High-Speed Living Anionic Polymerization of Methacrylic Esters with Aluminum Porphyrin Initiators. Organoaluminum Compounds as Lewis Acid Accelerators

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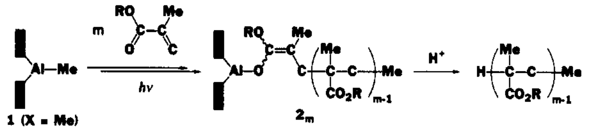
ABSTRACT: The polymerization of methacrylic esters initiated with methylaluminum tetraphenylporphyrin (**1**, X = Me) proceeded dramatically rapidly at room temperature in the presence of sterically crowded organoaluminum compounds such as methylaluminum *ortho*-substituted diphenolates (**3a**–**3g**), bis(triphenylmethanolate) (**4b**), and triphenylaluminum, where undesired reaction between the growing species (enolatoaluminum porphyrin, **2**) and the Lewis acids was sterically suppressed. Use of less hindered Lewis acids such as methylaluminum diphenolates having no *ortho* substituents (**3h**, **3i**), bis(diphenylmethanolate) (**4a**), trimethylaluminum, and triisobutylaluminum for the polymerization of methyl methacrylate under similar conditions resulted in termination of chain growth. However, this unfavorable termination was avoidable when the polymerization temperature was lowered to −40 °C.

Introduction

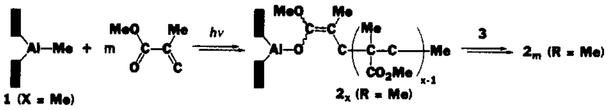
Potential utility of Lewis acids for promoting nucleophilic reactions via coordinative activation of substrates is well established in the field of organic chemistry,[1] but undesired attack of nucleophiles to the Lewis acidic (electrophilic) center, leading to destruction of these species, is usually inevitable. Thus, the application of this concept to the control of anionic (nucleophilic) polymerization has been essentially limited. Hatada *et al.* have utilized a mixture of *tert*-butyllithium and trialkylaluminum for the polymerization of methyl methacrylate (MMA), where the chain growth takes place with living character to give syndiotactic PMMA (poly(methyl methacrylate)) in a nonpolar solvent, but lowering the temperature to, *e.g.*, −78 °C is a prerequisite.[2] Very recently, another interesting example has been reported by Ballard *et al.*, who have utilized *tert*-butyllithium as initiator in conjunction with a bulky Lewis acid such as diisobutylaluminum 2,6-di-*tert*-butyl-4-methylphenolate, and achieved the living polymerization of methacrylic esters at 0 °C.[3] In these two examples, however, some aggregated species between the nucleophilic growing species and Lewis acids have been proposed as the active species.

In a previous communication,[4] we have already reported that the polymerization of MMA initiated with methylaluminum tetraphenylporphyrin (**1**, X = Me, (TPP)AlMe), proceeding via an enolatoaluminum porphyrin as the growing species (**2**, Scheme I),[5] is dramatically accelerated by the addition of a bulky Lewis acid such as methylaluminum bis(2,4-di-*tert*-butylphenolate) (**3b**) (Scheme II). On the basis of this finding, monodisperse, high molecular weight PMMA with M_n exceeding one million was synthesized.[6] The basic idea of this finding came from our interesting observation that the living anionic polymerization of δ-valerolactone (δ-VL) via an alcoholatoaluminum porphyrin (**1**, X = O-polymer) as the growing species is accelerated upon addition of a Lewis acidic chloroaluminum porphyrin (**1**, X = Cl)[7] which itself, however, has no ability to initiate the polymerization (Scheme III).

Scheme I

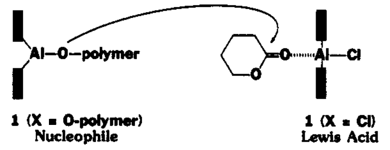


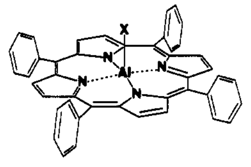
Scheme II



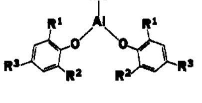
Scheme III

Accelerated Chain Growth

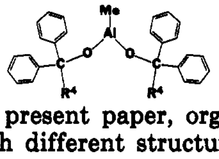




(TPP)AlX (**1**)



3a: $R^1 = {}^tBu$, $R^2 = R^3 = H$
3b: $R^1 = R^3 = {}^tBu$, $R^2 = H$
3c: $R^1 = {}^tBu$, $R^2 = H$, $R^3 = OMe$
3d: $R^1 = Ph$, $R^2 = R^3 = H$
3e: $R^1 = R^2 = {}^tBu$, $R^3 = Me$
3f: $R^1 = R^2 = R^3 = {}^tBu$
3g: $R^1 = R^2 = Cl$, $R^3 = H$
3h: $R^1 = R^2 = H$, $R^3 = {}^tBu$
3i: $R^1 = R^2 = H$, $R^3 = OMe$



4a: $R^4 = H$
4b: $R^4 = Ph$

In the present paper, organoaluminum-based Lewis acids with different structures were employed for the polymerization of various methacrylic esters initiated with **1** (X = Me), and the mode of acceleration was discussed in terms of the type of Lewis acid and the polymerization conditions.

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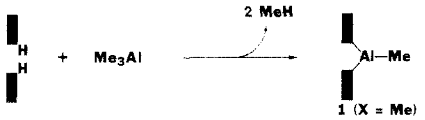
Scheme IV



Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine (TPPH$_2$) was synthesized from pyrrole (0.8 mol) and benzaldehyde (0.8 mol) in propionic acid (2.5 L) under reflux for 0.5 h, and the crude product, precipitated upon keeping the reaction mixture overnight at room temperature, was recrystallized from CHCl$_3$/MeOH (1/2 v/v) to give TPPH$_2$ in 20% yield.[8]

Dichloromethane (CH$_2$Cl$_2$) was washed successively with concentrated H$_2$SO$_4$, water, and aqueous NaHCO$_3$, dried over CaCl$_2$, and distilled over CaH$_2$ in a nitrogen atmosphere. Deuterated dichloromethane (CD$_2$Cl$_2$), stirred at room temperature with a small amount of triethylaluminum, was subjected to several freeze–thaw cycles, and collected in a trap cooled with a liquid nitrogen bath and stored under nitrogen. Benzene (C$_6$H$_6$), deuterated benzene (C$_6$D$_6$), hexane, and tetrahydrofuran (THF) were distilled in a nitrogen atmosphere over sodium benzophenone ketyl just before use. Diisopropylamine was distilled after refluxing over a mixture of CaH$_2$ and KOH under nitrogen. *tert*-Butyl isobutyrate was fractionally distilled over CaH$_2$ under reduced pressure in a nitrogen atmosphere. 2-*tert*-Butylphenol, 4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, 2,4,6-tri-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 2-phenylphenol, and 2,6-dichlorophenol were recrystallized from hexane. 4-Hydroxyanisole, 3-*tert*-butyl-4-hydroxyanisole, triphenylmethanol, and diphenylmethanol were recrystallized from toluene.

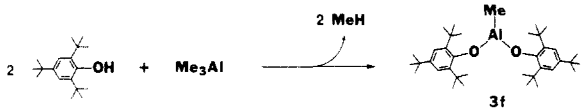
Methyl methacrylate (MMA), ethyl methacrylate (EMA), isopropyl methacrylate (^{i}PMA), *n*-butyl methacrylate (^{n}BMA), isobutyl methacrylate (^{i}BMA), *tert*-butyl methacrylate (^{t}BMA), benzyl methacrylate (BnMA), and dodecyl methacrylate (C$_{12}$-MA) were fractionally distilled over CaH$_2$ under reduced pressure in a nitrogen atmosphere.

Deuterated methyl methacrylate (MMA-d_8) was prepared as follows: To a D$_2$O solution (82.6 mL) of NaCN (0.96 mol) was added acetone-d_6 (0.68 mol) at room temperature, followed by a mixture of D$_2$O (88.3 mL) and D$_2$SO$_4$ (62.6 g, 0.63 mol) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h, and the organic layer extracted with ether was dried over magnesium sulfate, and subjected to fractional distillation under reduced pressure, affording acetone cyanohydrin-d_7 in 63% yield (39.4 g). Acetone cyanohydrin-d_7 was added dropwise at 60 °C to 98% H$_2$SO$_4$ (34.1 g, 0.35 mol) containing fuming H$_2$SO$_4$ (15.1 g) in the presence of metallic Cu (1.5 g) and CuCl (0.5 g), and the mixture was stirred at 140 °C for 1 h. After cooling to 100 °C, methanol-d_4 (0.78 mol) was added to the mixture, and stirring was continued for 20 h at the same temperature. Then, the reaction mixture was allowed to cool to room temperature, and water (49.6 mL) was added. The organic phase separated was dried over molecular sieves 4A, and fractionally distilled under nitrogen, affording MMA-d_8 in 10.4% yield (4.8 g), which was further distilled in the presence of triethylaluminum under nitrogen before use.[9]

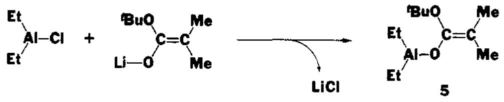
Trimethylaluminum (Me$_3$Al) and triisobutylaluminum (^{i}Bu$_3$Al) were fractionally distilled under reduced pressure in a nitrogen atmosphere.

Triphenylaluminum (Ph$_3$Al) was synthesized as follows: To an ether solution (24 mL) of AlCl$_3$ (53 mmol, 7.1 g) was added a hexane solution (1.8 M, 88 mL) of phenyllithium (159 mmol) at −78 °C by a hypodermic syringe in a nitrogen stream, and the mixture was stirred at −78 °C for 1 h under nitrogen and then allowed to warm to room temperature. After additional stirring for 30 min at room temperature, the reaction mixture was filtered under nitrogen to remove insoluble LiCl. Then, volatile fractions were removed under reduced pressure to leave a white powder, which was subjected to sublimation in vacuo, followed by recrystallization from benzene under nitrogen, affording Ph$_3$Al as white crystals (1.8 g, 13% yield based on AlCl$_3$).[10]

Scheme V



Scheme VI



Preparation of Methylaluminum 5,10,15,20-Tetraphenylporphine (1, X = Me) (Scheme IV). To a round-bottomed flask (50 mL) equipped with a three-way stopcock containing TPPH$_2$ (0.25 mmol) under dry nitrogen were successively added CH$_2$Cl$_2$ (10 mL) and Me$_3$Al (1.2 equiv, 0.03 mL) by means of hypodermic syringes in a nitrogen stream, and the mixture was stirred for 1 h in a nitrogen atmosphere. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave 1 (X = Me) as a purple powder.[11]

Preparation of Organoaluminum Olates. Methylaluminum Bis(2,4,6-tri-*tert*-butylphenolate) (3f) (Scheme V). To a 100-mL round-bottomed flask equipped with a three-way stopcock, containing 2,4,6-tri-*tert*-butylphenol (40.8 mmol, 10.7 g), were successively added hexane (52 mL) and Me$_3$Al (20.4 mmol, 1.96 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h, whereupon white precipitates were formed. The suspernatant was decanted, and the residual liquid phase (40 mL) separated was taken away by a syringe from the flask under nitrogen. Then, hexane (30 mL) was added to the residue at 60 °C, affording a clear solution, which was allowed to cool to room temperature, giving **3f** as white crystals in 45% yield (5.2 g). The crystals were dried under reduced pressure at room temperature under nitrogen.[12]

Other organoaluminum compounds (**3a–3e, 3g–3i, 4a, and 4b**) were similarly synthesized by the reactions of Me$_3$Al with the corresponding phenols or alcohols (2 equiv) in C$_6$H$_6$ or CH$_2$Cl$_2$ under nitrogen, and the reaction mixtures were used for polymerization.

1-*tert*-Butoxy-1-[(diethylaluminio)oxy]-2-methylpropene (5) (Scheme VI). To a 50-mL round-bottomed flask equipped with a three-way stopcock, containing a THF solution (4.5 mL) of diisopropylamine (5 mmol, 0.7 mL), was added dropwise a hexane solution (3.1 mL) of ^{n}BuLi (5 mmol) at −78 °C by a hypodermic syringe in a nitrogen stream, and the mixture was stirred at the same temperature for 30 min. Then, *tert*-butyl isobutyrate (5 mmol, 0.82 mL) was added by means of a syringe to the reaction mixture at −78 °C. After stirring for 30 min at −40 °C, Et$_2$AlCl (5 mmol, 0.63 mL) was added over a period of 5 min to the reaction mixture. Stirring the reaction mixture at −40 °C for 15 min led to the formation of **5** with deposition of LiCl.[13] The resulting suspension was settled, and the supernatant liquid phase separated was used for polymerization.

Polymerization. Polymerizations of Alkyl Methacrylates by the Methylaluminum Porphyrin–Organoaluminum Systems. A representative example is given below by the polymerization of methyl methacrylate (MMA) with (TPP)AlMe (1, X = Me). To a 100-mL round-bottomed flask attached to a three-way stopcock containing a CH$_2$Cl$_2$ solution (8 mL) of 1 (X = Me, 0.2 mmol) was added MMA (43.4 mmol, 4.6 mL) by a syringe in a nitrogen stream. This mixture was illuminated by xenon arc light (300 W) through a filter to cut out light of wavelength shorter than 420 nm. After 2.5-h irradiation at 35 °C, methylaluminum bis(2,4-di-*tert*-butylphenolate) (**3b**) was added (3 equiv with respect to 1 (X = Me)) at room temperature under diffuse light. An aliquot of the reaction mixture was taken out by a syringe in a nitrogen stream, and subjected to ^{1}H NMR and gel permeation chromatography (GPC) analyses to determine the monomer conversion and the average molecular weights of the produced polymer, respectively.

Two-Stage Polymerization of MMA in the Presence of Lewis Acid (3f). To a 100-mL round-bottomed flask attached to a three-way stopcock containing a CH$_2$Cl$_2$ solution (16 mL) of 1 (0.4 mmol) was added MMA (20 mmol, 2.1 mL) by a syringe in a nitrogen stream. The mixture was irradiated with xenon arc light (λ > 420 nm) at 35 °C. After 3-h irradiation, methylalu-

Table I. Polymerization of Methyl Methacrylate (MMA) via an Enolatoaluminum Porphyrin (2, R = Me) in the Presence of Methylaluminum Diolates ($MeAlX_2$)[a]

run	$MeAlX_2$	$[MeAlX_2]_0$/ $[2]_0$	time/ min	conv[b]/ %	M_n[c]	M_w/M_n[c]
1	**3a**	3	0.5	100	21 500	1.10
2	**3b**	0.2	3	100	26 300	1.07
3	**3b**	2	10	100	23 700	1.07
4	**3c**	3	0.5	100	22 000	1.10
5	**3d**	3	0.75	92	27 700	1.42
6	**3f**	3	5	100	24 300	1.11
7	**3g**	0.5	0.5	74	31 800	1.16
8	**3h**	0.5	60	7		
9	**3i**	0.5	60	8		
10	**4a**	3	60	6		
11	**4b**	3	60	91	24 000	1.04

[a] In CH_2Cl_2 under nitrogen, $[MMA]_0/[1\ (X = Me)]_0 = 200$, $[1\ (X = Me)]_0 = 16.2$ mM, $[1\ (X = Me)]_0 = [2\ (R = Me)]_0$. [b] Determined by ^1H NMR analysis of the reaction mixture. [c] Estimated by GPC based on polystyrene standards.

minum bis(2,4,6-tri-*tert*-butylphenolate) (**3f**) was added (1 equiv with respect to **1**) at room temperature under diffuse light. After 90 s, an aliquot of the reaction mixture was taken out by a syringe in a nitrogen stream and subjected to NMR and GPC analyses to confirm the complete monomer consumption and to estimate the average molecular weights of the produced polymer, respectively. The polymerization mixture remaining in the flask was allowed to stand at 25 °C for 4 h, and then the second part of the MMA (80 mmol) was fed. After 60 s, MeOH (5 mL) was added to the flask, and the reaction mixture was subjected to ^1H NMR and GPC analyses.

Measurements. Gel permeation chromatography (GPC) measurements were performed at 40 °C on a Toyo Soda Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector and a variable-wavelength UV–vis 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 = 2 890 000 (M_w/M_n = 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). ^1H and ^{13}C NMR measurements were performed in C_6D_6, $CDCl_3$, or CD_2Cl_2 using a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to C_6H_6 (δ 7.40), $CHCl_3$ (δ 7.28), or CH_2Cl_2 (δ 5.30), for ^1H, and CD_2Cl_2 (δ 54.0) for ^{13}C as internal standards.

Results and Discussion

Polymerization of Methacrylic Esters via Enolatoaluminum Porphyrins (2) in the Presence of Methylaluminum Diphenolates (3) and Dialcoholates (4). The polymerization of methyl methacrylate (MMA) was initiated with methylaluminum tetraphenylporphyrin (**1**, X = Me) under irradiation with visible light, and at the monomer conversion of 6–8%, Lewis acids such as methylaluminum diphenolates (**3a**–**3i**) and methylaluminum dialcoholates (**4a**, **4b**) were added to the system (Table I). Among the methylaluminum diphenolates examined, **3a**–**3g** having substituents at the *ortho* positions of the phenolate ligands were quite effective for acclerating the polymerization (runs 1–7), allowing the formation of narrow MWD PMMAs with M_n values in fair agreement with that (20 000) expected from the initial mole ratio of MMA to **1** (X = Me) of 200. In terms of both the power of acceleration and the cleanness of polymerization, the diphenolates having *o*-*tert*-butyl substituents (**3a**–**3c**, **3e**, and **3f**) are the most favorable. On the other hand, when methylaluminum diphenolates having no *ortho* substituents (**3h** and **3i**) were used, the polymerization was terminated just after they were added to the system (runs 8 and 9). As for methylaluminum dialcoholates (**4a**, **4b**), the tertiary alcoholate (**4b**) gave a satisfactory result (run 11), whereas use of the secondary alcoholate (**4a**) resulted in termination of chain growth (run 10). In runs 1–7, the dark red-purple color of the polymerization system, characteristic of the growing enolate species (**2**, R = Me), was observed to remain unchanged throughout the polymerization, while in runs 8–10, the polymerization systems immediately turned bright red-purple characteristic of **1** (X = OR, OAr) upon addition of the Lewis acids.

Table II. Polymerization of Methyl Methacrylate (MMA) via an Enolatoaluminum Porphyrin (2, R = Me) in the Presence of Methylaluminum Bis(2,4-di-*tert*-butylphenolate) (3b)[a]

run	$[3b]_0$/ $[2]_0$	time /s	conv[b]/ %	M_n[c] ($M_{n_{calcd}}$)	M_w/M_n[c]	magnitude of acceleration[d]
1	0.2	5	21	5500 (4300)	1.09	1400
2	1.0	5	62	14 400 (12 100)	1.10	14 000
3	3.0	3	100	25 500 (21 700)	1.07	46 200

[a] In CH_2Cl_2 under nitrogen, $[MMA]_0/[1\ (X = Me)]_0 = 200$, $[1\ (X = Me)]_0 = 16.2$ mM, $[1\ (X = Me)]_0 = [2\ (R = Me)]_0$. [b] Determined by ^1H NMR analysis of the reaction mixture. [c] Estimated by GPC based on polystyrene standards. [d] Mole ratio of MMA reacted per second before and after addition of **3b**.

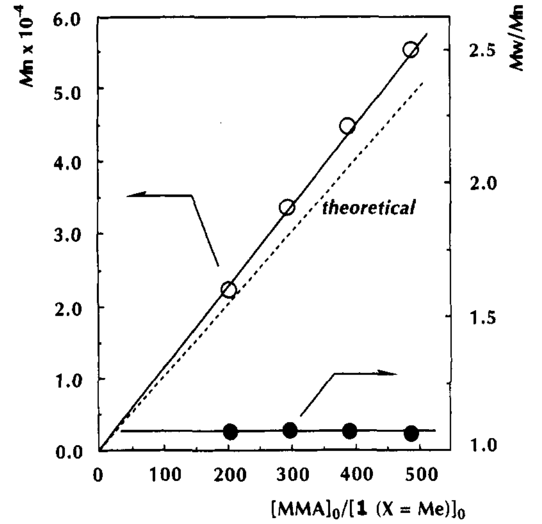


Figure 1. Polymerization of methyl methacrylate (MMA) initiated with (TPP)AlMe (**1**, X = Me) via an enolatoaluminum porphyrin (**2**, R = Me) in the presence of methylaluminum bis(2-*tert*-butyl-4-methoxyphenolate) (**3c**) ($[3c]_0/[2]_0 = 0.5$) in CH_2Cl_2 at room temperature. Relationship between M_n (●) (M_w/M_n (○)) of the polymer and the initial monomer-to-initiator mole ratio ($[MMA]_0/[1\ (X = Me)]_0$) at 100% conversion.

In the polymerization of MMA initiated with **1** (X = Me) ($[MMA]_0/[1]_0 = 200$), the degree of acceleration became more pronounced as the amount of **3b** was increased from 0.2 to 1.0 to 3.0 equiv with respect to **2** (R = Me) (Table II). If the added **3b** initiates the polymerization, the number of polymer molecules produced should increase proportionally to the amount of **3b**, and consequently, the M_n value should decrease. However, irrespective of the ratio of **3b** to **2**, all the polymers formed were of narrow MWD, and the observed M_n values were always close to those expected from the mole ratios of the monomer reacted to **2**. As shown in Figure 1, the M_n of the polymer could be precisely controlled by changing the monomer-to-initiator ratio in the presence of 0.5 equiv of **3c** with respect to the growing species **2** (R = Me). These results indicate that the added **3** does not initiate but only accelerates the polymerization. In this regard, all the produced polymers in Table II were silent in GPC when monitored at 263 nm (2,4-di-*tert*-butylphenol, λ_{max} 263 nm; anisole, 269 nm), indicating no incorporation of the

Table III. Polymerization of Methacrylic Esters via Enolatoaluminum Porphyrins (2) in the Presence of Methylaluminum Bis(2-*tert*-butyl-4-methoxyphenolate) (3c)^a

run	monomer	time/s	conv^b/%	$M_n{}^c$ ($M_{n_{calcd}}$)	$M_w/M_n{}^c$
1	EMA	30	100	27 700 (23 000)	1.09
2	^{i}PMA	30	100	30 900 (25 600)	1.10
3	^{n}BMA	30	100	34 900 (28 400)	1.07
4	^{i}BMA	30	100	36 300 (28 400)	1.07
5	^{t}BMA	90	11		
6	BnMA	90	100	32 900 (35 200)	1.08
7	C_{12}MA	90	64	30 600 (32 600)	1.09

^{a} In CH_2Cl_2 under nitrogen, [monomer]$_0$/[1 (X = Me)]$_0$/[**3c**]$_0$ = 200/1.0/0.5, [1 (X = Me)]$_0$ = 16.2 mM. ^{b} Determined by ^{1}H NMR analysis of the reaction mixture. ^{c} Estimated by GPC based on polystyrene standards.

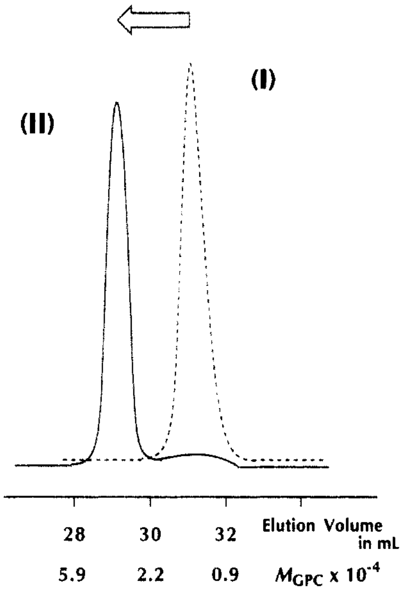


Figure 2. Two-stage polymerization of methyl methacrylate (MMA) in CH_2Cl_2 at room temperature with the enolatoaluminum porphyrin (2, R = Me)–methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**3f**) (1.0/1.0) system. GPC profiles of the polymers formed at the first stage (I) ([MMA]$_0$/[1 (X = Me)]$_0$ = 50, 100% conversion, M_n = 7000, M_w/M_n = 1.12) and the second stage (II) ([MMA]$_0$/[2]$_0$ = 200, 100% conversion, M_n = 47 600, M_w/M_n = 1.05).

phenolate unit of **3b** into the polymer terminal. Furthermore, with **3b** alone, the polymerization of MMA, did not take place at all under identical conditions.

In addition to MMA, a variety of methacrylic esters could be polymerized rapidly to the corresponding polymers with narrow MWDs in the presence of methylaluminum bis(2-*tert*-butyl-4-methoxyphenolate) (**3c**) (1 equiv relative to **2**). The successful examples include ethyl methacrylate (EMA), isopropyl methacrylate (^{i}PMA), *n*-butyl methacrylate (^{n}BMA), isobutyl methacrylate (^{i}BMA), benzyl methacrylate (BnMA), and dodecyl methacrylate (C_{12}MA), where the M_n values were all close to the predicted values (M_n(calcd)) with the M_w/M_n ratios below 1.1 (runs 1–4, 6, and 7, Table III). The polymerization of *tert*-butyl methacrylate (^{t}BMA) (run 5) is an only exceptional case, where the monomer conversion hardly increased even after 24 h.

The polymerization in the presence of bulky methylaluminum diphenolates proceeds with living character. Clear evidence for this was given by the sequential two-stage polymerization of MMA with the **2** (R = Me)–**3f** (1 equiv/1 equiv) system in CH_2Cl_2 at room temperature (Figure 2), where 50 equiv of MMA with respect to **1** (X = Me) were polymerized up to 100% conversion (90 s) at the first stage, and after a 4-h interval at 25 °C, 200 equiv of MMA were charged to the mixture. In spite of a long interval between the first and second monomer feeds, the second-stage polymerization ensued with heat evolution, and was completed within 60 s. The GPC profile showed a clear increase in molecular weight of the polymer from 7000 (the first stage, Figure 2 (I)) to 47 600 (the second stage (II)), retaining the narrow MWD (M_w/M_n, from 1.12 to 1.05).

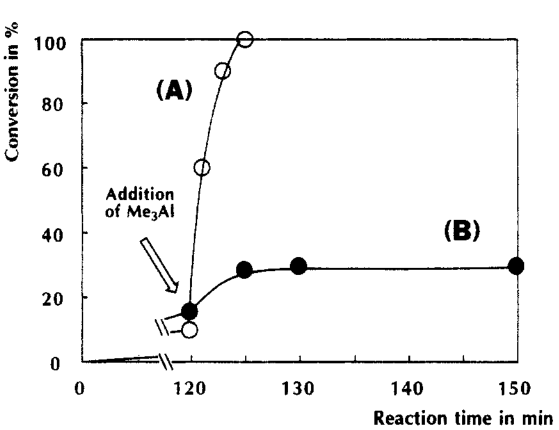


Figure 3. Polymerizations of *tert*-butyl methacrylate (^{t}BMA) (A) and methyl methacrylate (MMA) (B) initiated with (TPP)AlMe (1, X = Me; [monomer]$_0$/[1 (X = Me)]$_0$ = 100, [1 (X = Me)]$_0$ = 17.8 (A) and 19.6 (B) mM, CH_2Cl_2 as solvent, room temperature). Effect of trimethylaluminum (Me_3Al) ([Me_3Al]$_0$/[2]$_0$ = 3.0) on the rate of polymerization.

Polymerization of Methacrylic Esters via Enolatoaluminum Porphyrins (2) in the Presence of Trialkyl- and Triarylaluminum Compounds. Similarly to methylaluminum diphenolates (**3**), trialkylaluminums such as trimethylaluminum (Me_3Al), triisobutylaluminum ($^iBu_3Al$), and triphenylaluminum (Ph_3Al), by themselves, have no ability to initiate the polymerization of methacrylic esters under ordinary conditions. For investigating the acceleration effects of trialkylaluminums, the polymerization of *tert*-butyl methacrylate (^{t}BMA) was first chosen, since it proceeds slowly even in the presence of methylaluminum diphenolates (**3**) as Lewis acids. However, quite unexpectedly, the polymerization was dramatically accelerated when Me_3Al was added to the system. As exemplified in Figure 3A, the polymerization of ^{t}BMA (100 equiv) with **1** (X = Me), which had proceeded to 7% conversion by 2-h irradiation at 35 °C, proceeded rapidly with vigorous heat evolution as soon as 3 equiv of Me_3Al with respect to **2** (R = ^{t}Bu) was added at room temperature, and the complete consumption of ^{t}BMA was attained within only 5 min. The produced polymer exhibited a unimodal, sharp GPC peak, and the M_n value increased linearly along the theoretical line (dotted, Figure 4) calculated from the monomer-to-initiator (**1**, X = Me) mole ratio, keeping the M_w/M_n ratio in the range 1.05–1.06. It was also noted here that the addition of Me_3Al is accompanied by a rapid color change of the system from dark red-purple due to **2** to blue-purple characteristic of methylaluminum tetraphenylporphyrin (**1**, X = Me).

In contrast, when the monomer was methyl methacrylate (MMA), the polymerization was terminated upon addition of Me_3Al under similar conditions. For example, when 3 equiv of Me_3Al with respect to **2** (R = Me) was added to the system ([MMA]$_0$/[1 (X = Me)]$_0$ = 100, 9% conversion), heat evolution, although observed at the very early stage, subsided within only 1–2 min. At this stage, the color of the solution had already turned blue-purple. The monomer conversion after 5 min was only 30%, and it no longer increased upon prolonged reaction for 2 h (Figure 3B).

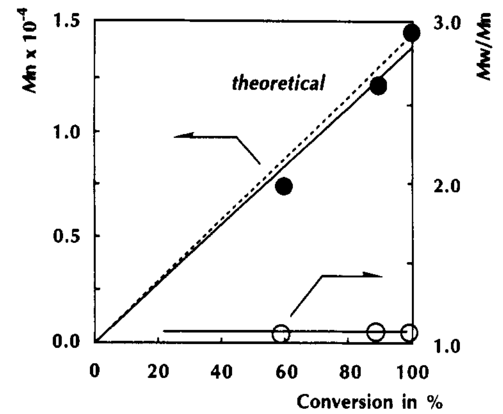


Figure 4. Polymerization of *tert*-butyl methacrylate (^{t}BMA) initiated with (TPP)AlMe (1, X = Me) via an enolatoaluminum porphyrin (2, R = ^{t}Bu) in the presence of trimethylaluminum (Me$_3$Al; [^{t}BMA]$_0$/[1 (X = Me)]$_0$/[Me$_3$Al]$_0$ = 100/1.0/3.0, [1]$_0$ = 17.8 mM, CH$_2$Cl$_2$ as solvent, room temperature). Relationship between M_n (●) (M_w/M_n (○)) of the polymer and conversion.

Table IV. Polymerization of Methyl Methacrylate (MMA) via an Enolatoaluminum Porphyrin (2, R = Me) in the Presence of Trialkylaluminums (R$_3$Al)[a]

run	R$_3$Al	time[d]/min	conv[b]/%	M_n[c]	M_w/M_n[c]
1	Me$_3$Al	0	4		
		10	9		
		30	9		
2	^{i}Bu$_3$Al	0	6		
		10	63	19 500	1.37
		30	64	20 200	1.41
3	Ph$_3$Al	0	3		
		30	46	8600	1.19
		60	79	16 700	1.17
		90	100	22 300	1.18

[a] In CH$_2$Cl$_2$ under nitrogen, [MMA]$_0$/[1 (X = Me)]$_0$/[R$_3$Al]$_0$ = 200/1.0/3.0, [1 (X = Me)]$_0$ = 16.2 mM. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Estimated by GPC based on polystyrene standards. [d] After addition of R$_3$Al.

Use of bulkier ^{i}Bu$_3$Al in place of Me$_3$Al for the polymerization of MMA ([MMA]$_0$/[2 (R = Me)]$_0$/[^{i}Bu$_3$Al]$_0$ = 200/1.0/3.0) gave an essentially similar result, although the monomer conversion finally attained was higher (64%) (run 2, Table IV). The M_n of the polymer formed at this conversion (20 200) was much higher than that expected from the ratio of MMA reacted to 1 (X = Me) (12 800), and the MWD was broad (M_w/M_n = 1.41). On the contrary, when Ph$_3$Al (3 equiv with respect to 2 (R = Me)) was added at room temperature to the system ([MMA]$_0$/[1]$_0$ = 200, 3% conversion), a fairly rapid polymerization took place with heat evolution, and the monomer was completely consumed within 90 min (run 3, Table IV). The M_n of the produced polymer (22 300) was close to the expected value of 20 000, and the MWD was satisfactorily narrow (M_w/M_n = 1.18). In this case, the system retained the original color characteristic of 2 (R = Me) throughout the polymerization.

At a lower temperature, in contrast, even Me$_3$Al was able to accelerate the polymerization of MMA. At −40 °C, for example, the polymerization with 1 (X = Me) alone as initiator ([MMA]$_0$/[1 (X = Me]$_0$ = 100) in CH$_2$Cl$_2$ proceeded to only 11% conversion in 1 h, but after 3 equiv of Me$_3$Al was added to the system, it attained 91% conversion in the next 1 h. Furthermore, the polymer formed here had a narrow MWD as indicated by the M_w/M_n ratio of 1.17, and the M_n value (9700) was close to that expected (9100) from the mole ratio of the monomer reacted to the initiator. In this case, the polymerization was observed to proceed without any change in color of the system.

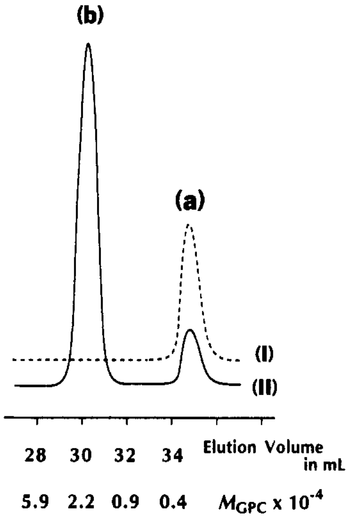


Figure 5. Polymerizations of *tert*-butyl methacrylate (^{t}BMA) initiated with (TPP)AlMe (1, X = Me; [^{t}BMA]$_0$/[1 (X = Me)]$_0$ = 100, [1]$_0$ = 17.8 mM, CH$_2$Cl$_2$ as solvent). GPC profiles of the polymers formed (I) after 90-h irradiation at 35 °C, 25% conversion, and (II) 60 min after addition of trimethylaluminum (Me$_3$Al; [Me$_3$Al]$_0$/[2 (R = ^{t}Bu)]$_0$ = 0.25) at room temperature, 100% conversion.

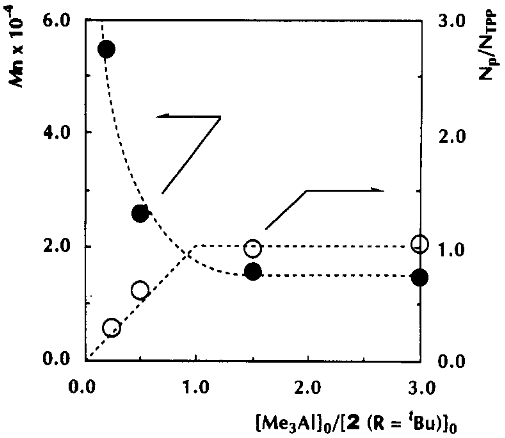


Figure 6. Polymerization of *tert*-butyl methacrylate (^{t}BMA) initiated with (TPP)AlMe (1, X = Me) via an enolatoaluminum porphyrin (2, R = ^{t}Bu) in the presence of trimethylaluminum (Me$_3$Al; [^{t}BMA]$_0$/[1 (X = Me)]$_0$ = 100, [1]$_0$ = 17.8 mM, CH$_2$Cl$_2$ as solvent, room temperature). Correlations of the number-average molecular weight (M_n) and the ratio of the numbers of polymer molecules to 2 (N_p/N_{TPP}) with the initial mole ratio of Me$_3$Al to 2.

Thus, the polymerization temperature is one of the important factors to achieve the clean and rapid polymerization with trialkylaluminums. In this regard, when 0.25 equiv of Me$_3$Al with respect to the growing species (2) was added *at room temperature* to the polymerization system of ^{t}BMA ([^{t}BMA]$_0$/[1 (X = Me)]$_0$ = 100) at 25% conversion, a part of the prepolymer (peak a in Figure 5 (I)) remained unreacted even after the complete monomer consumption was attained (Figure 5 (II)). When the amount of Me$_3$Al relative to 2 was increased from 0.25 to 0.5, peak a became much smaller, while the molecular weight corresponding to the major peak (peak b) decreased. On the other hand, when the ratio [Me$_3$Al]$_0$/[2]$_0$ exceeded unity (1.5 and 3.0), peak a disappeared completely to give a unimodal MWD product. At [Me$_3$Al]$_0$/[2]$_0$ $\geq$ 1, the M_n value of the final product was no longer affected by the ratio [Me$_3$Al]$_0$/[2]$_0$ (Figure 6). Thus, the number of polymer molecules versus 2 (N_p/N_{TPP}), calculated from

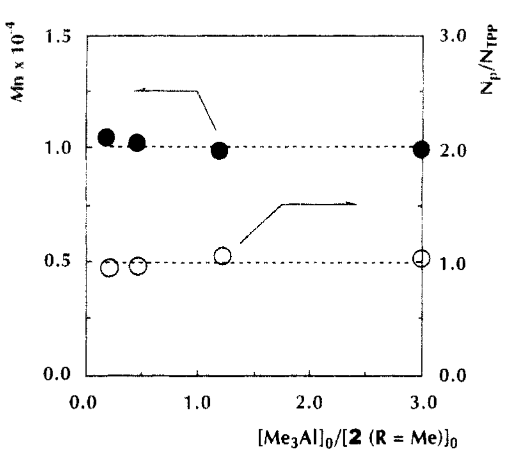


Figure 7. Polymerization of methyl methacrylate (MMA) initiated with (TPP)AlMe (1, X = Me) via an enolatoaluminum porphyrin (2, R = Me) in the presence of trimethylaluminum (Me_3Al; $[MMA]_0/[1\ (X = Me)]_0 = 100$, $[1]_0 = 19.6$ mM, CH_2Cl_2 as solvent, −40 °C). Correlations of the number-average molecular weight (M_n) and the ratio of the numbers of polymer molecules to 2 (N_p/N_{TPP}) with the initial mole ratio of Me_3Al to 2.

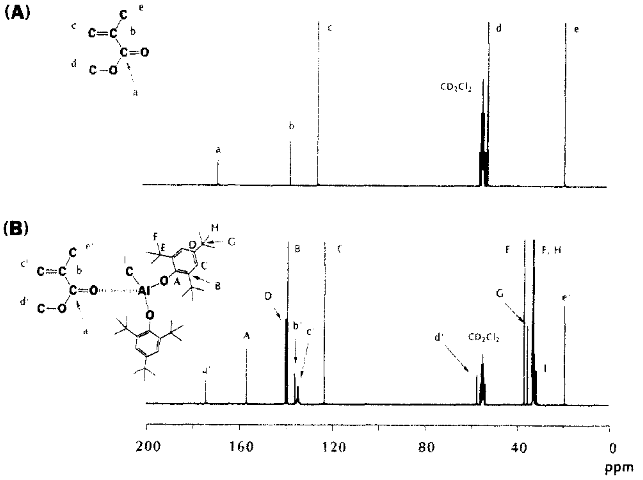
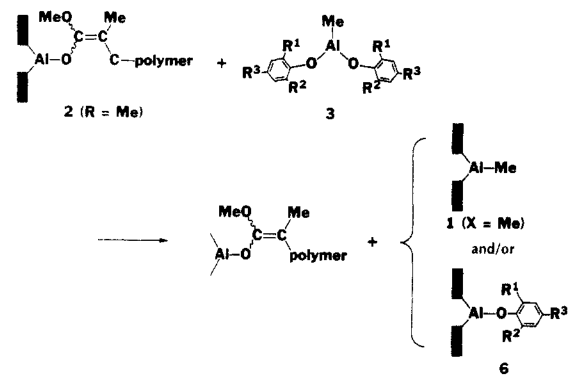


Figure 8. ^{13}C NMR spectra in CD_2Cl_2 at 25 °C of (A) methyl methacrylate (MMA) and (B) an equimolar mixture of MMA and methylaluminum bis(2,4,6-*tert*-butylphenolate) (3f).

the M_n of the polymer corresponding to peak b (Figure 5 (II)) and the initial monomer-to-initiator mole ratio, increased with increasing the ratio $[Me_3Al]_0/[2]_0$ up to unity, but no further increase in N_p/N_{TPP} resulted after the ratio $[Me_3Al]_0/[2]_0$ exceeded unity. In sharp contrast, in the case of the polymerization of MMA at −40 °C with varying mole ratios of $[Me_3Al]_0/[2]_0$, only the rate of polymerization was changed, but in any case the produced polymer exhibited a unimodal, sharp GPC peak with the M_n value close to that expected from the formation of one polymer molecule from every molecule of 2 (R = Me) (Figure 7).

NMR Studies. (I) Interaction between Monomer and Organoaluminum Compounds. In the ^1H NMR spectrum of an equimolar mixture of MMA and 3f in CD_2Cl_2 at 25 °C, all the signals due to MMA clearly shifted downfield from those of MMA alone, where the signals due to CH_2 (δ 6.00 and 5.49), CH_3O (δ 3.66), and CH_3 (δ 1.86) of MMA appeared at δ 6.41 and 5.81, 3.92, and 1.98, respectively. In the ^{13}C NMR spectrum, the signals due to, *e.g.*, $C{=}O$ (a, δ 168.3), CH_2 (c, δ 125.6), and CH_3O (d, 52.2) of MMA also shifted downfield to δ 173.3 (a′), 133.8 (c′), and 56.5 (d′), respectively, in the presence of an equimolar amount of 3f (Figure 8B). As for the signals of 3f,[14] the $C{-}O$ signal of the phenolate ligands most clearly shifted from δ 152.6 to δ 155.7 (A). These

Scheme VII



observations demonstrate the occurrence of a coordinative interaction between the carbonyl group of MMA and 3f.

In the ^{13}C NMR spectrum of an equimolar mixture of MMA and Me_3Al in CD_2Cl_2 at 25 °C, a downfield shift was again observed for the $C{=}O$ signal of MMA from δ 168.3 to δ 172.2. On the other hand, for an equimolar mixture of MMA and Ph_3Al, the downfield shift of the MMA $C{=}O$ signal was very small (0.1 ppm) compared with those for the MMA–3f and MMA–Me_3Al systems under similar conditions.

(II) Ligand Exchange Reaction between 2 and Organoaluminum Compounds. A C_6D_6 solution of an equimolar mixture of the living polymer of MMA (2, R = Me; $[MMA]_0/[1\ (X = Me)]_0 = 10$, 100% conversion) and 3f was studied by ^1H NMR. If the ligand exchange reaction took place between 2 (R = Me) and 3f, 1 (X = Me) and/or 6 ($R^1 = R^2 = R^3 = {}^tBu$) should be formed (Scheme VII), which are easily detectable by the characteristic signals at δ −5.79 and −0.26 due respectively to the MeAl group of 1 (X = Me) and the ^{t}Bu group of 6 ($R^1 = R^2 = R^3 = {}^tBu$). However, throughout the observation over a period of 24 h at 25 °C, neither of these two signals was detected.

In sharp contrast, when Me_3Al was mixed with 2 (R = ^{t}Bu; $[{}^tBMA]_0/[1\ (X = Me)]_0 = 5$, 100% conversion) under similar conditions, the color of the solution immediately turned from dark red-purple to blue-purple. The ^1H NMR spectrum of this mixture in C_6D_6 showed the appearance of a new signal due to 1 (X = Me) (f, δ −5.79) with the intensity ratio of 3:8 to that of the pyrrole β protons (8H) of the porphyrin ligand, while a characteristic signal at δ −0.33 ppm due to the enolate ^{t}Bu group of 2 (R = ^{t}Bu) (a)[15] completely disappeared (Figure 9). This observation indicates the occurrence of a rapid ligand exchange between 2 (R = ^{t}Bu) and Me_3Al (Scheme VIII). The ligand exchange reaction also occurred in the 2 (R = Me)–Me_3Al system. Figure 10A shows the ^1H NMR spectrum in CD_2Cl_2 at 25 °C of 2 (PMMA-d_8), prepared from MMA-d_8 and 1 (X = Me) with the ratio of 10:1, where only the terminal methyl group originating from 1 (X = CH_3) (δ 0.70) is observed besides the signals due to the porphyrin ligand of the aluminum enolate species (a, δ 9.10 (pyrrole β-*H*); b, δ 8.21 (Pho *o*-*H*); c, δ 7.80 Ph *m*,*p*-*H*)). Upon addition of 3 equiv of Me_3Al at 25 °C to this enolate solution, the spectrum was changed to Figure 10B, where a new signal (f′) due to the *Me*Al group of 1 (X = Me) appeared in addition to some new signals (e′, g′) assignable to the *Me*Al groups of the dimethylaluminum enolate and excess Me_3Al. Moreover, the signals due to the porphyrin ligand shifted slightly but definitely to those for 1 (X = Me) (a′, δ 9.05 (pyrrole β-*H*); b′, δ 8.19 (Ph *o*-*H*); c′, δ 7.77 (Ph *m*,*p*-*H*)), although the signal due to the terminal methyl group shifted only little from d to d′, as expected.

Contrary to the above results at 25 °C, the ligand exchange reaction (Scheme VIII) was found to be greatly

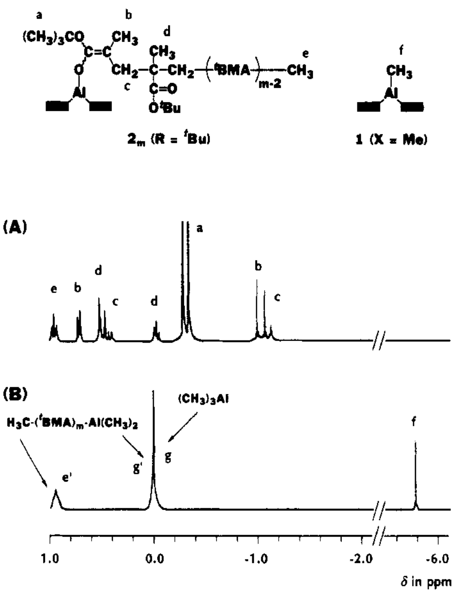


Figure 9. ^{1}H NMR spectra in CD_2Cl_2 at 25 °C of (A) the enolatoaluminum porphyrin (2, R = ^{t}Bu; [^{t}BMA]$_0$/[1 (X = Me)]$_0$ = 5, 100% conversion) and (B) the reaction mixture of 2 (R = ^{t}Bu) and trimethylaluminum (Me_3Al; [Me_3Al]$_0$/[2]$_0$ = 3.0, [2]$_0$ = 25.0 mM).

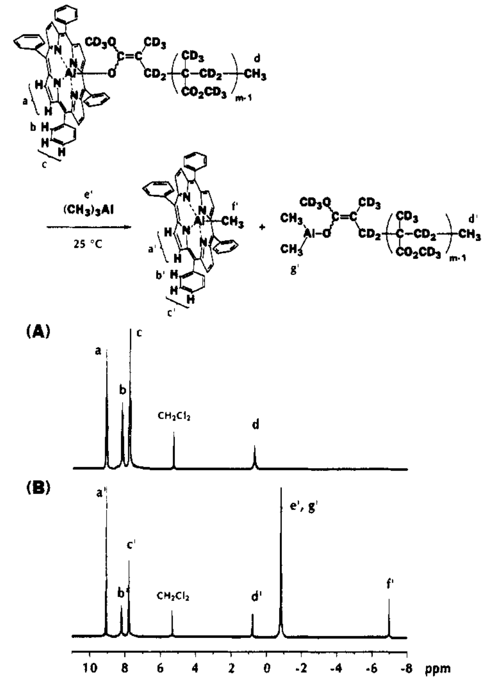
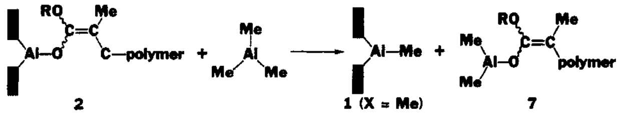


Figure 10. ^{1}H NMR spectra in CD_2Cl_2 at 25 °C of (A) the enolatoaluminum porphyrin (2, PMMA-d_8; [MMA-d_8]$_0$/[1 (X = Me)]$_0$ = 10, 100% conversion) and (B) the reaction mixture of 2 (PMMA-d_8) and trimethylaluminum (Me_3Al; [Me_3Al]$_0$/[2]$_0$ = 3.0, [2]$_0$ = 25.0 mM).

Scheme VIII



retarded by lowering the temperature. Figure 11 shows the change in mole fraction of 1 (X = Me): [1 (X = Me)]/([1 (X = Me)] + [2 (PMMA-d_8)]), as determined from the relative intensity of the signals f′ to a and a′ (Figure 10), after addition of 3 equiv of Me_3Al to 2 (PMMA-d_8) at −40 °C. Although a trace amount of 1 (X = Me) was accidentally generated at the initial stage until the probe temperature was settled, its mole fraction was never increased throughout the observation over a period of 75 min. On the other hand, when the probe temperature jumped at 25 °C, a steep increase in the mole fraction of 1 (X = Me) was observed.

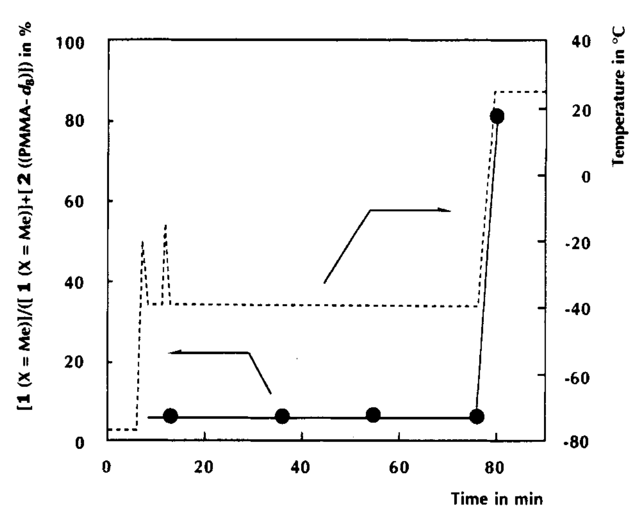


Figure 11. Time course of the reaction of the enolatoaluminum porphyrin (2, PMMA-d_8; [MMA-d_8]$_0$/[1 (X = Me)]$_0$ = 10, 100% conversion) with trimethylaluminum (Me_3Al) in CD_2Cl_2 at −40 to +25 °C ([Me_3Al]$_0$/[2]$_0$ = 3.0, [2]$_0$ = 25.0 mM), in an NMR tube (Φ = 5 mm). [1 (X = Me)]/([1 (X = Me)] + [2 ((PMMA-d_8)]: determined from the relative intensity of the ^{1}H NMR signals at δ −6.97 (1, $AlCH_3$) to δ 9.0–9.1 (f′ to a and a′ in Figure 10).

Polymerizations of Methacrylic Esters Initiated with 1-*tert*-Butoxy-1-[(diethylaluminio)oxy]-2-methylpropene (5). In connection with the ligand exchange reaction between the enolatoaluminum porphyrin (2) with Me_3Al (Scheme VIII), the diethylaluminum enolate (5), a model compound of the exchanged product, was synthesized according to Scheme VI, and tested as initiator for the polymerizations of methyl methacrylate (MMA) and *tert*-butyl methacrylate (^{t}BMA). For example, when 100 equiv of MMA was added to a CH_2Cl_2 solution of 5 at room temperature, the polymerization was actually initiated with heat evolution, but terminated only at 10.3% conversion, affording a low molecular weight PMMA possessing a very broad MWD as indicated by the M_w/M_n ratio of 5.6. On the other hand, as for ^{t}BMA under similar conditions ([^{t}BMA]$_0$/[5]$_0$ = 100), the enolate (5) brought about a very rapid polymerization, and the complete monomer consumption was attained within minutes, affording the narrow MWD polymer (M_w/M_n = 1.05) with an M_n of 34 600. The observed M_n value, although higher than expected, was observed to increase almost linearly to 77 100 and 102 000, retaining the narrow MWD (M_w/M_n = 1.05–1.13),[16] when the initial monomer-to-initiator mole ratio was increased to 200 and 300, respectively.

Mechanistic Aspects. To summarize the above results (Tables I, II, and IV), methylaluminum *ortho*-substituted phenolates (**3a**–**3g**), methylaluminum bis(triphenylmethanolate) (**4b**), and Ph_3Al as Lewis acid additives can dramatically acclerate, even at room temperature, the polymerization of MMA via 2 without damaging the living character of polymerization. On the other hand, when methylaluminum phenolates bearing no *ortho* substituents (**3h**, **3i**), methylaluminum bis(diphenylmethanolate) (**4a**), Me_3Al, and ^{i}Bu$_3$Al are used under similar conditions, the polymerization is terminated. When the temperature is lowered to, *e.g.*, −40 °C, even Me_3Al is usable for accelerating the polymerization of MMA without any loss of the living character. Together with the results of the NMR

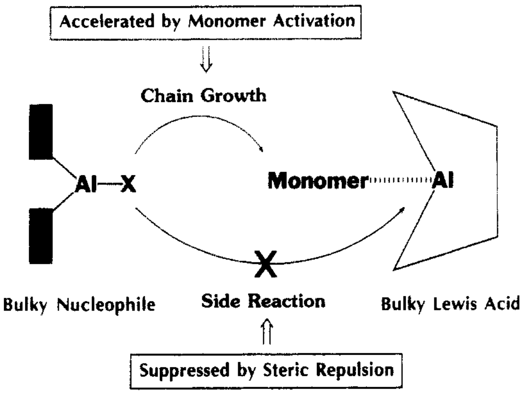


Figure 12. Basic concept of the Lewis acid-assisted "high-speed living anionic polymerization" of methacrylic esters.

investigations, the accelerated living polymerization of MMA with the 2–Lewis acid (**3a**–**3g**) systems is concluded to be the result of (1) coordinative activation of MMA for the nucleophilic attack of 2 (Figure 12) and (2) suppression of the undesired degradative attack of 2 to the Lewis acidic center (Scheme VII) because of the steric repulsion between the bulky porphyrin ligand of 2 and the substituents at the *ortho* positions of the phenolate ligands of **3a**–**3g**. The same may be true for the 2–Ph_3Al system.

When the substituents of the Lewis acid are smaller as typically in the case of Me_3Al, the undesired ligand exchange reaction (Scheme VIII) competitively occurs, leading to the formation of dimethylaluminum enolate (7) at the expense of the change of 2 into methylaluminum porphyrin (1, X = Me) (Figure 10). As already reported, 1 (X = Me) has no ability to initiate the polymerization of methacrylic esters without visible light irradiation. Furthermore, dimethylaluminum enolate is not a suitable growing species for the living polymerization of MMA, taking into account the fact that the polymerization initiated with the diethylaluminum enolate (5) at room temperature is terminated at the very early stage. Therefore, the ligand exchange reaction (Scheme VIII) leads to the termination of chain growth in the polymerization of MMA. Similarly to the above, the ligand exchange reaction (Scheme VIII) actually occurs at room temperature when the monomer is *tert*-butyl methacrylate (^{t}BMA) (Figure 9), but the resulting dimethylaluminum enolate (7, R = ^{t}Bu) can initiate the rapid polymerization of ^{t}BMA in a fairly controlled fashion, considering the quantitative formation of a narrow MWD P^{t}BMA using 5 as the initiator. Therefore, when Me_3Al is added to the living P^{t}BMA (2, R = ^{t}Bu) at the ratio below unity, only part of the polymer molecules are transformed into the more active form 7 (R = ^{t}Bu), and the formation of a bimodal MWD P^{t}BMA results (Figure 5). This is also supported by the results shown in Figure 6. At a lower temperature such as −40 °C, the ligand exchange reaction (Scheme VIII) is very much reluctant to occur (Figure 11), so that the polymerization is accelerated by Me_3Al without losing the living character (Figure 7), similarly to the case using the 2–bulky 3 systems.

Conclusion

The aluminum porphyrin initiators (1) provide one of the bulkiest families of nucleophilic growing species, which are very reluctant to undergo degradative reaction with bulky Lewis acids even at room temperature. By taking the advantage of this, the Lewis acid-assisted high-speed living anionic polymerization of methacrylic esters was realized (Figure 12). By lowering the polymerization temperature, even Lewis acids with poor steric bulk such as trialkylaluminums were usable as the accelerators.

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(14) The assigment was made according to Maruoka, K.; Araki, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 2650 (supplementary material).

(15) ^{1}H NMR for 2 (R = ^{t}Bu) (C_6D_6): δ 9.36 (pyrrole β-H), 8.46 (Ph *o*-H), 7.76 (Ph *m*,*p*-H), 2.7–2.3 (main chain CH_2), 1.9–1.4 (main chain CH_3 and $C(CH_3)_3$), 0.96 (terminal CH_3; e in Figure 9), 0.72 and 0.70 ($=CCH_3$; b), 0.51 ($=C(CH_3)CH_2CCH_3$; d), 0.43–0.40 ($=CCH_2$; c), 0.0 to −0.2 ($=C(CH_3)CH_2CCH_3$; d), −0.28 and −0.33 ($=COC(CH_3)_3$; a), −1.00 and −1.09 ($=CCH_3$; b), −1.14 ($=CCH_2$; c).

(16) A small shoulder was observed on the higher molecular weight side of the main peak in GPC.