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Lewis Acid-Driven Accelerated Living Polymerization of Lactones Initiated with Aluminum Porphyrins. Chemoselective Activation of Ester Groups by Lewis Acid

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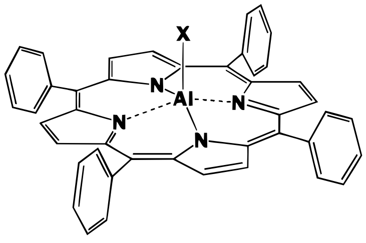
ABSTRACT: Ring-opening polymerization of δ-valerolactone (δ-VL) initiated with (5,10,15,20-tetraphenylporphinato)aluminum methoxide ((TPP)AlOMe, **1**; X = OMe) was dramatically accelerated upon addition of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) and bis(2,4,6-tri-*tert*-butylphenolate) (**2b**) via coordinative activation of monomer, but was accompanied by transesterification, resulting in broadening of the polymer molecular weight distribution (MWD) at the later stage of polymerization. On the contrary, when methylaluminum bis(2,6-di-X-phenolate)s (X = Cl (**2c**), Br (**2d**), I (**2e**), and Ph (**2f**)) were used as Lewis acids, the polymerization proceeded also rapidly, retaining the narrow MWD. ^{13}C NMR studies on the Lewis acid (**2b** or **2f**)−δ-VL and −poly(δ-VL) mixtures showed that the coordination abilities of **2b** and **2f** toward the monomer ester group are comparable to each other, while **2f** shows a lower affinity to the polymer ester group than **2b**. **2a** was also able to accelerate the polymerization of β-butyrolactone (β-BL) with (TPP)AlOMe or (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1**; X = Cl) to different extents depending on the mode of ring scission, where the MWD of the polymer remained narrow throughout the accelerated polymerization (M_w/M_n = 1.1−1.2).

Introduction

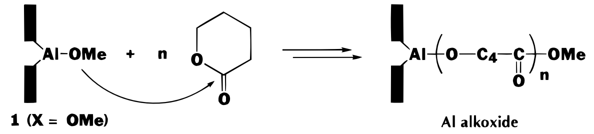
We have reported that aluminum porphyrins bring about the living polymerization of various monomers such as epoxides,[1] lactones,[2,3] methacrylic esters,[4] and acrylic esters,[5] affording polymers with narrow molecular weight distributions (MWD). Recently, we have discovered the new method "accelerated living polymerization" of methyl methacrylate, using enolate aluminum porphyrin (**1**, X = enolate) as the nucleophilic initiator in conjunction with organoaluminum compounds, such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**), as the Lewis acid monomer activator.[6] More recently, this method was successfully applied to the acceleration of the living and immortal polymerizations of epoxides.[7] The acceleration of these polymerizations is realized by the coordinative activation of the monomer by the Lewis acid for the nucleophilic attack of the growing species.

The polymerizations of six- and four-membered lactones initiated with aluminum porphyrins ((TPP)AlX, **1**) proceeds via (porphinato)aluminum alkoxide and carboxylate as the growing species, respectively (Schemes 1 and 2),[2,3] and to give polymers with narrow MWD, although it is well known that the polymerization of lactone initiated with boron trifluoride, ferric chloride, aluminum chloride, or aluminum isopropoxide cannot avoid inter- or intramolecular transesterification to cause degradation of the once-formed polyester by the attack of the active chain ends on the polymer ester groups.[8]

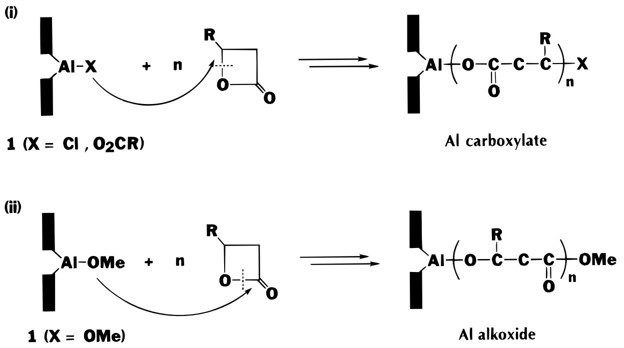


(TPP)AlX (1)

Scheme 1



Scheme 2



In the present study, the novel concept of "Lewis acid-assisted living polymerization with the aluminum porphyrin−methylaluminum diphenolate (**2**) system" was successfully extended from the accelerated living addition polymerization of alkyl methacrylates to the accelerated living ring-opening polymerizations of lactones.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine (TPPH$_2$) was synthesized from pyrrole (0.8 mol) and benzaldehyde (0.8 mol)

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in propionic acid (2.5 L) under reflux for 0.5 h. The reaction mixture was allowed to stand overnight at room temperature, and the crude product that precipitated was recrystallized from $CHCl_3$/MeOH (1/2 in v/v) to give $TPPH_2$ in 20% yield.[9]

2,6-Di-*tert*-butyl-4-methylphenol, 2,4,6-tri-*tert*-butylphenol, and 2,6-diphenylphenol were recrystallized from *n*-hexane. 2,4,6-Trichlorophenol, 2,4,6-tribromophenol, 2,4,6-triiodophenol, triphenylcarbinol, and 2,6-dimethoxyphenol were recrystallized from toluene.

Trimethylaluminum (Me_3Al) was fractionally distilled under reduced pressure in a nitrogen atmosphere.

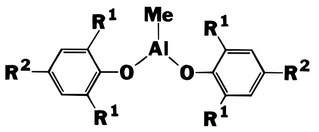
CH_2Cl_2 and 1,2-dichloroethane (DCE) were washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled over CaH_2 under nitrogen. Deuterated dichloromethane (CD_2Cl_2), stirred at room temperature with a small amount of triethylaluminum, was subjected to several freeze-to-thaw cycles, collected in a trap cooled in a liquid nitrogen bath, and stored under nitrogen. Benzene and *n*-hexane were distilled over sodium benzophenone ketyl in a nitrogen atmosphere, respectively. MeOH was purified as follows: 50 mL of MeOH was refluxed over the mixture of Mg (4 g) and I_2 (1 g) until all the Mg was converted to the methoxide, and then 1 L of MeOH was added, refluxed, and distilled under nitrogen.

δ-Valerolactone (δ-VL; purchased from Tokyo Chemical Industry) and β-D,L-butyrolactone (β-BL; purchased from Tokyo Chemical Industry) were dried over CaH_2 and then distilled under reduced pressure in a nitrogen atmosphere.

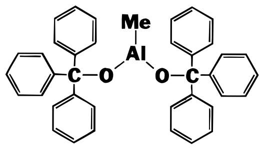
Preparation of (5,10,15,20-Tetraphenylporphinato)aluminum Methoxide (1, X = OMe). To a round-bottom flask (50 mL) equipped with a three-way stopcock containing $TPPH_2$ (0.5 mmol), CH_2Cl_2 (20 mL) and Me_3Al (0.048 mL, 1 equiv) were sucessively added by a hypodermic syringe in a nitrogen stream, and the mixture was stirred for 1 h in a nitrogen atmosphere at room temperature. The volatile fractions were removed from the reaction mixture under reduced pressure to leave **1** (X = Me) as a purple powder. Methoxyaluminum 5,10,15,20-tetraphenylporphine ((TPP)AlOMe; **1**, X = OMe) was prepared by the reaction of **1** (X = Me) with MeOH. To a CH_2Cl_2 (20mL) solution of (TPP)AlMe (0.5 mmol), MeOH (5 mL) was added by a syringe in a nitrogen stream, and the mixture was stirred for 15 h in a nitrogen atmosphere at room temperature. The solvent and the unreacted MeOH were removed from the reaction mixture under reduced pressure to leave **1** (X = OMe) as a purple powder.[10]

Preparation of (5,10,15,20-Tetraphenylporphinato)aluminum Chloride (1, X = Cl). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1.0 mmol) under dry nitrogen, CH_2Cl_2 (40 mL) and Et_2AlCl (1.2 equiv, 0.16 mL) were successively added by means of hypodermic syringes in a nitrogen stream, and the mixture was stirred for 2 h. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave **1** (X = Cl) as a purple powder.[11]

Preparation of Methylaluminum Diolates (2 and 3). Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) was prepared by the reaction of 2,6-di-*tert*-butyl-4-methylphenol with Me_3Al.[12] To a round-bottom flask (50 mL) equipped with a three-way stopcock containing 2,6-di-*tert*-butyl-4-methylphenol (20 mmol) was added *n*-hexane (15 mL). To this solution was added Me_3Al (0.95 mL, 0.5 equiv to the phenol) dropwise with stirring in a nitrogen stream at 0 °C to obtain white precipitates, and the mixture was stirred for 1 h in a nitrogen atmosphere at room temperature in the dark to complete the reaction. The white precipitates were recrystallized from *n*-hexane in a nitrogen atmosphere. The supernatant solution in the flask was taken out by a syringe in a nitrogen stream, and the residue was dried under reduced pressure. Similarly, methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**2b**) was prepared.[12] These were used as CH_2Cl_2 solutions (0.6 M), respectively. Methylaluminum bis(2,4,6-trichlorophenolate) (**2c**), bis(2,4,6-tribromophenolate) (**2d**), bis(2,4,6-triiodophenolate) (**2e**), bis(2,6-diphenylphenolate) (**2f**), bis(2,6-dimethoxyphenolate) (**2g**), and bis(triphenylcarbinolate) (**3**) were prepared by similar reaction of the corresponding phenol or alcohol with 0.5 equiv of Me_3Al in CH_2Cl_2 under nitrogen and used without further purification, respectively (**2c**, **2f**, **2g**: 0.3 M solution; **2d**, **3**: 0.3 M suspension; **2e**: 0.1 M suspension).



2a: R^1= ^{t}Bu, R^2= Me
2b: R^1= ^{t}Bu, R^2= ^{t}Bu
2c: R^1= Cl, R^2= Cl
2d: R^1= Br, R^2= Br
2e: R^1= I, R^2= I
2f: R^1= Ph, R^2= Ph
2g: R^1= OMe, R^2= OMe



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Polymerization. Polymerizations of δ-VL using (TPP)AlOMe (**1**, X = OMe) as an initiator in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) were carried out without solvent according to the following procedures. To a 50-mL round-bottom flask equipped with a three-way stopcock containing **1** (X = OMe), 200 equiv of δ-VL was added by a hypodermic syringe in a nitrogen stream, and the mixture was stirred in a nitrogen atmosphere at 50 °C for 91 h. To this flask was added a CH_2Cl_2 solution of **2a** (3 equiv with respect to (TPP)AlOMe). A small amount of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to ^{1}H NMR to determine the conversion of monomer and to gel permeation chromatography (GPC) to estimate the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymer formed.

A typical procedure for the polymerization of δ-VL with the **1** (X = OMe)−methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**2b**) system was as follows: To a 50-mL round-bottomed flask attached to a three-way stopcock containing a DCE solution (1.0 mL) of **1** (X = OMe) (0.25 mmol), δ-VL (50 mmol) and a DCE solution (0.5 mL) of **2b** (0.75 mmol) were successively added by syringes at 50 °C. A small amount of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to ^{1}H NMR to determine the conversion of monomer and to GPC to estimate M_n and M_w/M_n.

Polymerization of δ-VL (200 equiv) initiated with the **1** (X = OMe)−other methylaluminum diolate (**2c**−**2g**, and **3**) (1/3) systems in DCE at 50 °C and polymerization of β-BL (300 equiv) with the **1** (X = OMe, Cl)−**2a** (1/3) systems in CH_2Cl_2 at room temperature were carried out similarly to the polymerization of δ-VL with the (TPP)AlOMe−**2b** system mentioned above.

Measurements. ^{1}H and ^{13}C NMR measurements were performed using $CDCl_3$ or CD_2Cl_2 as solvent on a JEOL type GSX-270 spectrometer. The chemical shifts were determined with respect to $CHCl_3$ (δ 7.28 ppm) or CH_2Cl_2 (δ 5.31 ppm) for ^{1}H and with respect to CD_2Cl_2 (δ 54.0 ppm) for ^{13}C as internal standards. For the estimation of M_n and M_w/M_n of the polymers, gel permeation chromatography (GPC) was performed at 40 °C on a TOSOH Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent with a flow rate of 1.0 mL·min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes; M_n (M_w/M_n): 2 890 000 (1.09), 422 000 (1.04), 107 000 (1.07), 43 900 (1.01), 16 700 (1.02), 9000 (1.06), 6200 (1.04), 4000 (1.10), and 2800 (1.05).

Results and Discussion

1. Polymerization of δ-Valerolactone (δ-VL).

Polymerization of δ-VL Initiated with (TPP)AlOMe (1; X = OMe) in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (2a). We have already reported that aluminum porphyrin brings about the living ring-opening polymerization of δ-valerolactone to give polymers with narrow MWD.[3]

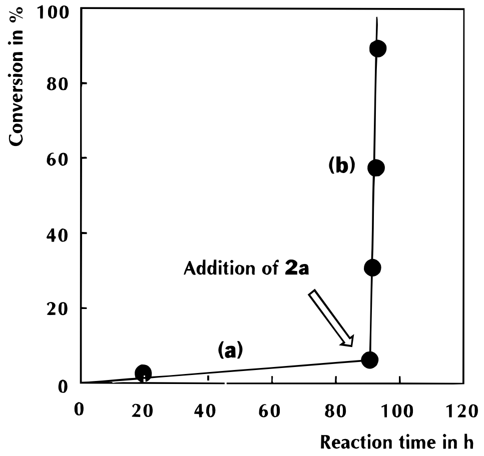

Figure 1. Polymerization of δ-valerolactone (δ-VL) initiated with **1** (X = OMe) at 50 °C without solvent ($[\delta\text{-VL}]_0/[\mathbf{1}, X = OMe]_0 = 200$, $[\mathbf{1}]_0 = 42.4$ mM). Time−conversion relationships (a) before and (b) after addition of **2a** ($[\mathbf{2a}]_0/[\mathbf{1}, X = OMe]_0 = 3$).

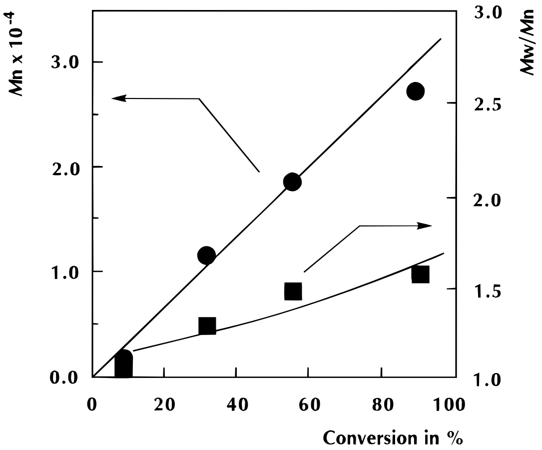

Figure 2. Polymerization of δ-valerolactone (δ-VL) initiated with **1** (X = OMe) at 50 °C without solvent. Relationships between the monomer conversion and M_n (●) [M_w/M_n (■)].

A representative initiator is (TPP)AlOMe (**1**, X = OMe), and the growing species is an aluminum alkoxide complex of porphyrin (Scheme 1). However, as shown by the time−conversion curve (Figure 1), the polymerization of δ-VL with **1** (X = OMe) ($[\delta\text{-VL}]_0/[\mathbf{1}\ (X = OMe)]_0 = 200$) at 50 °C without solvent proceeded rather slowly to attain only 7% conversion in 91 h (Figure 1a). On the other hand, when 3 equiv of **2a** with respect to **1** was added at 50 °C to this reaction mixture, a remarkable rise in the viscosity of the polymerization system was observed to attain 89% conversion in only 15 min after the addition of **2a** (Figure 1b). This corresponds to a 2100-fold acceleration of polymerization.

As shown in Figure 2, in the case of the polymerization of δ-VL, the number-average molecular weight (M_n) increased proportionally to the conversion of monomer along with the theoretical line. The degree of polymerization of the polymer was in good agreement with the mole ratio of the monomer reacted to the initiator, indicating that every initiator molecule produces one polymer molecule. The MWD of the polymer was very narrow at the earlier stage of the polymerization ($M_w/M_n = 1.05$ [$M_n = 2200$] at 7% monomer conversion) but tended to become broader at the later stage ($M_w/M_n = 1.58$ [$M_n = 27\,000$] at 89% conversion). This broadening of the MWD is attributed to the possible activation of the ester carbonyl group of the formed polymer by **2a**, which would lead to the accelerated intra- and/or intermolecular attack of the growing species on the ester groups in the polymer main chain. In order to examine this possibility, the polymerization of δ-VL (50 equiv) initiated with **1** (X = OMe) in CH_2Cl_2 at room temperature was brought to 89% conversion in 330 h to give a polymer with M_w/M_n of 1.20 ($M_n = 5400$). Then 3 equiv of **2a** was added to the mixture, and it was kept for 50 h, where the MWD became much broader ($M_w/M_n = 1.50$ [$M_n = 4200$]).

Table 1. Polymerization of δ-VL with (TPP)AlOMe (1, X = OMe) in the Presence of Various Methylaluminum Diphenolates (2) and Methylaluminum Bis(triphenylcarbinolate) (3)[a]

run	2 or 3	time/h	conv/%[b]	M_n[c]	M_w/M_n[c]
1[d]	**2b**	1.0	67.9	26000	1.32
2	**2c**	3.5	70.1	21000	1.19
3	**2d**	4.8	64.7	25000	1.21
4[e]	**2e**	9.0	73.7	19000	1.17
5	**2f**	3.5	74.0	24000	1.13
6	**2g**	5.2	66.2	28000	1.47
7	**3**	63.0	83.3	15000	1.50
8	*f*	147	3.6		

[a] DCE as solvent, 50 °C, $[\delta\text{-VL}]_0/[\mathbf{2}\text{ or }\mathbf{3}]_0/[\mathbf{1}]_0 = 200/3/1$, $[\mathbf{1}]_0 = 14.6$ mM. [b] Determined by ^1H NMR. [c] Estimated by GPC based on polystyrene standards. [d] $[\mathbf{1}]_0 = 15.7$ mM. [e] $[\mathbf{1}]_0 = 11.3$ mM. [f] Without **2** or **3**.

2a itself could polymerize δ-VL at 50 °C ($[\delta\text{-VL}]_0[\mathbf{2a}]_0 = 400$, without solvent), more slowly (8.1% conversion in 2 h) than the (TPP)AlOMe−**2a** system, and control of the molecular weight was not possible, the MWD being broad ($M_n = 64\,300$, $M_w/M_n = 1.46$).

Polymerization of δ-VL Initiated with (TPP)AlOMe (1, X = OMe) in the Presence of Various Methylaluminum Diolates (2 and 3). Polymerization of δ-VL initiated with the **1** (X = OMe)−methylaluminum diphenolate (**2b**−**g**) systems was carried out in DCE at 50 °C with an initial mole ratio $[\delta\text{-VL}]_0/[\mathbf{2}]_0/[\mathbf{1}\ (X = OMe)]_0$ of 200/3/1. As shown in Table 1, all the methylaluminum diphenolates (**2b**−**g**) brought about the accelerated polymerization of δ-VL corresponding to the acceleration by a factor of 100−4800 (**2b**−**g**) compared with the rate of polymerization in the absence of **2** under similar conditions (Table 1, run 8), where the M_n of the produced polymer was about 25 000 at 65−75% conversion (**2b**−**f**) except for the case using **2g**. On the other hand, a remarkable difference in the MWD of the produced polymers at about 70% conversion was observed. In the case of using **2b**, the MWD became broader at the later stage (Figure 3, □) to give a polymer with an M_w/M_n of 1.32 at 68% conversion (Table 1, run 1). A similar phenomenon was observed in the polymerization in the presence of 2g. However, the polymerizations in the presence of **2c**−**f** gave polymers with narrow MWD ($M_w/M_n = 1.1$−1.2) at 65−75% conversion, respectively (Table 1, runs 2−5). In particular, in the case of using 2f (Table 1, run 5), the MWD was kept very narrow throughout the polymerization ($M_w/M_n = 1.12$−1.14) (Figure 3, ■).

In contrast, when using methylaluminum bis(triphenycarbinolate) (**3**), the MWD of the produced polymer was broad, though the polymerization in the presence of **3** was less accelerated (Table 1, run 7) than in the presence of methylaluminum diphenolates (**2b**−**g**), indicating that the broadening of the MWD was independent of the accelerating power of the methylaluminum diolates.

Coordinative Interaction between Methylaluminum Diphenolates (2b and 2f) and δ-VL or Poly-

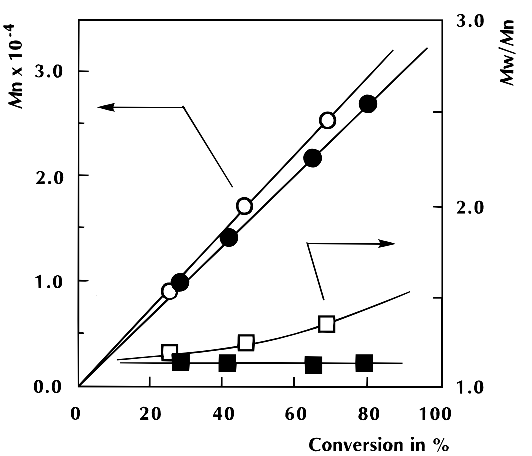

Figure 3. Polymerization of δ-valerolactone (δ-VL) initiated with **1** (X = OMe) in the presence of **2b** and **2f** at 50 °C in DCE [$(\delta\text{-VL})_0/[\mathbf{2}]_0/[\mathbf{1}, \text{X} = \text{OMe}]_0$ = 200/3/1, $[\mathbf{1}]_0$ = 15.7 mM (**2b**), 14.6 mM (**2f**). Relationships between the monomer conversion and M_n (**2b**, ○; **2f**, ●) [M_w/M_n (**2b**, □; **2f**, ■)].

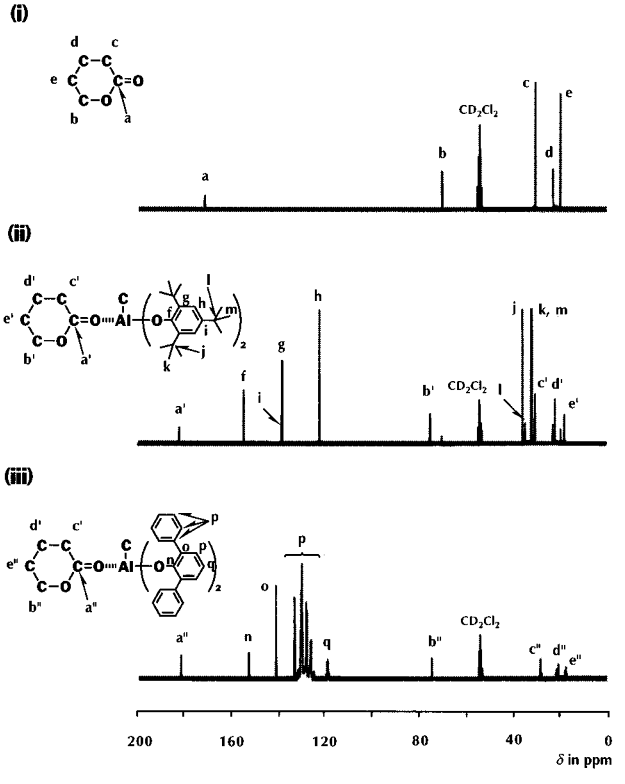

Figure 4. ^{13}C NMR spectra in CD_2Cl_2 at 23 °C of (i) δ-valerolactone (δ-VL) ($[\delta\text{-VL}]_0$ = 0.3 M), (ii) a mixture of **2b** and δ-VL, and (iii) a mixture of **2f** and δ-VL ($[\delta\text{-VL}]_0/[\mathbf{2}]_0$ = 1.5, $[\delta\text{-VL}]_0$ = 0.3 M).

(δ-VL). ^{13}C NMR Studies. Coordinative interaction between methylaluminum diphenolates (**2b** and **2f**) and δ-VL or poly(δ-VL) was investigated by ^{13}C NMR in CD_2Cl_2 at 23 °C. The spectrum of δ-VL alone is shown in Figure 4i, where the signals a (δ 170.7 ppm), b (δ 69.1 ppm), and c, d, and e (δ 29.5, 22.0, and 18.8 ppm) were due to *C*=O, *C*H$_2$O, and other *C*H$_2$ groups, respectively. When the spectrum of the mixture at the molar ratio of **2b** to δ-VL of 1.5:1 (Figure 4ii) was compared with that of δ-VL alone (Figure 4i), each signal for δ-VL in the mixture shifted to the signals a′ (δ 181.5 ppm), b′ (δ 74.3 ppm), and c′, d′, and e′ (δ 29.9, 21.1, and 17.2 ppm), respectively. The extent of the shift was most remarkable for the signal due to the carbonyl carbon (Δδ 10.8 ppm). Similar shifts were observed in the case of the mixture of **2f** and δ-VL ($[\mathbf{2f}]_0/[\delta\text{-VL}]_0$ = 1.5), where the signal assigned to the *C*=O shifted most remarkably (downfield shift of 10.1 ppm) (Figure 4iii). Figure 5 shows the ^{13}C NMR spectra of poly(δ-VL) alone (i), poly(δ-VL) in the mixtures of **2b** and poly(δ-VL) (ii), and **2f** and poly(δ-VL) (iii) ($[\mathbf{2}]_0$/[monomer units in poly(δ-VL)]$_0$ = 1.0).[13] When the spectrum of the mixture was compared with that of poly(δ-VL) alone, each signal due to poly(δ-VL) in the mixture turned out to shift similarly to δ-VL in the presence of **2**, and the extent of the shift was most noticeable in the signal assigned to the carbonyl carbon, where the signal A (δ 173.6 ppm) shifted to the signal A′ (δ 182.8 ppm) and A″ (δ 183.6 ppm) in the presence of **2b** and **2f** (downfield shifts of 9.2 and 10.0 ppm), respectively. However, there was observed a clear difference in these two spectra. In the spectrum of the mixture of **2b** and poly(δ-VL) (Figure 5ii), no signals were observed at the same chemical shift as those due to poly(δ-VL) in the absence of **2b** (Figure 5i). On the other hand, the spectrum of the mixture of **2f** and poly(δ-VL) (Figure 5iii showed the signals at the original chemical shifts (Figure 5i) in addition to the shifted signals, where the relative intensity ratio of the shifted signals to the original signals was 4:6. These observations indicate that **2f** interacts more strongly with δ-VL than with poly(δ-VL), while **2b** possible interacts almost equally with δ-VL and poly(δ-VL).

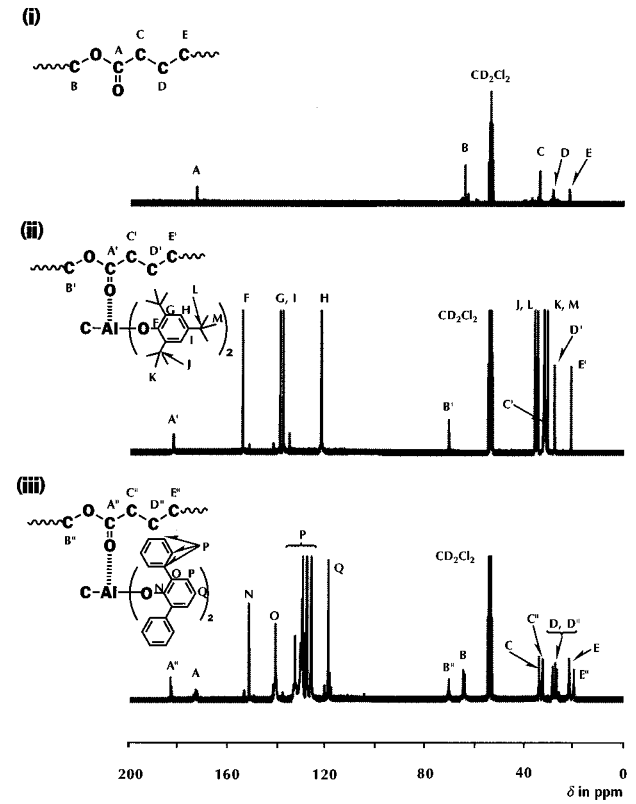

Figure 5. ^{13}C NMR spectra in CD_2Cl_2 at 23 °C of (i) poly(δ-valerolactone) (poly(δ-VL)) ([monomer units in poly(δ-VL)]$_0$ = 0.6 M), (ii) a mixture of **2b** and poly(δ-VL), and (iii) a mixture of **2f** and poly(δ-VL) ([monomer units in poly(δ-VL)]$_0/[\mathbf{2}]_0$ = 1.0, [monomer units in poly(δ-VL)]$_0$ = 0.3 M).

Polymerization of δ-VL with the (TPP)AlOMe (1; X = OMe)−Methylaluminum Diphenolate (2) Systems. Mechanistic Aspect. As described above, methylaluminum diolates (**2a**−**g** and **3**) accelerate the polymerization of δ-VL initiated with **1** (X = OMe) (Figure 1 and Table 1). Together with the results of the NMR observations, the accelerated polymerization of δ-VL with the **1** (X = OMe)−**2** systems is concluded

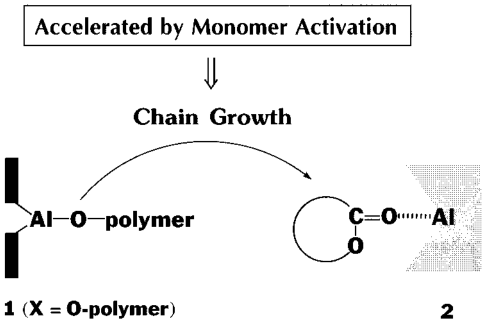

Figure 6. Basic concept of the "accelerated living polymerization" of lactone with the aluminum porphyrin (**1**)–methylaluminum diphenolate (**2**) initiating system.

to be the result of (1) coordinative activation of δ-VL by **2** for the nucleophilic attack of **1** (X = O-polymer) (Figure 6) and (2) suppression of the undesired degradative attack of **1** on the Lewis acid center of **2** because of the steric repulsion between the bulky porphyrin ligand of **1** and the substituents at the *ortho* positions of the phenolate ligands of **2**.

The substituents on the phenolate ligand of **2** are considered to affect the ability of promoting the possible side reaction in the later stage of the polymerization of δ-VL such as transesterification. The NMR analysis of the mixture of **2b** and poly(δ-VL) (Figure 5) indicated the coordinative interaction between **2b** and poly(δ-VL) similar to that between **2b** and δ-VL. This coordinative interaction between **2b** and poly(δ-VL) probably promotes the attack of the growing species on the ester groups in the produced polymer main chain (transesterification) proceeding in competition with the accelerated propagation and thus results in the broadening of the MWD at the later stage of the polymerization. On the other hand, **2f** coordinates selectively with the δ-VL monomer and thus effectively accelerates the polymerization of δ-VL; however, the interaction of **2f** with poly(δ-VL) is not enough to promote the unfavored transesterification (Figure 5iii), where the MWD of the produced polymer is kept very narrow throughout the polymerization.

2. Polymerization of β-Butyrolactone (β-BL). β-lactone has been known to undergo the living polymerization initiated by aluminum porphyrins such as (TPP)AlCl (**1**, X = Cl) and (TPP)AlO$_2$CR (**1**, X = O$_2$CR).[2] The reaction proceeds via the cleavage of the CO$_2$–C bond, and the growing species is an aluminum carboxylate (Scheme (2i)). On the other hand, we have revealed more recently that the polymerization of β-lactone also takes place with (TPP)AlOR (**1**, X = OR) as initiator though more slowly, where the ring is cleaved at the O–C=O bond, the growing species being an aluminum alkoxide, as evidenced by the ^{1}H NMR studies of the reaction mixture (Scheme (2ii)). The ^{1}H NMR spectrum in CDCl$_3$ for the reaction mixture of β-BL and **1** (X = Cl) (10/1) for 200 h showed signals due to (TPP)AlOCH(C*H*$_3$), (TPP)AlOC*H*(CH$_3$), and (TPP)AlOCH(CH$_3$)C*H*$_2$ at δ −1.95 (d, 3H), −1.84 (m, 1H), and −1.21 and −0.39 (dq, 2H) ppm, respectively,[14] while the signals due to (TPP)AlOC(=O)C*H*$_2$CH(CH$_3$) and (TPP)AlOC(=O)CH$_2$CH(C*H*$_3$) overlapping at δ −0.4 to −0.6 ppm (5H)[2a] were not observed.

Of interest to note is the fact that the methylaluminum diphenolate such as **2a** exhibits the accelerating effect also on the polymerization of β-lactone, and the extent of acceleration depends on the mode of the ring scission. For example, in the polymerization of β-butyrolactone (β-BL, 300 equiv) initiated with **1** (X = Cl) in CH$_2$Cl$_2$ at room temperature, the addition of **2a** (1 equiv) brought about a 2-fold acceleration (Figure 7, ■ → □). The M_n (5100 [M_w/M_n = 1.1] at 22% conversion; 288 h) of the polymer formed in the absence of **2a** and that (15 600 [M_w/M_n = 1.2] at 57% conversion; 384 h) of the polymer obtained in the presence of **2a** were close to the expected values (5700 and 14 700, respectively) from the initial β-BL-to-**1** (X = Cl) mole ratio and the monomer conversion by assuming that every molecule of **1** produced one polymer molecule.

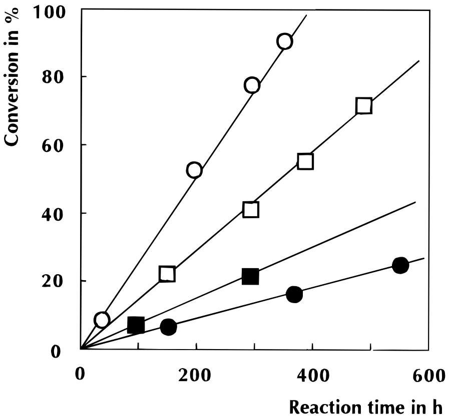

Figure 7. Polymerizations of β-butyrolactone (β-BL) initiated with **1** (X = Cl) in the absence (■) and presence (□) of **2a**, and with **1** (X = OMe) in the absence (●) and presence (○) of **2a** at room temperature in CH$_2$Cl$_2$ ([β-BL]$_0$/[**1**, X = Cl or OMe]$_0$ = 300, [**1**]$_0$ = 29.4 mM, [**2a**]$_0$/[**1**, X = Cl or OMe]$_0$ = 0 (■ and ●) or 3 (□ and ○)).

In contrast, the polymerization initiated with (TPP)AlOMe was slower (26% conversion in 552 h; M_n = 6100 [M_w/M_n = 1.2]) than by **1** (X = Cl), but the accelerating effect of **2a** was more remarkable (6 times) for **1** (X = OMe)-initiated polymerization (86% conversion in 362 h; M_n = 19 500 [M_w/M_n = 1.2]) (Figure 7, ● → ○). The polymerization of β-BL took place by **2a** alone, but the polymerization did not proceed to high conversion and the polymer was of broad molecular weight distribution.

The acceleration by **2a** is also considered to be due to the coordination of the carbonyl group of β-BL to **2a**, as indicated by the broadening of the *C*=O signal (δ 167.7 ppm) of β-BL in the ^{13}C NMR spectrum when mixed with **2a** (1/1) in CD$_2$Cl$_2$. The coordination of monomer is considered to affect the reactivity directly when the carbonyl group is attacked by the growing species, while the attack at the β-carbon remote from carbonyl group is less affected by the coordination, resulting in the different extents of acceleration depending on the mode of ring cleavage.

Irrespective of the structure of the initiator employed (**1**, X = OMe, Cl), the MWD of the poly(β-BL) remained narrow throughout the accelerated polymerization in the presence of **2a** (M_w/M_n = 1.1–1.2), in sharp contrast to the broadened MWD of the poly(δ-VL) at the later stage of the polymerization with **1** (X = OMe) in the presence of **2a** (M_w/M_n ~ 1.5).

Conclusion

The accelerated polymerization of δ-valerolactone (δ-VL) affording a polyester was achieved by the aluminum porphyrin (**1**)–methylaluminum diphenolate (**2**) system. For the precise control of the molecular weight of the produced polyester, it was important to tune the structure of **2** in order that **2** can exclusively interact with

δ-VL monomer in the presence of the ester groups of the produced polymer.

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(13) Poly(δ-VL) was synthesized by the polymerization of δ-VL with the (TPP)AlOMe−**2a** system ($M_n = 24\,000$ [$M_w/M_n = 1.57$]), purified by precipitation from $CHCl_3$−hexane, and subjected to the ^{13}C NMR studies.

(14) The signals were assigned by reference to the signals for the model compound (TPP)AlOCH(CH_3)CH_2C(=O)OEt (**1**, X = OCH(CH_3)CH_2C(=O)OEt) prepared by the reaction of (TPP)AlMe (**1**, X = Me) and HOCH(CH_3)CH_2C(=O)OEt.

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