in aqueous solution were pulverized and allowed to swell in benzene/methanol (1:1). They were placed in glass columns and subjected to separation of two kinds of dyes, a basic dye (methylene blue) and an acidic dye (sudan red), the same mixed solvent being used as the elution solvent. For comparison, separation by the original chitin was also attempted. The DEAE-chitins swelled so much that the necessary amounts of the derivatives with ds of 0.56 and 1.20 to pack the columns were 1/11 and 1/14 of that of the original chitin, respectively.

The separation behavior for each column is illustrated in Figure 4. In the chitin column, sudan red was eluted first and then methylene blue, but the separation was poor. When DEAE-chitins were used, the development order was reversed, methylene blue being eluted first. With the DEAE-chitin with a ds of 0.56, the separation was not sharp. The DEAE-chitin with ds of 1.20, however, showed improved separation with little tailing and promises to have high potential for use as an adsorbent and separating agent.

Conclusion

DEAE-chitins have been prepared in organic solvents as well as in aqueous solution. Since both reactions proceeded fairly reproducibly under appropriate conditions, the substitution extents were controlled easily. Properties of the products depended on the mode of preparation and substitution extent. DEAE-chitins prepared in aqueous solution showed especially high affinity for both polar and nonpolar solvents. This would be a useful property to explore new advanced utilizations. The high swelling ability in common solvents was of advantage for separation use in that only a very small amount was necessary and that high efficiency was achieved.

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Ring-Opening Polymerizations of Lactone and Epoxide Initiated with Aluminum Complexes of Substituted Tetraphenylporphyrins. Molecular Design of Highly Active Initiators

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ABSTRACT: Ring-opening polymerization of β-propiolactone with a series of aluminum complexes of substituted tetraphenylporphyrins gave polymer with narrow molecular weight distribution, where the aluminum porphyrins (tetrakis(2′,4′,6′-trimethoxyphenyl)porphinato)aluminum chloride, (tetrakis(2′,6′-dimethoxyphenyl)porphinato)aluminum chloride, and (tetrakis(2′,6′-dichlorophenyl)porphinato)aluminum chloride were much more active than nonsubstituted (tetraphenylporphinato)aluminum chloride. These aluminum ortho-disubstituted tetraphenylporphyrins were also active as initiators for the polymerizations of δ-valerolactone and 1,2-epoxypropane both in the absence and presence (immortal polymerization) of methanol as a protic chain-transfer agent.

Introduction

Aluminum porphyrins initiate the living polymerizations of a wide variety of monomers such as lactones,[1] epoxides,[2] and methacrylic esters,[3] affording the corresponding polymers of controlled molecular weight with narrow molecular weight distribution. In these cases, the chain growth takes place at the central aluminum atom–axial ligand bond of the initiator. For example, the polymerization of β-propiolactone initiated with aluminum porphyrin proceeds by the repeated reactions of the monomer with the aluminum–carboxylate bond of (porphina-

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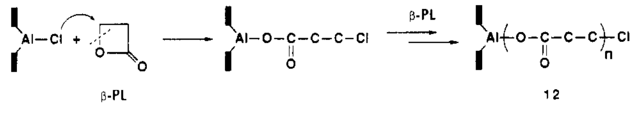
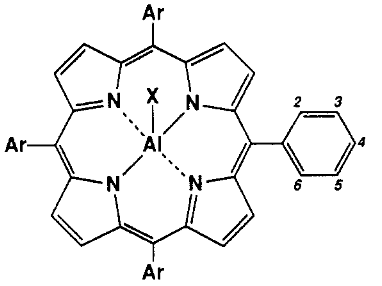
Scheme I



to)aluminum carboxylate (12) as the growing species[1] (Scheme I). Thus, the rate of polymerization is expected to be affected by the structure of the porphyrin ligand.

In this study, the polymerizations of lactones such as β-propiolactone (β-PL) and δ-valerolactone (δ-VL) and an epoxide such as 1,2-epoxypropane (propylene oxide, PO) were investigated by using as initiators the aluminum porphyrins bearing substituted phenyl groups on the porphyrin ring (1–11).



a; X = Cl
b; X = Me
c; X = OMe

Formula No.	Abbreviation	2	3	4	5	6
1	(TPP)AlX	H	H	H	H	H
2	(T(2,4,6-MeO)PP)AlX	OMe	H	OMe	H	OMe
3	(T(3,4,5-MeO)PP)AlX	H	OMe	OMe	OMe	H
4	(T(2,6-MeO)PP)AlX	OMe	H	H	H	OMe
5	(T(2,4-MeO)PP)AlX	OMe	H	OMe	H	H
6	(T(2-MeO)PP)AlX	OMe	H	H	H	H
7	(T(4-MeO)PP)AlX	H	H	OMe	H	H
8	(T(2,3,4,5,6-F)PP)AlX	F	F	F	F	F
9	(T(2,6-Cl)PP)AlX	Cl	H	H	H	Cl
10	(T(2,4,6-Me)PP)AlX	Me	H	Me	H	Me
11	(T(2,4,6-Ph)PP)AlX	Ph	H	Ph	H	Ph

Experimental Section

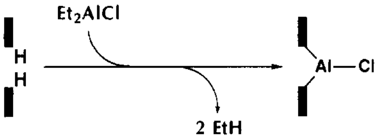
Materials. Free-base porphyrins (abbreviations defined in ref 4) such as $TPPH_2$,[5] T(2,4,6-MeO)PPH_2,[6] T(3,4,5-MeO)PPH_2,[7] T(2,6-MeO)PPH_2,[5] T(2,4-MeO)PPH_2,[5] T(2-MeO)PPH_2,[8] T(4-MeO)PPH_2,[9] and T(2,3,4,5,6-F)PPH_2[10] were synthesized respectively from pyrrole and the corresponding substituted benzaldehydes in refluxing propionic acid and recrystallized from $CHCl_3$/MeOH. The yields were respectively 17%, 4.6%, 15%, 2.6%, 0.42%, 0.77%, 20%, and 4.9%.

T(2,6-Cl)PPH_2 was obtained by treating the zinc complex from pyrrole and 2,6-dichlorobenzaldehyde in the presence of anhydrous zinc acetate in refluxing 2,4,6-trimethylpyridine for 3 h with 6 N HCl.[11] The porphyrin fraction was isolated from the reaction mixture by column chromatography (Wakogel C-100 silica gel, 40–100 mesh, CH_2Cl_2 as eluent) and recrystallized from $CHCl_3$/MeOH. The yield of T(2,6-Cl)PPH_2 was 0.75%.

T(2,4,6-Me)PPH_2 was synthesized according to Lindsey's method[12] from pyrrole and mesitaldehyde in $CHCl_3$ (distilled over K_2CO_3) under nitrogen at room temperature and recrystallized from $CHCl_3$/MeOH after chromatographing on silica gel (Wakogel C-100) with $CHCl_3$ as eluent. The yield of T(2,4,6-Me)PPH_2 was 30%.

For the preparation of T(2,4,6-Ph)PPH_2, 2,4,6-triphenylbromobenzene was prepared by treating 1,3,5-triphenylbenzene with bromine in carbon disulfide at 30 °C for 24 h, and the product was recrystallized from MeOH (83% yield).[13] 2,4,6-Triphenylbenzaldehyde was prepared by quenching the reaction mixture of 2,4,6-triphenylbromobenzene and n-butyllithium with N,N-dimethylformamide in refluxing benzene in a nitrogen atmosphere.[14] The reaction mixture was chromatographed on silica gel (Wakogel C-300, 200–300 mesh) with CH_2Cl_2/n-hexane (1:4) as eluent, and the separated yellow fraction was recrystallized from MeOH to give the aldehyde as yellow needles in 41% yield. T(2,4,6-Ph)PPH_2 was synthesized according to Lindsey's method[15] with some modifications: To a 3-L two-necked round-bottom flask connected with a three-way stopcock and a reflux condenser, 2,4,6-triphenylbenzaldehyde (8.36 g, 25 mmol), 2.5 L of $CHCl_3$,[16] and pyrrole (1.75 mL, 25 mmol) were added successively, and the flask was wrapped in aluminum foil. After the solution was purged with dry nitrogen, $BF_3 \cdot OEt_2$ (3.08 mL, 25 mmol) was added via a hypodermic syringe, and the mixture was stirred for 20 h at room temperature in a nitrogen atmosphere. Then, 2,3,5,6-tetrachloro-1,4-benzoquinone (4.61 g, 18.8 mmol) was added to the reaction mixture, and the resulting dark purple solution was gently refluxed for 1 h. Triethylamine (3.48 mL, 25 mmol) was added, and the mixture was concentrated to a volume of approximately 200 mL, from which excess quinone was removed by shaking with a 2% aqueous NaOH solution (1.5 L) containing $Na_2S_2O_4$ (3.0 g). The organic layer, washed with water and dried over $MgSO_4$, was charged onto 20 g of silica gel (Wakogel C-300), which was then subjected to flash chromatography on silica gel with CH_2Cl_2/n-hexane (1:2) as eluent. The third fraction with orange color was collected and flash-chromatographed on silica gel in a similar way as above, and the second fraction with red color containing the porphyrin was collected and chromatographed again on acidic alumina (Merck Art.1078) with CH_2Cl_2 as eluent. The second fraction with green color was collected and charged onto 1 g of basic alumina (Merck Art.1097), which was then subjected to column chromatography with n-hexane as eluent to remove a light-yellow fraction, followed by CH_2Cl_2/n-hexane (1:4) to elute a reddish-brown fraction. This fraction was subjected to preparative thin-layer chromatography on a silica gel plate (Merck Art.13973, 20 × 20 cm) with CH_2Cl_2 as eluent, where the reddish-brown area was scraped off the plate and subjected to Soxhlet extraction with CH_2Cl_2 for 12 h. The extract was evaporated to dryness, and the residue was recrystallized from $CHCl_3$/n-hexane to give T(2,4,6-Ph)PPH_2[17] in 0.046% yield (4.4 mg). The above procedures were repeated several times to obtain 55 mg of T(2,4,6-Ph)PPH_2.

Scheme II



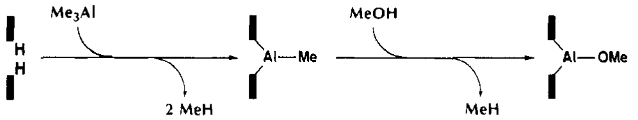
Dichloromethane (CH_2Cl_2) was washed successively with sulfuric acid, water, and aqueous $NaHCO_3$, dried over calcium chloride, and distilled over calcium hydride in a nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) was distilled over calcium hydride under nitrogen. Methanol (MeOH) was distilled over magnesium treated with iodine under nitrogen.

Diethylaluminum chloride (Et_2AlCl) and trimethylaluminum (Me_3Al) were distilled under reduced pressure in a nitrogen atmosphere.

β-Propiolactone (β-PL, from Sigma) and δ-valerolactone (δ-VL, from Nacalai Tesque) were dried over calcium hydride and then distilled under reduced pressure in a nitrogen atmosphere. 1,2-Epoxypropane (propylene oxide, PO, from Nacalai Tesque) was distilled after refluxing over a mixture of calcium hydride and potassium hydroxide under nitrogen. Pyrrole and benzaldehydes were used as received from commercial sources (Tokyo Kasei, Aldrich).

Procedures. Preparation of Aluminum Porphyrins. (Porphinato)aluminum chlorides **1a**–**10a** were prepared by the reaction of Et_2AlCl and the corresponding free-base porphyrins, respectively (Scheme II).[18] To a round-bottom flask (50 mL) equipped with a three-way stopcock containing a free-base porphyrin (0.2 mmol) under dry nitrogen, CH_2Cl_2 (4 mL) and Et_2AlCl (0.030 mL, 1.2 equiv) were successively added by means of a hypodermic syringe in a nitrogen stream, and the mixture was stirred at room temperature for 2 h in a nitrogen atmosphere. Then, the volatile fractions were removed from the reaction mixture under reduced pressure to leave the corresponding (porphinato)aluminum chloride as a purple powder. **11a** was pre-

Scheme III



pared as follows: To a 10-mL round-bottom flask connected with a three-way stopcock containing T(2,4,6-Ph)PPH$_2$ (23 mg, 0.015 mmol), a CH$_2$Cl$_2$ solution of Et$_2$AlCl (0.03 mmol in 0.75 mL) was added by a syringe in a nitrogen stream. The mixture was stirred for 4 h at 35 °C under nitrogen and then evaporated to dryness under reduced pressure at room temperature to leave **11a**[19] as a purple powder.

(Porphinato)aluminum methyls **1b**, **3b**, and **5b–10b** were prepared similarly to the above by the reaction of the corresponding free-base porphyrins (0.2 mmol) and 1.2 equiv of Me$_3$Al (0.023 mL) in CH$_2$Cl$_2$ at room temperature in a nitrogen atmosphere (Scheme III).[20] **2b** and **4b** were prepared respectively by the reaction of the corresponding free-base prophyrins (0.2 mmol) with 3 equiv of Me$_3$Al (0.058 mL) in CH$_2$Cl$_2$ at room temperature in a nitrogen atmosphere. After 2 h, the reaction mixture was evaporated to dryness, and the residue was heated at 75 °C under reduced pressure for 5 h to remove unreacted Me$_3$Al. For the preparation of **11b**, a 10-mL round-bottom flask equipped with a three-way stopcock containing T(2,4,6-Ph)PPH$_2$ (7.6 mg, 0.005 mmol) was purged with dry nitrogen, and a CH$_2$Cl$_2$ solution (0.5 mL) of Me$_3$Al (0.01 mmol) was added to this flask by a syringe in a nitrogen stream. After stirring for 4 h at room temperature, the volatile fractions were removed from the reaction mixture under reduced pressure at room temperature to give **11b** as a purple powder.

(Porphinato)aluminum methoxides **1c–10c** were prepared as follows:[21] To 4 mL of CH$_2$Cl$_2$ containing a (porphinato)aluminum methyl (0.2 mmol), MeOH (2 mL) was added, and the mixture was stirred for 24 h at room temperature in a nitrogen atmosphere. The volatile fractions were removed from the reaction mixture under reduced pressure (Scheme III).

Aluminum porphyrins thus prepared were characterized by ^{1}H and ^{27}Al NMR.[22]

Polymerization. Polymerizations of β-propiolactone (β-PL) using aluminum porphyrins (**1a–11a**) as initiators were carried out according to the following procedures: To a 50-mL round-bottom flask attached to a three-way stopcock containing a CH$_2$Cl$_2$ solution of the aluminum porphyrin initiator, 50 equiv of β-PL was added via a syringe in a nitrogen stream, and the mixture was stirred at 30 °C in a nitrogen atmosphere. Polymerizations of δ-valerolactone (δ-VL) using the aluminum porphyrin initiators (**1c**, **2c**, **3c**, **4c**, **8c**, **9c**, and **10c**) were similarly carried out without solvent at 50 °C with the initial monomer-to-initiator mole ratio of 200. Polymerizations of 1,2-epoxypropane (PO) using the aluminum porphyrin initiators (**1a**, **2a**, **4a**, **9a**, and **10a**) were carried out in CH$_2$Cl$_2$ at 25 °C with the initial monomer-to-initiator mole ratio of 200. An aliquot of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to gel permeation chromatography (GPC) to determine the conversion of monomer, number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) of the polymer formed. In the case of the polymerization of PO, the conversion was determined by the weight of the nonvolatile fraction.

The immortal polymerizations of PO with aluminum porphyrins (**1a** and **2a**) were carried out as follows: To a 50-mL round-bottom flask equipped with a three-way stopcock containing the initiator, MeOH (9 equiv) and PO (400 equiv) were added successively in a nitrogen stream, and the mixture was stirred at 30 °C. The conversion, M_n and M_w/M_n were determined as in the polymerization of PO in the absence of MeOH. The immortal polymerizations of δ-VL with aluminum porphyrins (**1c** and **2c**) were similarly carried out in CH$_2$Cl$_2$ at 30 °C. The conversion of the monomer and the M_n and M_w/M_n of the produced polymer were determined by GPC.

Measurements. Absorption spectra (UV-vis) were recorded on a Hitachi Type-340 or Jasco Ubest-50 spectrophotometer. ^{1}H and ^{27}Al NMR spectra were measured with a JEOL Type GSX-270 or GX-400 spectrometer, where the chemical shifts were determined with respect to CHCl$_3$ (δ 7.28 ppm) for ^{1}H and with respect to Al(NO$_3$)$_3$ (δ 0.0 ppm) for ^{27}Al. For the estimation of average molecular weight and molecular weight distribution of polymers, gel permeation chromatography (GPC) was performed at 38 °C on a Toyo Soda Model HLC-802A high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent at the flow rate of 1.1 mL·min^{-1}. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000–3000 (two), 3000 (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes; 107 000 (M_w/M_n = 1.07), 43 900 (1.01), 39 000 (1.07), 18 000 (1.10), 16 700 (1.02), 6200 (1.04), and 2800 (1.05) from Toyo Soda Manufacturing Co., Ltd., and 10 000 (1.06), 9000 (1.06), 4000 (1.10), and 2100 (1.10) from Pressure Chemical Co.

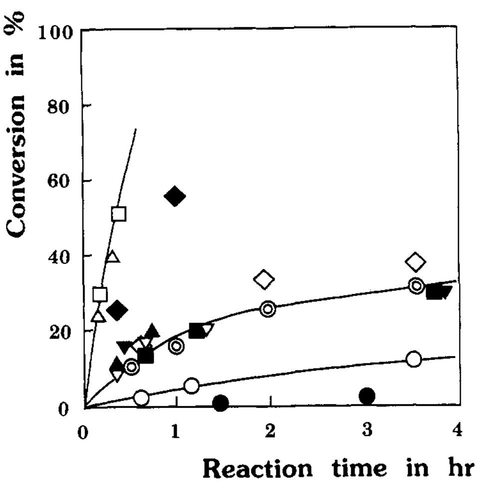


Figure 1. Polymerizations of β-propiolactone (β-PL) initiated with (porphinato)aluminum chlorides **1a** (◎), **2a** (□), **3a** (■), **4a** (△), **5a** (▲), **6a** (▽), **7a** (▼), **8a** (◇), **9a** (◆), **10a** (○), and **11a** (●), at 30 °C in CH$_2$Cl$_2$, [β-PL]$_0$/[initiator]$_0$ = 50 ([initiator]$_0$ = 76.1 mM). Time–conversion curve.

Results

Polymerization of β-Propiolactone (β-PL). The polymerization of β-propiolactone (β-PL) was carried out by using a series of aluminum porphyrins bearing an axial Cl group (**1a–11a**) as initiators in CH$_2$Cl$_2$ at 30 °C with an initial mole ratio [β-PL]$_0$/[initiator]$_0$ of 50. As clearly shown by the time–conversion curves (Figure 1), some of the aluminum porphyrins brought about the polymerization of β-PL very rapidly. For example, the polymerization with chloroaluminum porphyrin carrying 2,4,6-trimethoxyphenyl groups, (T(2,4,6-MeO)PP)AlCl (**2a**), was observed to proceed up to 51% conversion in only 24 min, while the polymerization with (TPP)AlCl (**1a**) carrying nonsubstituted phenyl rings proceeded to 13% conversion under the same conditions. The polymer formed with **2a** as initiator was of narrow molecular weight distribution, as exemplified by the gel permeation chromatogram (GPC) of the polymer obtained at 51% conversion (Figure 2). The number-average molecular weight (M_n) of the polymer, as estimated from the chromatogram, was 2000 (M_w/M_n = 1.19), which is very close to the M_n expected by assuming that every molecule of **2a** produces one polymer molecule (M_n = 1800). Among the series of aluminum tetrakis(methoxy-substituted-phenyl)porphyrins (**2a–7a**), (T(2,6-MeO)PP)AlCl (**4a**) with ortho-dimethoxy-substituted phenyl groups was also brought about the polymerization very rapidly, where the conversion of the monomer in 20 min was 39%. In sharp contrast, the rates of polymerizations initiated with (T(3,4,5-MeO)PP)AlCl (**3a**), (T(2,4-MeO)PP)AlCl (**5a**), (T(2-MeO)PP)AlCl (**6a**), and (T(4-MeO)PP)AlCl (**7a**) were

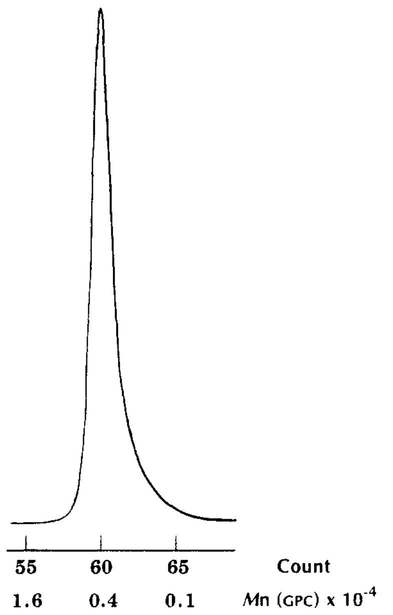


Figure 2. Polymerization of β-propiolactone (β-PL) initiated with (T(2,4,6-MeO)$_3$PP)AlCl (**2a**), at 30 °C for 24 min in CH_2Cl_2, $[\beta\text{-PL}]_0/[\mathbf{2a}]_0$ = 50 ($[\mathbf{2a}]_0$ = 76.1 mM), 51% conversion. GPC curve of the polymer (M_n = 2000 and M_w/M_n = 1.19; based on polystyrenes as standards).

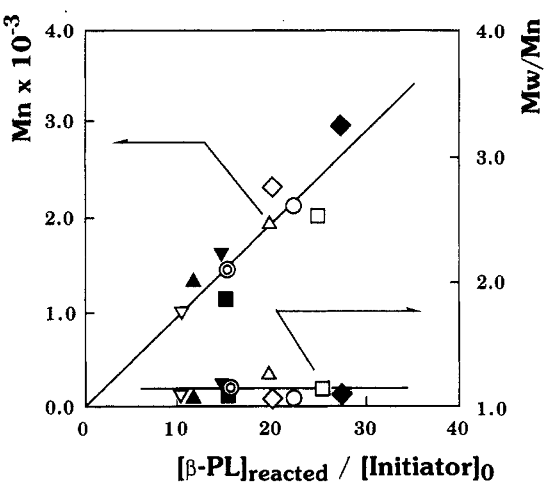
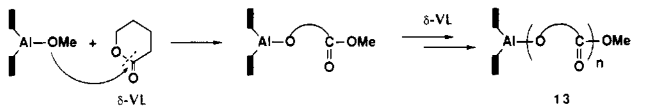


Figure 3. Polymerizations of β-propiolactone (β-PL) initiated with (porphinato)aluminum chlorides **1a** (◎), **2a** (□), **3a** (■), **4a** (△), **5a** (▲), **6a** (▽), **7a** (▼), **8a** (◇), **9a** (◆), and **10a** (○). Relationships between M_n (M_w/M_n) and the mole ratio of the monomer reacted to initiator ($[\beta\text{-PL}]_{reacted}/[\text{initiator}]_0$). M_n and M_w/M_n as estimated by GPC using polystyrenes as standards.

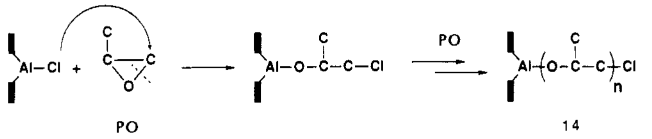
comparable to that observed with the nonsubstituted aluminum porphyrin **1a** as initiator irrespective of the number and position of methoxy substituents on the peripheral phenyl rings; the conversions of the polymerizations with **3a**, **5a**, **6a**, and **7a** were 14%, 12%, 10%, and 17%, respectively, after 40, 20, 20, and 25 min.

As is the case for the polymerizations initiated with **1a** and **2a**, all the polymers formed with **3a**–**7a** as initiators were of narrow molecular weight distribution (M_w/M_n = 1.14~1.28) with the number-average molecular weights (M_n) close to the values estimated from the mole ratio of the monomer reacted and initiator (Figure 3). This fact indicates that the polymerizations of β-PL using **1a**–**7a** are initiated with 100% efficiency and proceed without any side reactions (living character). Thus, the observed difference in the rates of polymerization in Figure 1 can be directly attributed to the difference in the reactivities of the (porphinato)aluminum carboxylate growing species (**12** in Scheme I).

Scheme IV



Scheme V



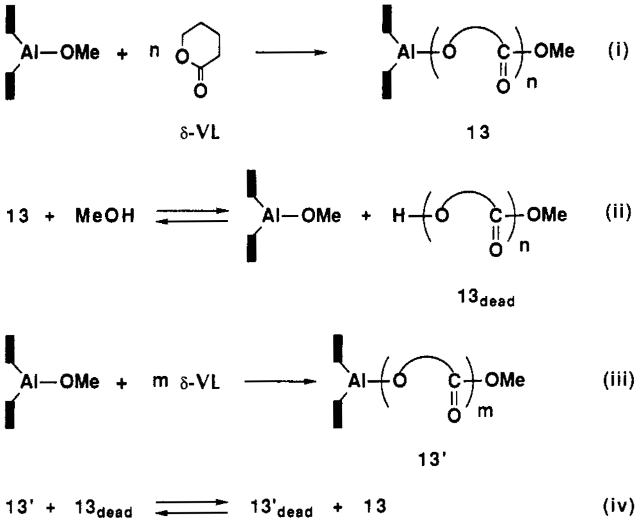
Taking into account the notably high activities of the aluminum porphyrins (T(2,4,6-MeO)PP)AlCl (**2a**) and (T(2,6-MeO)PP)AlCl (**4a**), the polymerization of β-PL was further investigated by using as initiators (T(2,3,4,5,6-F)PP)AlCl (**8a**), (T(2,6-Cl)PP)AlCl (**9a**), (T(2,4,6-Me)PP)AlCl (**10a**), and (T(2,4,6-Ph)PP)AlCl (**11a**), all of which bear substituents at the 2,6-ortho positions of the peripheral phenyl rings. The polymerization initiated with (T(2,6-Cl)PP)AlCl (**9a**) was found to take place as rapidly as those with **2a** and **4a** and proceeded up to 55% conversion in 1 h. On the other hand, the polymerization with (T(2,4,6-Me)PP)AlCl (**10a**) was much slower than with **1a**; the conversion in 1.2 h was only 6%. It should be also noted that the polymerization with (T(2,4,6-Ph)PP)AlCl (**11a**) hardly took place under similar conditions. The polymerization with (T(2,3,4,5,6-F)-PP)AlCl (**8a**) with perfluorinated phenyl rings proceeded with a rate comparable to that with **1a** (17% conversion in 33 min). In these cases using **8a**–**10a** as initiators, the polymers with narrow molecular distributions were also obtained with the number of the polymer molecules equal to that of the initiator molecules (Figure 3).

Polymerization of δ-Valerolactone and 1,2-Epoxypropane (PO). Similar results were obtained in the polymerizations of δ-valerolactone (δ-VL) and 1,2-epoxypropane (PO), which proceed via (porphinato)aluminum alkoxides (**13** and **14**) as the growing species[1,2] (Schemes IV and V).

In the case of the polymerizations of δ-VL using (TPP)AlOMe (**1c**), (T(2,4,6-MeO)PP)AlOMe (**2c**), (T(3,4,5-MeO)PP)AlOMe (**3c**), (T(2,6-MeO)PP)AlOMe (**4c**), (T(2,3,4,5,6-F)PP)AlOMe (**8c**), (T(2,6-Cl)PP)AlOMe (**9c**), or (T(2,4,6-Me)PP)AlOMe (**10c**) as initiator, the rates of polymerizations with **2c** and **4c** were observed to be much higher than those with other aluminum porphyrin initiators. For example, the polymerizations with **2c** and **4c** at 50 °C proceeded up to 98% and 97% conversions in 5.5 and 6.5 h, respectively, while the polymerization with **1c** proceeded to only 26% in 144 h under the same conditions. On the other hand, the polymerizations initiated with **3c**, **8c**, and **9c** proceeded with comparable rates to that with **1c**, where the conversions were 19%, 26%, and 34% after 118, 168 and 128 h, respectively. The polymerization with **10c** took place slower than with **1c**, to attain 24% conversion in 191 h.

The polymerization of PO was investigated using as initiators (TPP)AlCl (**1a**), (T(2,4,6-MeO)PP)AlCl (**2a**), (T(2,6-MeO)PP)AlCl (**4a**), (T(2,6-Cl)PP)AlCl (**9a**), and (T(2,4,6-Me)PP)AlCl (**10a**).[23] In this case, **2a**, **4a**, and **9a** were found to polymerize PO much more rapidly than **1a**; the polymerizations with **2a** and **4a** at 25 °C both proceeded up to 90% conversion in 30 min, that with **9a** proceeded to 75% conversion in 1 h, and that with **1a**

Scheme VI



attained 82% conversion in 19 h. In contrast, the polymerization with **10a** proceeded much slower than with **1a**, where the conversion after 19 h was only 30%.

The polymers from δ-VL and PO obtained by using substituted aluminum porphyrin initiators were of relatively broad molecular weight distribution as indicated by the ratio M_w/M_n ranging from 1.3 to 2.5.

Polymerization of δ-Valerolactone (V-VL) and 1,2-Epoxypropane (PO) with Aluminum Porphyrins in the Presence of Methanol. The polymerizations of lactones and epoxides initiated with aluminum porphyrin in the presence of an appropriate protic compound give polymers of narrow molecular weight distribution, where the number of the polymer molecules is equal to the sum of those of the aluminum porphyrin and the protic compound.[24] This is due to the reversible chain-transfer reaction between the molecules of the growing polymer and the protic compound, which takes place much faster than the propagating reaction (*immortal* character) (Scheme VI).

The aluminum porphyrin (T(2,4,6-MeO)PP)AlX (**2**) was also an active initiator for the polymerizations of δ-valerolactone (V-VL) and 1,2-epoxypropane (PO) in the presence of MeOH. As shown in Table I, the polymerization of δ-VL initiated with **2c** with the mole ratio $[\delta\text{-VL}]_0/[\text{MeOH}]_0/[\mathbf{2c}]_0$ of 400/9/1 proceeded up to 96% conversion in 2 h at 30 °C (run 2), while that with **1c** proceeded to only 9% conversion in 7 h under the same conditions (run 1). The polymer formed with **2c** was of narrow molecular weight distribution ($M_w/M_n = 1.14$), and the number of the polymer molecules relative to that of the initiator molecules (N_p/N_{Al}) of 8, as estimated from the number-average molecular weight ($M_n = 4700$), was in fair agreement with that (10) expected when all the molecules of the initiator (**2c**) and MeOH participate in initiating the polymerization. Thus, the polymerization of δ-VL initiated with a highly active initiator **2c** is of an immortal character.

Similarly, in the polymerization of PO initiated with **2a** with the mole ratio $[\text{PO}]_0/[\text{MeOH}]_0/[\mathbf{2a}]_0$ of 400/9/1 at 30 °C, the monomer conversion after 19 h was 88%, affording the polymer with M_w/M_n and N_p/N_{Al}, respectively, of 1.35 ($M_n = 3100$) and 7 (run 4), while the polymerization with **1a** under the same conditions proceeded slowly to attain 49% conversion (run 3).

Narrow molecular weight distributions of the polymers in the above polymerizations indicate that not only the propagating reaction (i and iii in Scheme VI) but also the exchange reaction (chain-transfer reaction, ii and iv) are accelerated by the presence of the methoxy groups on the phenyl rings of the initiator (**2**).

Discussion

The results mentioned above clearly demonstrate that the rates of polymerization of lactone (β- and δ-lactones) and epoxide initiated with aluminum complexes of substituted tetraphenylporphyrins are affected by the types of substituents and the modes of substitution. For the interpretation of the differences in the activities of the initiators, the first thing to be considered is the fact that the substituent effect is remarkable only when the substituents are located on all the ortho positions of the peripheral phenyl groups. This is well demonstrated by the polymerizations of β-propiolactone using a series of aluminum methoxy-substituted tetraphenylporphyrins (**2**–**7**), where the aluminum porphyrins carrying 2,6-dimethoxyphenyl and 2,4,6-trimethoxyphenyl groups, (T(2,6-MeO)PP)AlCl (**4a**) and (T(2,4,6-MeO)PP)AlCl (**2a**), exhibit very high activities, while the activities of other aluminum porphyrins ((T(3,4,5-MeO)PP)AlCl (**3a**), (T(2,4-MeO)PP)AlCl (**5a**), (T(2-MeO)PP)AlCl (**6a**), and (T(4-MeO)PP)AlCl (**7a**)) are almost comparable to that of nonsubstituted (TPP)AlCl (**1a**) regardless of the number of methoxy substituents on the phenyl rings. The second thing to be considered is the type of substituents. When the activities of aluminum porphyrins with fully ortho-substituted phenyl groups are compared with the activity of (TPP)AlX (**1**), the aluminum porphyrins carrying polar substituents such as methoxy and chlorine groups ((T(2,4,6-MeO)PP)AlX (**2**), (T(2,6-MeO)PP)AlX (**4**), and (T(2,6-Cl)PP)AlX (**9**)) have very high activities, while the activities of (T(2,4,6-Me)PP)AlX (**10**), and (T(2,4,6-Ph)PP)AlX (**11**) with nonpolar substituents are extremely low. The activity of (T(2,3,4,5,6-F)PP)AlX (**8**) carrying polar but small substituents is almost comparable to **1**.

The substituents are expected to affect the reactivity of the Al–X bond of aluminum porphyrin and/or the coordination of monomer to the aluminum atom. The electronic effect of the substituents on the phenyl groups could affect the reactivity of aluminum porphyrin, particularly when the phenyl groups are oriented coplanar with the porphyrin macrocycle establishing good π-overlap. However, if the phenyl groups have little chance to take a coplanar orientation with the porphyrin macrocycle, such an electronic effect will not be remarkable.

In view of the structure–reactivity relationship of a series of aluminum porphyrins, it is particularly interesting to note that (T(2,4,6-MeO)PP)AlX (**2**) and (T(2,4,6-Me)PP)AlX (**10**), though the substituent methoxy and methyl groups are both of electron-donating capabilities,[25] exhibit very different reactivities from each other. **2** is of much higher reactivity, and **10** exhibits very low reactivity compared with nonsubstituted (TPP)AlX (**1**). Including these examples, the aluminum porphyrins with much different reactivities from (TPP)AlX are characterized by having substituents at all the ortho positions of the phenyl groups. In these cases, the phenyl groups hardly take a coplanar orientation with the porphyrin macrocycle because of steric repulsion between the ortho substituents and the porphyrin disk (Figure 4),[26] so the electronic effect is unlikely. From the CPK model studies, a direct coordinative interaction seems also unlikely between the ortho substituents such as methoxy groups and the aluminum atom. In fact, the chemical shift values of various aluminum porphyrins in ^{27}Al NMR were not very much different from one another.[22]

Table I
Immortal Polymerization of δ-VL and PO with Aluminum Porphyrin in the Presence of Methanol (MeOH)[a]

run	monomer (M)	initiator (I)	$[M]_0/[MeOH]_0/[I]_0$	time, h	conversion, %	M_n[d]	M_w/M_n[d]	N_p/N_{Al}[e]
1	δ-VL[b]	**1c**	400/9/1	7	9	600	1.16	7
2	δ-VL	**2c**	400/9/1	2	96	4700	1.14	8
3	PO[c]	**1a**	400/9/1	19	49	1500	1.10	8
4	PO	**2a**	400/9/1	19	88	3100	1.35	7

[a] At 30 °C under N_2. [b] In CH_2Cl_2 ($[I]_0$ = 21.2 mM). [c] Without solvent ($[I]_0$ = 35.7 mM). [d] Estimated by GPC. [e] Number of polymer molecules (N_p)/number of initiator molecules (N_{Al}).

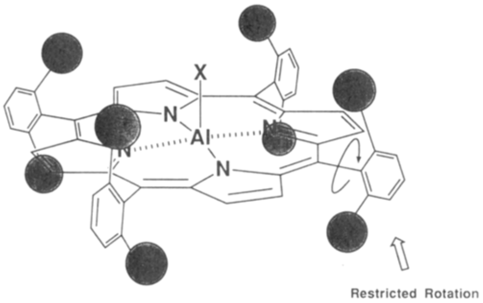


Figure 4. Schematic structure of aluminum porphyrin with fully ortho-substituted phenyl rings.

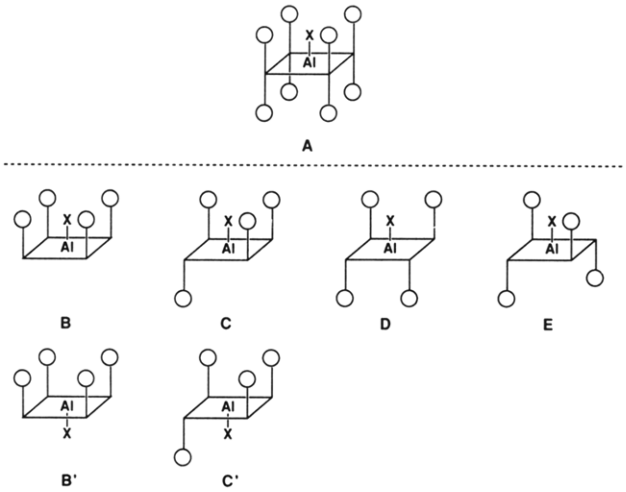


Figure 5. Schematic structures of ortho-substituted aluminum tetraphenylporphyrins.

The difference in the reactivity of aluminum porphyrins with fully ortho-substituted phenyl groups is considered to be due to the steric effect of the substituents. As mentioned above, the peripheral phenyl groups with bulky substituents at 2,6-positions are very reluctant to rotate around the phenyl group–porphyrin axis,[26] so the ortho substituents are projected above and below the porphyrin plane (A in Figure 5). When the substituents are polar groups such as methoxy and chlorine groups, the aluminum porphyrins ((T(2,4,6-MeO)PP)AlX (**2**), (T(2,6-MeO)PP)AlX (**4**), and (T(2,6-Cl)PP)AlX (**9**)) are considered to have polar pockets on both faces, where the incoming monomer is activated by polarization and/or the reactivity of the Al–X bond is enhanced. Consequently, the reaction between the Al–X bond and the monomer takes place very easily. On the other hand, nonpolar substituents such as methyl or phenyl groups provide the aluminum porphyrins with nonpolar pockets ((T(2,4,6-Me)PP)AlX (**10**)) or sterically hindered, nonpolar pockets ((T(2,4,6-Ph)PP)AlX (**11**)), where the reaction of the Al–X bond with the monomer takes place with some difficulties.

Also noticeable is the difference in the reactivity of (T(2,6-MeO)PP)AlX (**4**), (T(2,4-MeO)PP)AlX (**5**), and (T(2-MeO)PP)AlX (**6**). The aluminum porphyrins **5** and **6** are considered to be the mixtures of six atropisomers (B–E) due to the restricted rotation of the peripheral phenyl rings,[26] where the statistical population of the isomer B, which is expected to have an activity comparable to that of **2** or **4**, is calculated to be only 6.3%. Thus, **5** and **6** are not more active than (TPP)AlX (**1**). For the aluminum porphyrins bearing phenyl rings with no ortho substituents ((T(3,4,5-MeO)PP)AlX (**3**) and (T(4-MeO)PP)AlX (**7**)) or small ortho-substituents such as fluorine groups (T(2,3,4,5,6-F)PP)AlX (**8**), the construction of the pockets as proposed for **2**, **4**, and **9** may hardly be expected due to the nonrestricted rotation of the phenyl rings.[27] In these cases, the electronic effect of the substituent would be expected. However, the almost comparable activities of **3**, **7**, and **8** to nonsubstituted (TPP)AlX (**1**) may indicate the low probability of the coplanar orientation between the phenyl ring and the porphyrin macrocycle.

Conclusion

The present studies demonstrate that the aluminum tetraphenylporphyrins carrying polar substituents at the 2,6-ortho positions of the phenyl rings serve as very active initiators for the polymerizations of lactone and epoxide. This interesting observation provides a methodology for molecular design of highly active metalloporphyrin initiators for controlled polymer syntheses.

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(4) Abbreviations used: $TPPH_2$, 5,10,15,20-tetraphenylporphine; $T(2,4,6\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(2′,4′,6′-trimethoxyphenyl)porphine; $T(3,4,5\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(3′,4′,5′-trimethoxyphenyl)porphine; $T(2,6\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(2′,6′-dimethoxyphenyl)porphine; $T(2,4\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(2′,4′-dimethoxyphenyl)porphine; $T(2\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(2′-methoxyphenyl)porphine; $T(4\text{-}MeO)PPH_2$, 5,10,15,20-tetrakis(4′-methoxyphenyl)porphine; $T(2,3,4,5,6\text{-}F)PPH_2$, 5,10,15,20-tetrakis(2′,3′,4′,5′,6′-pentafluorophenyl)porphine; $T(2,6\text{-}Cl)PPH_2$, 5,10,15,20-tetrakis(2′,6′-dichlorophenyl)porphine; $T(2,4,6\text{-}Me)PPH_2$, 5,10,15,20-tetrakis(2′,4′,6′-trimethylphenyl)porphine; $T(2,4,6\text{-}Ph)PPH_2$, 5,10,15,20-tetrakis(2′,4′,6′-triphenylphenyl)porphine.

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(16) Use of either commercial $CHCl_3$ or distilled $CHCl_3$ (over K_2CO_3) gave T(2,4,6-Ph)PPH_2 in comparable yields.

(17) UV–vis ($CHCl_3$, λ in nm): 439, 533, 569, 611, and 669 (ref 14b: 438, 530, 565, 606, 655 in C_6H_6.). ^1H NMR ($CDCl_3$, δ in ppm): 8.50 (s, pyrrole-H), −3.32 (s, N-H).

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(22) For (porphinato)AlCl, ^{27}Al NMR ($CDCl_3$, $Al(NO_3)_3$ (δ 0.0) as standard): **1a**, 102.6 (*Al*-Cl); **2a**, 91.6; **3a**, 103.0; **8a**, 94.6; **9a**, 94.5; **10a**, 100.7. For (porphinato)AlMe, ^1H NMR ($CDCl_3$, $CHCl_3$ (δ 7.28) as standard): **1b**, −6.84 (Al-CH_3); **2b**, −6.75; **3b**, −6.84; **4b**, −6.71; **5b**, −6.76, −6.83, −6.88, −6.94 (mixture of atropisomers); **6b**, −6.72, −6.78, −6.84, −6.91; **7b**, −6.92; **8b**, −6.93; **9b**, −6.77; **10b**, −6.88; **11b**, −7.84.

(23) The polymer obtained with **1a** was rich in isotactic sequences (i:s = 0.68:0.32, I:H:S = 0.46:0.41:0.13, as determined by ^{13}C NMR (see Oguni, N.; Lee, K.; Tani, H. *Macromolecules* **1972**, *5*, 819), while that with **2a** was virtually atactic (i:s = 0.49:0.51, I:H:S = 0.23:0.50:0.27).

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Registry No. **1a**, 71102-37-9; **1c**, 66945-43-5; **2a**, 126296-46-6; **2c**, 126296-56-8; **3a**, 126296-47-7; **3c**, 126296-57-9; **4a**, 126296-48-8; **4c**, 126296-58-0; **5a**, 126296-49-9; **6a**, 126296-50-2; **7a**, 126296-51-3; **8a**, 126296-52-4; **8c**, 126296-59-1; **9a**, 126296-53-5; **9c**, 126296-60-4; **10a**, 126296-54-6; **10c**, 126296-61-5; **11a**, 126296-55-7; PO (SRU), 25322-69-4; β-PL (homopolymer), 25037-58-5; β-PL (SRU), 24938-43-0; δ-valerolactone (homopolymer), 26354-94-9; δ-valerolactone (SRU), 26499-05-8.

Synthesis and Characterization of Poly(1,4-phenylenevinylene) Derivatives

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ABSTRACT: We report the synthesis of functionalized poly(*p*-phenylenevinylenes), in which α and β positions are substituted with oxygen-containing groups. These functionalized poly(*p*-phenylenevinylenes) were synthesized by the reaction of polybenzoin, synthesized by the benzoin-type reaction of terephthalaldehyde, with Schlosser's base, KO*t*-Bu/*n*-BuLi, to generate a polydianion, which on further reaction with acetyl chloride and dimethyl sulfate yields the corresponding poly(1,4-phenylenevinylene α,β-diol diacetate) and poly(1,4-phenylene-α,β-dimethoxyvinylene), respectively. These materials were characterized by IR, NMR, and elemental analysis. The conductivity was measured in the pristine state ($\sim 10^{-10}$ S/cm) as well as after doping with iodine ($\sim 10^{-6}$ S/cm).

Poly(1,4-phenylenevinylene) (PPV) forms the basis of an important class of nondegenerate, conducting polymers in which conjugation is extended by the aromatic rings included directly in the chain.[1] In this class of polymers two structures arising due to resonance—benzenoid and quinonoid—do not have the same energy. The quinonoid structure has higher energy than the benzenoid structure. Other examples of such nondegenerate systems are polyphenylene, polypyrrole, and polythiophene.[1]

PPV was first synthesized by Drefahl et al.[2] and later by Kossmehl et al.[3] using the Wittig reaction. Kanbe et al.[4] and Wessling et al.[5] used sulfonium salts to synthesize the PPV, and Lillya et al.[6] have used both the Wittig reaction and the dehydrohalogenation reaction to synthesize PPV. Moshchinskaya et al.[7] have synthesized PPV through the ammonium salts, whereas Karasz et al.[8-11] have studied the sulfonium reaction extensively to make PPV and its analogues with substituents on the aromatic ring.

PPVs synthesized by the Wittig reaction and by dehydrohalogenation are insoluble and infusible and probably of low molecular weight (DP 11).[11] However, the use

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