPH$_2$) was prepared by reaction between pyrrole and benzaldehyde in propionic acid at about 140 °C and was purified by recrystallization from chloroform–methanol.[7] β-Propiolactone and β-butyrolactone were dried over calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. Dichloromethane (CH$_2$Cl$_2$) was washed successively with sulfuric acid, water, and aqueous sodium bicarbonate, dried over calcium chloride, and distilled over calcium hydride in a nitrogen atmosphere. Diethylaluminum chloride (Et$_2$AlCl) and triethylaluminum (Et$_3$Al) were purified by distillation under reduced pressure in a nitrogen atmosphere.

Measurement. Gel permeation chromatogrpahy (GPC) was performed on a Toyo Soda Model HLC-820UR gel permeation chromatograph equipped with a differential refractometer detector using tetrahydrofuran as the eluent: flow rate, 1.2 mL·min^{-1};

columns, 60-cm length with pore size 7000–3000 (two), 3000 (one), and 2000 Å (one). The molecular weight and molecular weight distribution were calculated on the basis of the calibration curve obtained by using standard poly(propylene glycols) (PPG) for the lower molecular weight region and standard poly(ethylene oxides) (PEO) for the higher molecular weight region. Standard poly(ethylene oxides) were obtained from Toyo Soda Manufacturing Co., Ltd.: $\bar{M}_n = 22000$ ($\bar{M}_w/\bar{M}_n = 1.14$), $\bar{M}_n = 39000$ ($\bar{M}_w/\bar{M}_n = 1.03$), and $\bar{M}_n = 72000$ ($\bar{M}_w/\bar{M}_n = 1.02$). Standard poly(propylene glycols) were obtained from Lion Fat and Oil Co., Ltd.: $\bar{M}_n = 1000$ and 2000 ($\bar{M}_w/\bar{M}_n \simeq 1$).

The ^{1}H-NMR spectrum of the reaction mixture (living oligomer) was measured in dichloromethane or deuterated chloroform in a sealed tube in a nitrogen atmosphere, using a JEOL Type 4H-A spectrometer operating at 100 MHz. ^{13}C{^{1}H}-NMR measurement on the living oligomer was performed in deuterated chloroform in a sealed tube in a nitrogen atmosphere using a JEOL PFT-100 spectrometer. The spectrum pattern was recorded on a JEOL data terminal, Model Silent 700ASR connected to a spectrometer at 25.03 MHz. The off-resonance decoupling was carried out in the ^{13}C-NMR measurement.

Preparation of TPPAlCl. TPPAlCl (1, X = Cl) was prepared



1

TPPAlX

by reaction of Et_2AlCl with $TPPH_2$ as described previously.[3] $TPPH_2$ (1 mmol) was placed in a Pyrex tear-drop type flask (100 mL) connected with a three-way cock and purged by 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 at room temperature. From the above reaction mixture, volatile materials were removed under reduced pressure to give TPPAlCl as a purple solid with a metallic luster. CH_2Cl_2 (20 mL) was added to dissolve TPPAlCl, and the solution was used as the polymerization catalyst.

Polymerization. To the catalyst solution, β-propiolactone or β-butyrolactone was introduced by syringe with an initial mole ratio of monomer to catalyst of 100, and the mixture was kept at room temperature with magnetic stirring. After a definite time, a large excess of methanol was added to the reaction mixture to stop the polymerization, and then volatile materials (residual monomer, solvent, and methanol) were removed under reduced pressure. The conversion was calculated from the amount of residue by subtracting the amount of catalyst. In order to determine the molecular weight and molecular weight distribution, a part of the obtained polymer was dissolved in tetrahydrofuran, the insoluble part (the catalyst residue) was filtered off with a Teflon filter with a pore size 0.45 μm, and the solution was subjected to GPC analysis.

Oligomerization. The reaction was carried out in a similar way, with an initial mole ratio of monomer to catalyst of 1–10. After a definite time, the volatile materials were removed from the reaction mixture under reduced pressure, deuterated chloroform was added to dissolve the "living" oligomer, and the solution was subjected to NMR analysis.

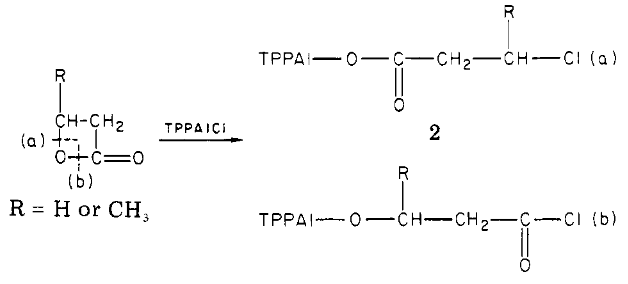
Equimolar Reaction Product between (Tetraphenylporphinato)aluminum Ethyl and Carboxylic Acid. (α,β,γ,δ-Tetraphenylporphinato)aluminum ethyl (TPPAlEt, 1; X = C_2H_5) was obtained by reaction between $TPPH_2$ and triethylaluminum (Et_3Al) as described previously.[8] The tear-drop type flask equipped with a three-way cock containing $TPPH_2$ (1 mmol) was purged by dry nitrogen, CH_2Cl_2 (20 mL) was introduced into the flask using a syringe, and Et_3Al (0.14 mL, 1 mmol) was added to the solution at room temperature with stirring. After the reaction mixture was kept for about an hour, the volatile materials were removed under reduced pressure, and CH_2Cl_2 (20 mL) was introduced into the flask to dissolve the product, TPPAlEt. To this solution, 3-chloropropionic acid, for example, was added at room temperature with magnetic stirring, where rapid reaction was observed by the disappearance of the ^{1}H-NMR signals due to the ethyl group of TPPAlEt. The reaction mixture was allowed to stand overnight. After completion of the reaction, the color of the solution turned to purple from the green color of TPPAlEt. The volatile materials were removed under reduced pressure from the above reaction mixture to give a purple solid. In the ^{1}H-NMR spectrum of this product in CH_2Cl_2, triplet signals probably due to methylene protons of $TPPAl{-}OOCCH_2CH_2Cl$ were observed at −0.7 and 1.4 ppm (for 3-chloropropionic acid, 2.85 and 3.8 ppm).

Table I
Polymerization of β-Propiolactone (PL) and β-Butyrolactone (BL) with TPPAlCl

monomer	$\frac{[\text{mon}]_0}{[\text{TPPAlCl}]_0}$	reacn time, days	convrsn, %	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[a]
PL	100	13	≃100	2800	1.13
BL	100	14	86	6200	1.07

[a] $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were estimated by GPC, using poly(ethylene oxide) and poly(propylene glycol) as standards.[15]

Scheme III



Results and Discussion

Polymerization of β-Propiolactone and β-Butyrolactone Catalyzed by (Tetraphenylporphinato)aluminum Chloride (TPPAlCl). As described in the preliminary communication,[6] TPPAlCl is a good catalyst for the polymerization of β-propiolactone and β-butyrolactone, as exemplified in Table I. The molecular weight distribution of the polymers obtained with TPPAlCl is very narrow, as indicated by the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$). Molecular weight increases linearly with conversion. The formation of one polymer chain from one catalyst molecule was confirmed in the polymerization of β-butyrolactone.[6] Thus, the polymerization of β-lactone catalyzed by TPPAlCl is of a living nature.

Structure of the Living Propagating End in the Polymerization of β-Propiolactone with TPPAlCl. Equimolar Reaction Product between TPPAlCl and β-Propiolactone. It is very interesting to investigate the structure of the propagating end formed in the living polymerization of β-propiolactone with TPPAlCl, since two different modes of cleavage are possible for β-lactone ring, as illustrated in Scheme III (R = H) for the reaction of the lactone with TPPAlCl. One is cleavage at the alkyl-oxygen bond (Scheme IIIa), and the other is cleavage at the acyl-oxygen bond (Scheme IIIb). In the former, a (porphinato)aluminum carboxylate will be produced as the propagating end. In the latter, on the other hand, the formation of a (porphinato)aluminum alkoxide carrying

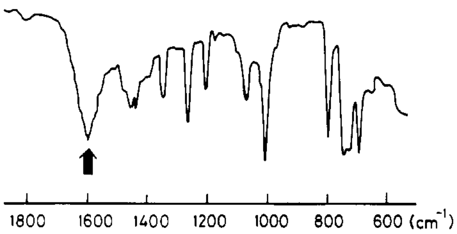


Figure 1. IR spectrum of the equimolar reaction product between TPPAlCl and β-propiolactone in CH_2Cl_2.

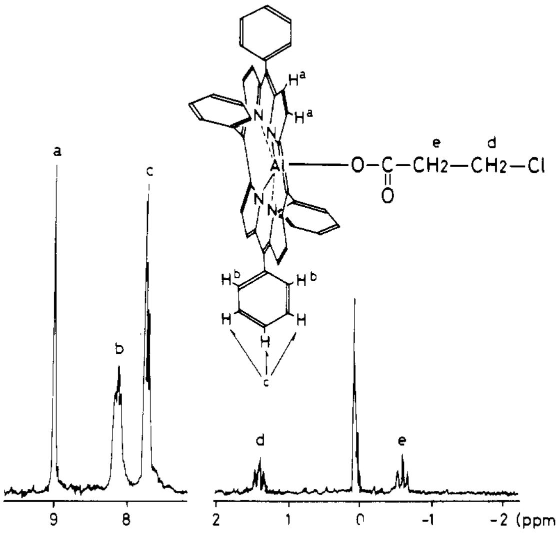


Figure 2. ^{1}H-NMR spectrum of the equimolar reaction product between TPPAlCl and β-propiolactone in $CDCl_3$.

an acyl chloride group will result.

In the IR spectrum of the equimolar reaction product between β-propiolactone and TPPAlCl (Figure 1), a strong absorption due to the carboxylate group is observed at 1600 cm^{-1}, but not the absorption due to the acyl chloride group at 1800 cm^{-1}.

The ^{1}H-NMR spectrum of the equimolar reaction product between β-propiolactone and TPPAlCl in $CDCl_3$ is illustrated in Figure 2, which is characterized by a triplet signal at a high magnetic field (−0.7 ppm (e)), probably due to the protons of the methylene group being strongly influenced by the large magnetic effect of the porphyrin ring. If the ring opening of β-propiolactone occurred at the acyl-oxygen bond (Scheme IIIb, R = H), the ^{1}H-NMR spectrum of the product would exhibit a triplet signal due to the $TPPAlOCH_2CH_2$ group at about −1.4 ppm, but not at −0.7 ppm, since a similar alkoxide obtained by reaction of ethylene oxide and TPPAlCl ($TPPAlOCH_2CH_2$...) is known to show a triplet signal at −1.4 ppm.[5] Therefore, the present NMR observation indicates the ring opening of β-propiolactone at the alkyl-oxygen bond (Scheme IIIa), but not at the acyl-oxygen linkage. The intensity ratio of the signals due to the methylene protons (d, 1.4 ppm, 1.7 H; e, −0.7 ppm, 1.9 H) to the porhyrin protons (a, 9.0 ppm, 8 H; b, 8.1 ppm, 8.1 H; c, 7.7 ppm, 12.2 H) is in agreement with the calculated value for the formation of $TPPAlOOCCH_2CH_2Cl$.

In order to further confirm the mode of ring opening, the equimolar reaction between TPPAlEt and 3-chloropropionic acid was carried out. The ^{1}H-NMR spectrum of this reaction product, which is considered to have the structure 2 (R = H), was identical with the spectrum of the equimolar reaction product between TPPAlCl and β-propiolactone.

Structure of the Living Oligomer of β-Propiolactone Obtained with TPPAlCl. Further information on the structure of the propagating end was obtained by NMR studies on the living oligomer of β-propiolactone. The ^{1}H-NMR spectrum of the living oligomer of β-propiolactone shown in Figure 3 is characterized by a triplet signal observed at high magnetic field (−0.7 ppm) due to methylene protons at the living propagating end, influenced by the large magnetic effect of the porphyrin. Besides signals due to the methylene protons of the oxycarbonylethylene ($OCOCH_2CH_2$) unit in the chain at 2.6 (i) and 4.3 ppm (f),[9] a signal due to the methylene proton of the terminal chloromethyl group appears at 3.6 ppm (h).[10] The signals observed at 3.9 (g) and 2.0 ppm (j) are considered to be due to the methylene protons of the penultimate unit of the living oligomer.

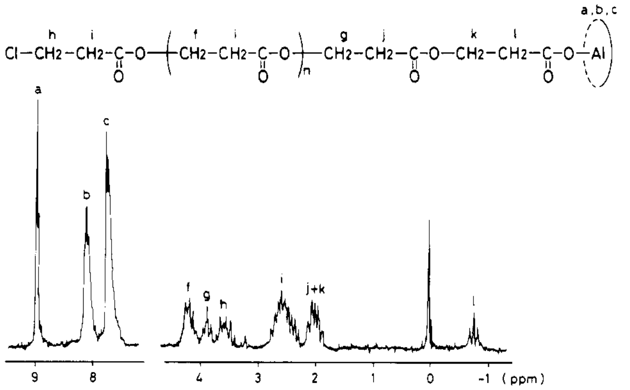


Figure 3. ^{1}H-NMR spectrum of living β-propiolactone (PL) oligomer obtained with TPPAlCl in $CDCl_3$, $[PL]_0/[TPPAlCl]_0 = 5$.

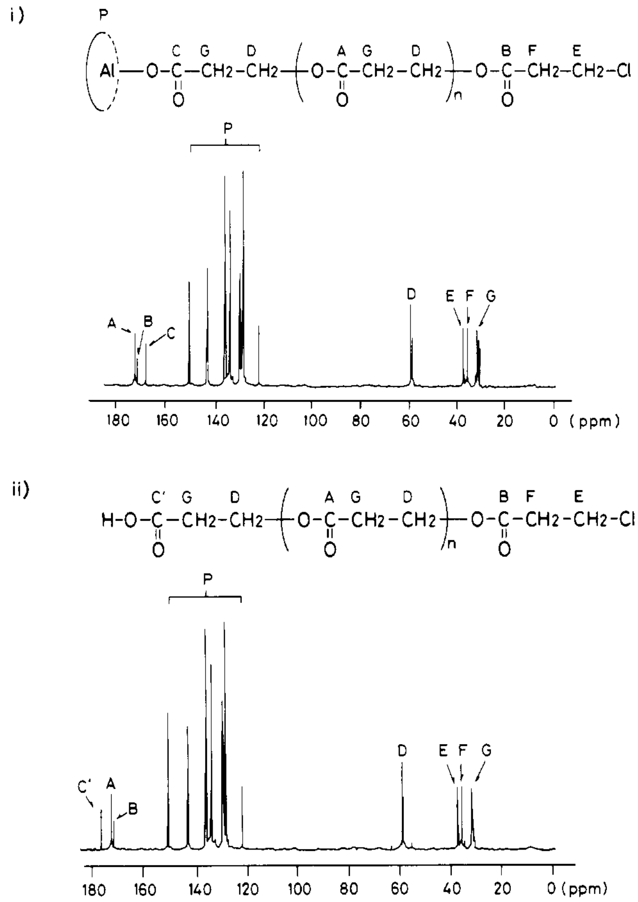


Figure 4. (i) $^{13}C\{^1H\}$-NMR spectrum of living β-propiolactone (PL) oligomer obtained with TPPAlCl in $CDCl_3$ ($[PL]_0/[TPPAlCl]_0 = 5$; (ii) after treatment with HCl.

Table II
Polymerization of β-Propiolactone (PL) and β-Butyrolactone (BL) with the Equimolar Reaction Product between TPPAlEt and Carboxylic Acid

carboxylic acid	monomer	$[\text{mon}]_0/[\text{cat}]_0$	reacn time, days	convrsn, %	$\overline{M}_n{}^a$	$\overline{M}_w/\overline{M}_n{}^a$
$ClCH_2CH_2COOH$	PL	200	4	≃100	5900	1.19
$ClCH(CH_3)CH_2COOH$	BL	100	21	≃100	5700	1.06

[a] $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ were estimated by GPC using poly(ethylene oxide) and poly(propylene glycol) as standards.

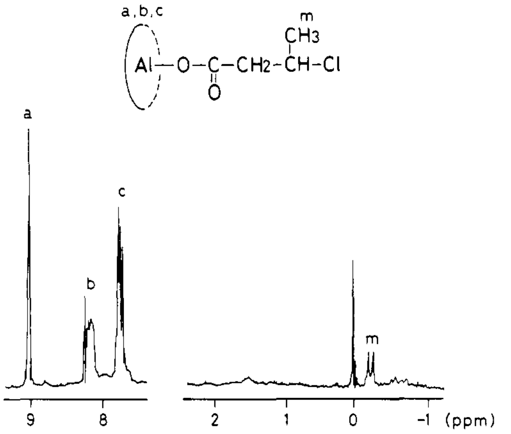


Figure 5. ^{1}H-NMR spectrum of the equimolar reaction product between TPPAlCl and β-butyrolactone in $CDCl_3$.

Figure 4i) shows the $^{13}C\{^1H\}$-NMR spectrum of the living oligomer of β-propiolactone. Signals P are assigned to the carbons in the porphyrin ring and signals D (60.0 ppm) and G (33.2 ppm) to methylene groups in the oligomer chain, respectively.[11] Other signals E (38.8 ppm) and F (37.4 ppm) are assigned to methylene groups of the terminal unit attached to chlorine.[12] Signals A (169.9 ppm), B (169.0 ppm), and C (165.7 ppm) are considered to be due to the carbonyl carbons. Upon treatment of the living oligomer of β-propiolactone with hydrochloric acid, signal C (165.7 ppm) disappeared and a new signal C′ appeared at lower magnetic field (176.7 ppm), while no change was observed as to other signals (Figure 4ii)). Therefore, signal C is considered to be due to the carboxylate group attached to TPPAl, and C′ due to the free carboxyl group. Signals A and B are assigned to the ester carbonyl.

Thus, in the initiation step of the polymerization of β-propiolactone with TPPAlCl, (tetraphenylporphinato)aluminum 3-chloropropionate is produced. The living oligomer of β-propiolactone has a (tetraphenylporphinato)aluminum carboxylate group as the propagating end.

Structure of the Living Propagating End in the Polymerization of β-Butyrolactone. In the IR spectrum of the equimolar reaction product between β-butyrolactone and TPPAlCl, an absorption due to carboxylate is observed at 1600 cm^{-1}, similarly to the case of β-propiolactone. In the ^{1}H-NMR spectrum of this reaction product (Figure 5), the signal at −0.2 ppm (m) is considered to be due to the methyl proton influenced by the large magnetic effect or porphyrin. This NMR spectrum is identical with that of the equimolar reaction product between TPPAlEt and 3-chlorobutyric acid, $TPPAlOOCCH_2CH(CH_3)Cl$.

In the $^{13}C\{^1H\}$-NMR spectrum of the living oligomer of β-butyrolactone by TPPAlCl, as illustrated in Figure 6i), signals J (163.6 ppm) is considered to be due to aluminum carboxylate at the living end, since this signal disappeared upon treatment of the system with hydrochloric acid, when a new signal due to the free carboxyl group is observed (Figure 6ii), J′, 171.9 ppm), while no change was observed with respect to any other signal. The signals H (167.6 ppm), K (66.5 ppm), N (39.7 ppm), and Q (18.5 ppm) are assigned to the ester carbonyl, methine, methylene, and methyl groups in the oligomer chain, respectively.[13] Signals I (166.5 ppm), L (51.8 ppm), M (44.0 ppm), and O (23.6 ppm) are considered to be due to the carbonyl, methine, methylene, and methyl groups of the terminal unit attached to chlorine,[14] respectively. Therefore, the living oligomer of β-butyrolactone is considered to have the structure of $TPPAl\text{–}(O\text{–}OC\text{–}CH_2CH(CH_3))_n\text{–}Cl$.

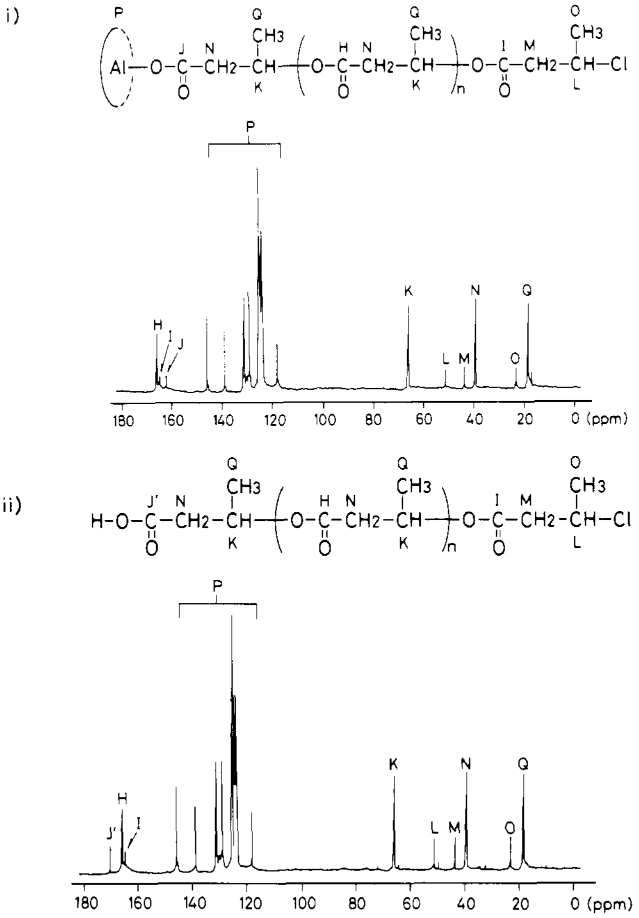


Figure 6. (i) $^{13}C\{^1H\}$-NMR spectrum of the living β-butyrolactone (BL) oligomer obtained with TPPAlCl in $CDCl_3$ ($[BL]_0/[TPPAlCl]_0$ = 10; (ii) after treatment with HCl.

Polymerization of β-Propiolactone and β-Butyrolactone with the (Tetraphenylporphinato)aluminum Ethyl–Carboxylic Acid System. Since the growing end in the polymerization of β-lactone by TPPAlCl is a (porphinato)aluminum carboxylate, similar compounds obtained by reaction between (tetraphenylporphinato)aluminum ethyl and carboxylic acid are also considered active as initiators for the polymerization of β-lactone. In fact, the equimolar reaction mixture between TPPAlEt and 3-chloropropionic acid or 3-chlorobutyric acid was found to be a good initiator for the polymerization of β-propiolactone and β-butyrolactone (Table II). As shown in Figure 7, the polymer obtained has a very narrow molecular weight distribution.

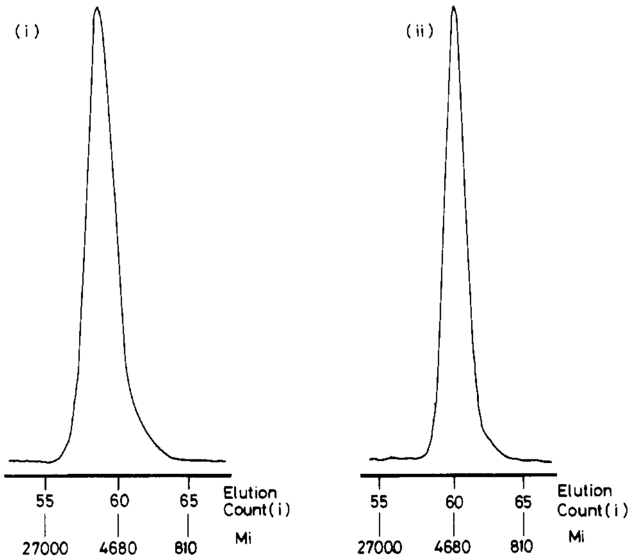
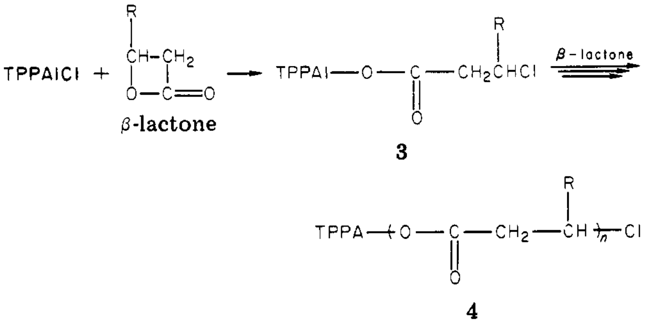


Figure 7. GPC curves of (i) poly(β-propiolactone) obtained with the TPPAlEt–$ClCH_2CH_2COOH$ system ($\bar{M}_n$ = 5900, $\bar{M}_w/\bar{M}_n$ = 1.19) and (ii) of poly(β-butyrolactone) obtained with the TPPAlEt–$ClCH(CH_3)CH_2COOH$ system ($\bar{M}_n$ = 5700, $\bar{M}_w/\bar{M}_n$ = 1.06. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were estimated by using poly(ethylene oxide) and poly(propylene glycol) as standards.

Scheme IV



Conclusion

The polymerization of β-lactone with TPPAlCl is concluded to proceed as follows. The first step in the polymerization is the attack of chlorine on the carbon atom adjacent to the ester oxygen, leading to the insertion of β-lactone with alkyl-oxygen scission into the aluminum–chlorine bond to give a (tetraphenylporphinato)aluminum carboxylate (**3**, Scheme IV). **3** attacks subsequently as a nucleophile on β-lactone with alkyl-oxygen scission to regenerate a (porphinato)aluminum carboxylate. Repetition of this reaction leads to the living polymerization of β-lactone with the aluminum carboxylate group as the growing end (**4**) to give the polymer with narrow molecular weight distribution.

Registry No. PL (homopolymer), 25037-58-5; BL (homopolymer), 36486-76-7; PL (SRU), 24938-43-0; BL (SRU), 26744-04-7; TPPAlCl, 71102-37-9.

References and Notes

(1) (a) Ohse, H.; Cherdron, H. *Makromol. Chem.* **1966**, *97*, 139. (b) Yamashita, Y.; Hane, T. *J. Polym. Sci.* **1973**, *11*, 425. (c) Lenz, R. W.; D'Hondt, C. G.; Bigdeli, E. *ACS Symp. Ser.* **1977**, *No. 59*, 210.

(2) (a) Stomkowski, S.; Penczek, S. *Macromolecules* **1976**, *9*, 367. (b) Stomkowski, S.; Penczek, S. *Ibid.* **1980**, *13*, 229.

(3) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. *Makromol. Chem.* **1981**, *182*, 1073.

(4) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162.

(5) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166.

(6) Yasuda, T.; Aida, T.; Inoue, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 585.

(7) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(8) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 948.

(9) For the high polymer of β-propiolactone obtained by TPPAlCl with a monomer to catalyst ratio of 300, 2.7 (CH_2CO) and 4.3 ppm (OCH_2), in $CDCl_3$.

(10) For 3-chloropropionic acid, 3.8 ppm ($ClCH_2$) in $CDCl_3$.

(11) For the high polymer of β-propiolactone obtained by TPPAlCl with a monomer to catalyst ratio of 300, 170.3 (CO), 60.2 (CH_2CO), and 33.7 ppm (OCH_2), in $CDCl_3$.

(12) For 3-chloropropionic acid, 38.9 and 37.6 ppm, in $CDCl_3$.

(13) For the high polymer of β-butyrolactone obtained by TPPAlCl with a monomer to catalyst ratio of 300, 168.3 (CO), 66.7 (CH), 39.7 (CH_2), and 18.6 ppm (CH_3), in $CDCl_3$.

(14) For 3-chlorobutyric acid, 176.2 (CO), 51.9 (CH), 44.3 (CH_2), and 24.3 ppm (CH_3), in $CDCl_3$.

(15) Agreement between the observed and the calculated molecular weights has been confirmed by vapor pressure osmometry for poly(β-butyrolactone).[6]