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Aluminum Thiolate Complexes of Porphyrin as Excellent Initiators for Lewis Acid-Assisted High-Speed Living Polymerization of Methyl Methacrylate

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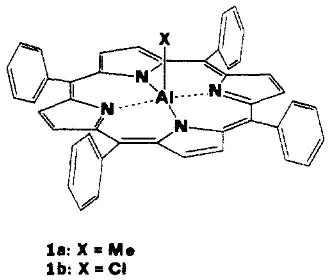
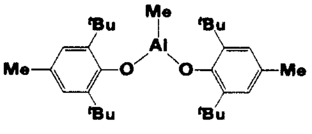
ABSTRACT: Thiolatealuminum porphyrins ((propylthio)- and (phenylthio)aluminum 5,10,15,20-tetraphenylporphyrins ((TPP)AlSPr (**1c**) and (TPP)AlSPh (**1d**))) as nucleophiles in conjunction with a bulky Lewis acid such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) served as excellent initiating systems for the high-speed synthesis of poly(methyl methacrylate) (PMMA) with controlled molecular weight. The living character of polymerization was demonstrated by the two-stage polymerization of MMA. In contrast with the method using methylaluminum porphyrin ((TPP)AlMe (**1a**)) as initiator, the new system features initiation of polymerization with no need for irradiation owing to the high nucleophilicity of the initiator, thereby allowing "one-shot" high-speed polymerization by simple mixing of MMA, Lewis acid (**2**), and initiator (**1c** or **1d**). Other aluminum porphyrins such as (TPP)AlX (**1**, X = Cl, O$_2$CMe, OC$_6$H$_3$(2,4-^{t}Bu$_2$), OMe) did not bring about the polymerization at all even in the presence of **2**. Use of lithium thiolate as initiator in combination with **2** resulted in a rather slow polymerization of MMA to give a polymer with a broad MWD and much higher M_n than expected.

Introduction

Controlled synthesis of polymers with a well-defined architecture is one of the ultimate goals of synthetic polymer chemistry. As for the synthesis of poly(methacrylic esters) with uniform, controlled molecular weights, several excellent initiators have been exploited, which include biphenylsodium,[1] silyl ketene acetal coupled with nucleophilic or Lewis acid catalysts,[2] ammonium enolates,[3] (1,1-diphenylhexyl)lithium/LiCl,[4] ^{t}BuMgBr/MgBr$_2$,[5] ^{t}BuLi/R$_3$Al,[6,7] methylaluminum porphyrin,[8] and organolanthanides[9] as representative examples. Methylaluminum porphyrin initiator (**1a**), which was discovered by us in 1987, is unique in the sense that the polymerization is initiated only under irradiation with visible light.[8] The propagation reaction, which involves an enolatealuminum porphyrin (**3**) as the growing species, can occur even in the absence of light (Scheme I), but the rate was unfortunately low.



1a: X = Me
1b: X = Cl
1c: X = SPr
1d: X = SPh
1e: X = O$_2$CMe
1f: X = OC$_6$H$_3$(2,4-di-*tert*-Bu)
1g: X = OMe



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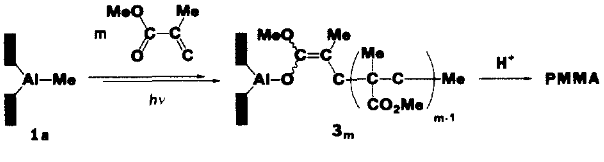
Recently, we have found that the polymerization of methyl methacrylate (MMA) via **3** is dramatically accelerated upon addition of hindered organoaluminum diphenolates such as **2** as Lewis acids, affording narrow MWD PMMAs only within seconds under appropriate conditions.[10] On the basis of this finding, the high-speed synthesis of a narrow MWD PMMA with M_n exceeding 10^6 was realized.[11] The present polymerization is actually a "Lewis acid-assisted coordinate anionic polymerization", which proceeds via clean repetition of the accelerated attack of the nucleophilic growing species to the activated monomer through coordination with the Lewis acid. Although Lewis acid-mediated nucleophilic reactions are generally accompanied by degradative attack of nucleophile to Lewis acid, such an undesired reaction is suppressed in our system due to the large steric barrier for the access of the nucleophilic growing species bearing a bulky porphyrin ligand to the sterically crowded Lewis acidic center (Figure 1).

Scheme I



Scheme II shows the general procedure for the high-speed polymerization of methyl methacrylate using (TPP)AlMe (**1a**) as initiator, where the photoinitiation prior to the addition of Lewis acid is required. This is because (1) (TPP)AlMe (**1a**) without irradiation has no ability to initiate the polymerization even in the presence of Lewis acid and (2) "all-at-once" polymerization by direct irradiation of a mixture of MMA, (TPP)AlMe (**1a**), and Lewis acid results in the formation of a relatively broad MWD PMMA with M_n much higher than expected. In this sense, the procedure using methylaluminum porphyrin (**1a**) as initiator is not convenient for practical application.

In the present study, aluminum porphyrins with various axial ligands (**1b–g**) were tested as initiators to realize more convenient, "one-shot" high-speed living polymerization of methyl methacrylate with no need for irradiation with visible light.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine (TPPH$_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from CHCl$_3$/MeOH (1/2 (v/v)) to give TPPH$_2$ as a purple powder.[12]

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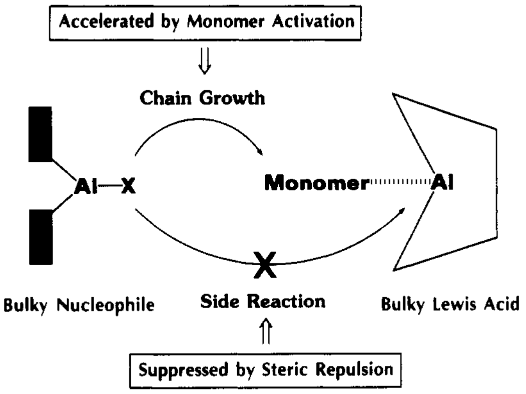
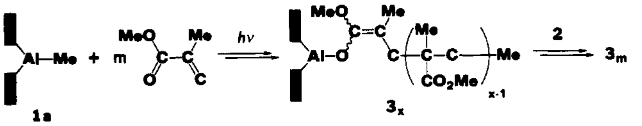
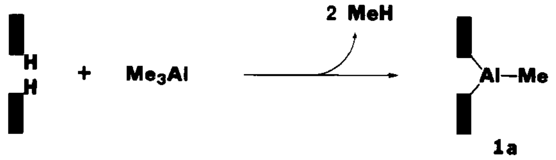


Figure 1. Basic concept of the "high-speed living polymerization" of methacrylic esters via steric separation of nucleophile and Lewis acid.

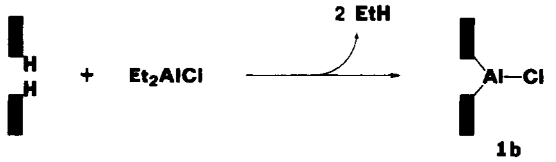
Scheme II



Scheme III



Scheme IV



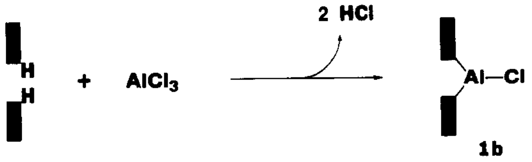
Dichloromethane (CH_2Cl_2) was washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, dried over $CaCl_2$, and distilled over CaH_2 in a nitrogen atmosphere. Benzene (C_6H_6), deuterated benzene (C_6D_6), and hexane were distilled, respectively, over sodium benzophenone ketyl in a nitrogen atmosphere. 1-Propanethiol (PrSH) was fractionally distilled over anhydrous $CaSO_4$ under nitrogen. Benzenethiol (PhSH) was distilled under reduced pressure over anhydrous $CaSO_4$ in a nitrogen atmosphere. Methyl methacrylate (MMA) was fractionally distilled under reduced pressure over CaH_2 in a nitrogen atmosphere. 2,6-Di-*tert*-butyl-4-methylphenol was recrystallized from hexane.

Trimethylaluminum (Me_3Al) and diethylaluminum chloride (Et_2AlCl) were fractionally distilled, respectively, under reduced pressure in a nitrogen atmosphere.

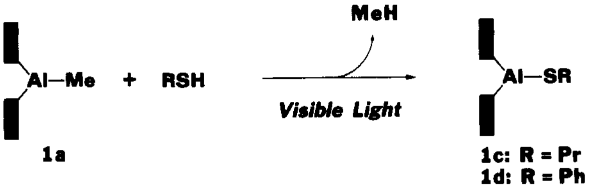
Preparation of Aluminum Porphyrins. Methyl(5,10,15,-20-tetraphenylporphinato)aluminum ((TPP)AlMe (1a)) (Scheme III). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) under dry nitrogen, CH_2Cl_2 (40 mL) and Me_3Al (1.2 equiv, 0.12 m) were successively added by means of hypodermic syringes in a nitrogen stream, and the mixture was stirred for 1 h. Then volatile fractions were removed from the reaction mixture under reduced pressure to leave **1a** as a purple powder.[13]

Chloro(5,10,15,20-tetraphenylporphinato)aluminum ((TPP)AlCl (1b)). From $TPPH_2$ and Et_2AlCl (Method I, Scheme IV). **1b** was prepared similarly to the above by the reaction of $TPPH_2$ (1 mmol) and 1.2 equiv of Et_2AlCl (0.16 mL) in CH_2Cl_2 (20 mL) at room temperature in a nitrogen atmosphere. After 2 h, the reaction mixture was evaporated to dryness under reduced pressure to leave **1b** as a purple powder.[14] **From $TPPH_2$ and $AlCl_3$ (Method II, Scheme V).** A benzonitrile (80 mL) solution of a mixture of $TPPH_2$ (0.5 g, 0.8 mmol) and $AlCl_3$ (0.5 g, 3.7 mmol) was refluxed until no further change in UV–vis absorption was detected. Then the reaction mixture was cooled to room temperature and filtered to remove excess $AlCl_3$. Hexane was added to the filtrate, and the precipitates formed were collected by filtration, washed with hexane, and dissolved in MeOH. The MeOH solution was filtered, and 3 N HCl was added to the filtrate, whereupon precipitates were formed. The precipitates were collected and subjected to recrystallization from acetone/hexane, affording **1b** as purple crystals, which were dried at 150 °C for 2 h under reduced pressure.[15,16]

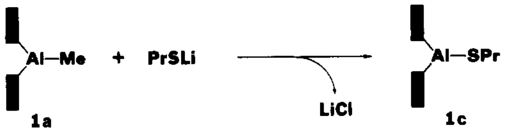
Scheme V



Scheme VI



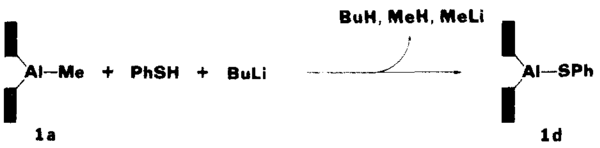
Scheme VII



(1-Propanethiolato)(5,10,15,20-tetraphenylporphinato)-aluminum ((TPP)AlSPr (1c)). From (TPP)AlMe (1a) and 1-Propanethiol (PrSH) (Method I, Scheme VI). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing **1a** (0.3 mmol) under dry nitrogen, CH_2Cl_2 (12 mL) and PrSH (5 equiv) were successively added by syringe in a nitrogen stream. The mixture was stirred for 12 h at room temperature under irradiation with a xenon arc light ($\lambda > 420$ nm), where the bluish-purple solution gradually turned reddish-brown, characteristic of **1c**. Then the mixture was evaporated to dryness under reduced pressure to leave **1c** as a purple powder.[17] ^1H NMR in C_6D_6 (C_6H_6 (δ 7.40) as internal standard): δ −1.42 (t, SCH_2), −0.55 (m, $CH_2CH_2CH_3$), and −0.10 (t CH_3). **From (TPP)AlCl (1b) and Lithium 1-Propanethiolate (PrSLi) (Method II, Scheme VII).** To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing hexane (8 mL) and PrSH (2.8 mmol, 0.25 mL), a hexane solution (1.2 mL) of BuLi (2.0 mmol) was added in a nitrogen stream at −23 °C. The mixture was stirred for 30 min at the same temperature and then allowed to warm to room temperature. After stirring for an additional 30 min, volatile fractions were removed under reduced pressure at room temperature to leave PrSLi as a white powder. To this flask was added a C_6H_6 solution (16 mL) of (TPP)AlCl (**1b**, 0.4 mmol) in a nitrogen stream, and the mixture was stirred at 50 °C for 2 h in the dark. Then the reaction mixture was filtered off under nitrogen from insoluble substances such as LiCl and PrSLi, affording **1c** (C_6H_6 solution) almost quantitatively.

(Benzenethiolato)(5,10,15,20-tetraphenylporphinato)aluminum ((TPP)AlSPh (1d)). From (TPP)AlMe (1a) and Benzenethiol (PhSH) (Method I, Scheme VI). Similarly to the case of (TPP)AlSPr (**1c**), a CH_2Cl_2 solution of a mixture of (TPP)AlMe (**1a**) and PhSH ($[1a]_0[PhSH]_0 = 3$) was irradiated with a xenon arc light ($\lambda > 420$ nm) for 12 h at room temperature in a nitrogen atmosphere, and then the reaction mixture was evaporated under reduced pressure at 80 °C to leave **1d** as a purple powder.[17] ^1H NMR in C_6D_6: δ 4.58 (d, SPh-*o*-H), 6.50 (t, SPh-*m*-H), and 6.76 (t, SPh-*p*-H). **From (TPP)AlMe (1a), Benzenethiol (PhSH), and Butyllithium (BuLi) (Method**

Scheme VIII



Scheme IX

II, Scheme VIII). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing **1a** (0.4 mmol), C_6H_6 (16 mL) and PhSH (1.2 mmol) were successively added in a nitrogen stream. After the mixture was cooled to 5 °C, a hexane solution (0.1 mL) of BuLi (0.16 mmol) was added, and the mixture was stirred for 30 min at the same temperature and an additional 2 h at 75 °C for completion of the ligand exchange reaction.

Aluminum Porphyrins with Other Axial Ligands ((TPP)-AlO_2CMe (1e), (TPP)$AlOC_6H_3(2,4\text{-}^tBu_2)$ (1f), and (TPP)-AlOMe (1g)). Aluminum 5,10,15,20-tetraphenylporphines having acetate (**1e**),[18] phenolate (**1f**),[13] and methanolate (**1g**)[19] as axial ligands were prepared according to the reported procedures by the reactions of (TPP)AlMe (**1a**) with acetic acid, 2,4-di-*tert*-butylphenol, and methanol, respectively, under diffuse light at room temperature.

Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (2) (Scheme IX). To a 50-mL round-bottomed flask equipped with a three-way stopcock containing 2,6-di-*tert*-butyl-4-methylphenol (25 mmol, 5.51 g), hexane (20 mL) and Me_3Al (12.5 mmol, 1.2 mL) were successively added at 0 °C. Upon stirring at room temperature, the reaction mixture gradually became turbid with evolution of methane. After 1 h of stirring, the suspension was allowed to stand without stirring at room temperature, and the supernatant upper layer (9 mL) was taken out by a syringe in a nitrogen stream. To this flask containing the wet powdery residue, hexane was added at 60 °C in a nitrogen stream until all the powder dissolved (5.5 mL), and the solution was cooled to room temperature, affording **2** as white crystals (3.7 g, 62% yield), which were dried under reduced pressure at room temperature.[20]

Polymerization. Polymerizations of MMA Initiated with Aluminum Porphyrins (1) or the 1–Lewis Acid (2) Systems. A typical example is given below by the polymerization of methyl methacrylate (MMA) with (TPP)AlSPr (**1c**). To a 100-mL round-bottomed flask attached to a three-way stopcock containing a CH_2Cl_2 solution (8 mL) of **1c** (0.2 mmol), MMA (40 mmol, 4.3 mL) was added by a syringe in a nitrogen stream under diffuse light at 35 °C. An aliquot of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to ^1H NMR and gel permeation chromatography (GPC) analyses to determine the monomer conversion and to estimate the average molecular weights (M_w, M_n) of the produced polymer, respectively. The polymerization in CH_2Cl_2 at 80 °C was carried out in a 50-mL sealed ampule. For the polymerization of MMA in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**), a C_6H_6 solution (6.3 mL) of a mixture of **2** (0.6 mmol) and MMA (40 mmol) was added by a syringe to a C_6H_6 solution (16 mL) of **1c** (0.4 mmol) under diffuse light at room temperature.

The polymerizations of MMA initiated with **1e**, **1f**, and **1g** in the absence and presence of **2** were carried out similarly.

Two-Stage Polymerization of MMA Initiated with the (TPP)AlSPr (1c)–Lewis Acid (2) System. To a 50-mL round-bottomed flask attached to a three-way stopcock containing a C_6H_6 solution (16 mL) of **1c** (0.4 mmol), **2** (0.2 mmol) dissolved in C_6H_6 (0.7 mL) and MMA (20 mmol, 2.1 mL) were successively added by syringes at 0 °C in a nitrogen stream. After 5 min, an aliquot of the reaction mixture was taken out by a syringe in a nitrogen stream and subjected to NMR analysis to confirm the complete monomer consumption and to GPC analysis to estimate the average molecular weights of the produced polymer. The reaction mixture at 100% conversion was allowed to stand at 0 °C for 1 h, and then the second feed of MMA (40 mmol) was added. After 5 min, MeOH (5 mL) was added to the flask, and the reaction mixture was subjected to ^1H NMR and GPC analyses to determine the monomer conversion and average molecular weights of the produced polymer, respectively.

Isolation of Polymers. To isolate the produced polymer from the polymerization mixture, volatile fractions were removed under reduced pressure at room temperature. The nonvolatile residue was dissolved in a minimum volume of $CHCl_3$, and the solution was added dropwise into a large volume of MeOH with vigorous stirring. The slightly colored precipitates formed were collected and reprecipitated similarly to give the polymer as white precipitates, which were collected and dried under reduced pressure at room temperature.

Measurements. Gel permeation chromatography (GPC) was 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 (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). ^1H and ^{13}C NMR measurements were performed using C_6D_6 or $CDCl_3$ as solvent on a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) or C_6H_6 (δ 7.40) for ^1H and $CDCl_3$ (δ 77.1) for ^{13}C as internal standards.

Results and Discussion

Polymerization of Methyl Methacrylate Initiated with Aluminum Porphyrins (1) under Diffuse Light. Aluminum porphyrins ((TPP)AlX (**1**)) having axial ligands such as chloride (X = Cl (**1b**)), acetate (X = O_2CMe (**1e**)), phenolate (X = $OC_6H_3(2,4\text{-}^tBu_2)$ (**1f**)), methanolate (X = OMe (**1g**)), propanethiolate (X = SPr (**1c**)), and benzenethiolate (X = SPh (**1d**)) were tested as initiators for the polymerizations of MMA (200 equiv with respect to **1**) in the absence and presence (3 equiv with respect to **1**) of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) as Lewis acid under diffuse light in CH_2Cl_2 at room temperature. The aluminum porphyrins carrying aluminum–chlorine (**1b**) and –oxygen bonds (**1e–g**) did not bring about the polymerization at all in the absence and even in the presence of the Lewis acid (**2**). On the contrary, aluminum porphyrins bearing aluminum–sulfur bonds (**1c** and **1d**) were found to initiate the polymerization without irradiation[21] even in the absence of **2**.

For example, the polymerization of MMA using (TPP)-AlSPr (**1c**) as initiator ($[MMA]_0/[\mathbf{1c}]_0 = 200$) in CH_2Cl_2 at 35 °C started upon addition of MMA to the initiator solution under diffuse light and proceeded up to 100% conversion in 18 h. The number-average molecular weight (M_n) of the produced polymer, as estimated from GPC based on polystyrene standards, was 22 000 (M_w/M_n = 1.12), which is close to that expected from the monomer-to-initiator mole ratio (20 000).[22]

Similar results were obtained when an aromatic thiolate complex such as (TPP)AlSPh (**1d**) was used as initiator. When the initial monomer-to-initiator mole ratio ($[MMA]_0/[\mathbf{1d}]_0$) was increased, M_n of the polymer formed at 100% conversion also increased linearly along the theoretical line (broken line in Figure 2) based on the assumption that every initiator molecule produces one polymer molecule, while the M_w/M_n ratio remained in the range 1.1–1.2. When the polymerization temperature was raised to 80 °C, the polymerization ($[MMA]_0/[\mathbf{1d}]_0 = 200$, CH_2Cl_2 as solvent) was accelerated to attain 80% in only 2 h, affording a polymer with M_n and M_w/M_n, respectively, of 15 000 and 1.18.

These observations strongly indicate that thiolatealuminum porphyrins (**1c** and **1d**) as initiators are possible

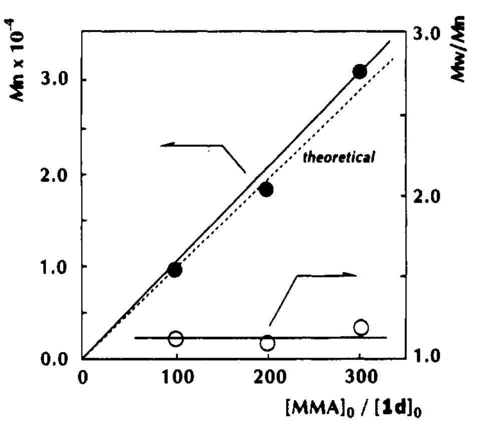


Figure 2. Polymerization of methyl methacrylate initiated with (TPP)AlSPh (**1d**) in CH_2Cl_2 at room temperature: Relationship between M_n (●) (M_w/M_n (○)) of the polymer and the initial monomer-to-initiator mole ratio ($[MMA]_0/[\mathbf{1d}]_0$) at 100% conversion.

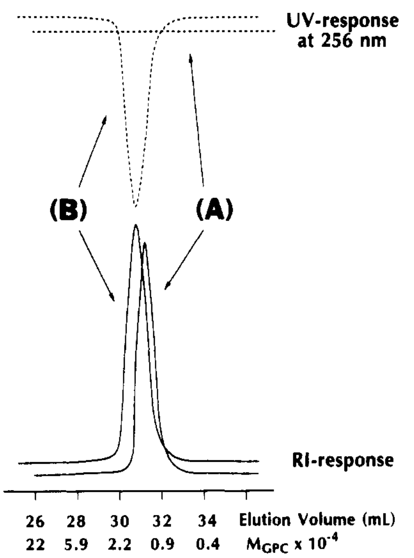


Figure 3. GPC profiles of poly(methyl methacrylate)s obtained with the (TPP)AlSPr (**1c**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) (A) and (TPP)AlSPh (**1d**)–**2** systems (B). $[MMA]_0/[\mathbf{1}]_0/[\mathbf{2}]_0$ = 100/1.0/1.0, C_6H_6 as solvent, room temperature, 100% conversion.

candidates for the "one-shot" high-speed living polymerization of methyl methacrylate without irradiation.

"One-Shot" Polymerization of Methyl Methacrylate Initiated with the Thiolatealuminum Porphyrin–Lewis Acid (2) Systems. Using (TPP)AlSPr (**1c**) as initiator, the polymerization of MMA in the presence of the Lewis acid (**2**) was attempted by direct addition of a mixture of MMA and **2** to a C_6H_6 solution of **1c** at room temperature under diffuse light. For example, when 100 equiv of MMA containing 1.5 mol % of **2** was added to the initiator, the color of the solution immediately turned from reddish-brown to reddish-purple, characteristic of an enolatealuminum porphyrin species (**4**). The polymerization took place rapidly with heat evolution and was completed within only 90 s, affording a polymer with M_n and M_w/M_n, as estimated by GPC (trace A in Figure 3), of 11 200 and 1.13, respectively. The M_n value of the polymer thus estimated is close to the expected one (10 000), indicating the participation of all the molecules of **1c** in initiating the polymerization.

To follow the time course of the polymerization with ease, the polymerization was slowed down by applying lower concentrations of the Lewis acid (**2**) and initiator (**1c**). At the ratio $[MMA]_0/[\mathbf{1c}]_0/[\mathbf{2}]_0$ of 300/1.0/0.2, more than 20 min was required for the completion of polymerization. The time–conversion curve observed here (Figure 4) shows that the monomer consumption is linear with time throughout the polymerization. As shown in Figure 5, M_n of the produced polymer increased linearly with conversion, retaining the ratio M_w/M_n in the range 1.1–1.2. A good agreement between the observed and expected M_n's of the polymer (solid and broken lines, respectively) again indicates quantitative initiation from every molecule of the initiator (**1c**).

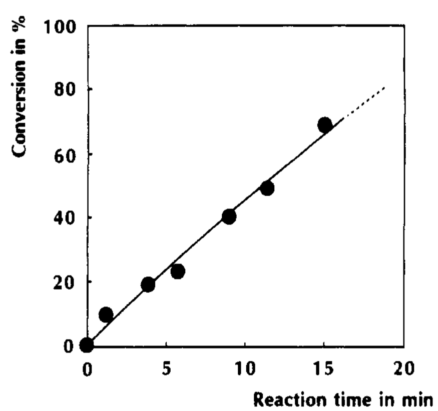


Figure 4. Polymerization of methyl methacrylate initiated with the (TPP)AlSPr (**1c**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate (**2**) system at a low concentration of **2**. $[MMA]_0/[\mathbf{1c}]_0/[\mathbf{2}]_0$ = 300/1.0/0.2, $[\mathbf{1c}]_0$ = 13.9 mM, C_6H_6 as solvent, room temperature. Time–conversion curve.

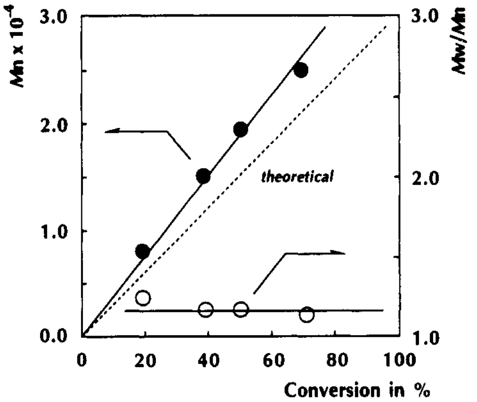


Figure 5. Polymerization of methyl methacrylate initiated with the (TPP)AlSPr (**1c**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) system: Relationship between M_n (●) (M_w/M_n (○)) of the polymer and conversion (reaction conditions, see Figure 4).

(TPP)AlSPh (**1d**) was also applicable as initiator to the "one-shot" high-speed polymerization of MMA in C_6H_6 under diffuse light, where a polymer with M_n and M_w/M_n, respectively, of 16 400 and 1.15 (GPC: trace B in Figure 3) was quantitatively formed within 5 min after the direct addition of a mixture of MMA (100 equiv) of **1d** (1 equiv) to the initiator solution.

To confirm the living nature of the polymerization with the thiolatealuminum porphyrin–Lewis acid (**2**) systems, the two-stage polymerization of MMA was attempted. Thus, after 50 equiv of MMA was completely polymerized at the first stage with the **1c**–**2** system ($[\mathbf{1c}]_0/[\mathbf{2}]_0$ = 1.0/0.5) at 0 °C in C_6H_6 (100% conversion within 5 min), the polymerization mixture was allowed to stand for an additional 1 h at the same temperature, and then 100 equiv of MMA was again added. As soon as the second part of MMA was fed, a rapid polymerization ensued with heat evolution and reached 100% conversion within 5 min. The GPC chromatogram of the polymer formed at the first stage (trace I in Figure 6 (M_n = 6020, M_w/M_n = 1.22))

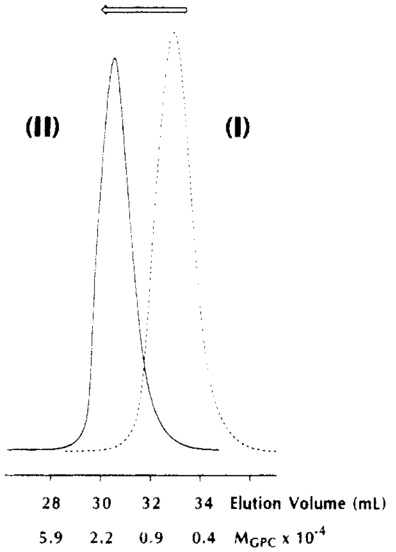


Figure 6. Two-stage polymerization of methyl methacrylate in C_6H_6 at room temperature with the (TPP)AlSPr (**1c**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) ($[\mathbf{1c}]_0/[\mathbf{2}]_0 = 1.0/0.5$) system. GPC profiles of the polymers formed at the first (I) ($[MMA]_0/[\mathbf{1c}]_0 = 50$, 100% conversion $M_n = 6020$, $M_w/M_n = 1.22$) and the second stages (II) ($[MMA]_0/[\mathbf{1c}]_0 = 100$, 100% conversion $M_n = 16\,400$, $M_w/M_n = 1.14$).

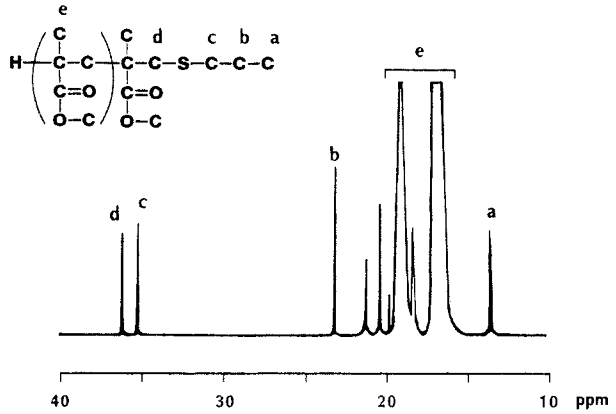
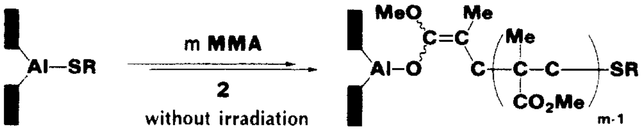


Figure 7. ^{13}C NMR spectrum in $CDCl_3$ of the poly(methyl methacrylate) ($M_{n,GPC} = 6900$, $M_w/M_n = 1.13$) obtained with the (TPP)AlSPr (**1c**)–methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2**) system ($[MMA]_0/[\mathbf{1c}]_0/[\mathbf{2}]_0 = 30/1.0/0.5$, 100% conversion).

entirely shifted toward the higher molecular weight region after the second-stage polymerization, to provide again a unimodal, sharp elution pattern (trace II) ($M_n = 16\,400$, $M_w/M_n = 1.14$). Thus, the living character of the polymerization was clearly demonstrated.

For the end-group analysis of the polymer, 30 equiv of MMA was polymerized with **1c** in the presence of 0.5 equiv of **2** in C_6H_6 at room temperature (10 min, 100% conversion), and a polymer with M_n of 6900 ($M_w/M_n = 1.13$) was isolated by repeated precipitations from $CHCl_3$/MeOH (see Experimental Section). Figure 7 shows the ^{13}C NMR spectrum (10–40 ppm) in $CDCl_3$ of the polymer thus obtained, where a set of weak signals assignable to the propylthio group attached to the polymer terminal (a, δ 13.4 (CH_3); b, δ 23.2 (CH_2CH_3); c, δ 35.3 ($SCH_2CH_2CH_3$))[23] and that due to the methylene group of the terminal MMA unit attached to the SPr group (d, δ 36.3 ppm (CH_2SPr)) were observed in addition to the signals due to the methyl group in the polymer main chain (e, δ 18.8 and 16.4).[24] The ^1H NMR spectrum also showed signals attributable to the terminal structure $C(CH_3)(CO_2CH_2)CH_2SPr$ (SCH_2Et, δ 2.41; CH_2SPr, δ 2.51 and 2.75),[25] and the number-average degree of polymerization, as calculated from the intensity ratio of the signal due to the main-chain CH_2 group (δ 1.4–2.1)[24] to that due to SCH_2Et, was 73, which is close to the value estimated by GPC (69). Thus, every terminal of the polymer molecule carries a propylthio group originating from the initiator (**1c**). Incorporation of the thiolate group of the initiator into the polymer terminal was also demonstrated for the polymerization with the (TPP)AlSPh (**1d**)–**2** system. As can be seen from the GPC chromatogram (trace B) in Figure 3, the polymer, purified by repeated precipitations, exhibits a clear UV response when monitored at 256 nm.[26] On the other hand, the polymers prepared with the systems **1a**–**2** and **1c**–**2** (trace A in Figure 3) were both silent at 256 nm.[27] Thus, the clear UV response observed for the polymer formed with the **1d**–**2** system (trace B in Figure 3) indicates the presence of an aromatic sulfide moiety at the polymer terminal. From the NMR and GPC observations described above, the polymerization of MMA with the thiolatealuminum porphyrin–Lewis acid (**2**) systems is initiated by the nucleophilic attack of the thiolate group of the initiator to the monomer, leading to the formation of sulfide moiety at the polymer terminal.

Scheme X



The Lewis acid (**2**) alone did not give rise to the polymerization of MMA under identical conditions. Although lithium propanethiolate (PrSLi) under similar conditions brought about the polymerization of MMA in the presence of the Lewis acid (**2**) ($[MMA]_0/[PrSLi]_0/[\mathbf{2}]_0 = 100/1.0/1.5$, C_6H_6 as solvent, room temperature), the propagation reaction was rather slow and completed in 40 min, giving a polymer with a broad MWD ($M_w/M_n = 1.45$) and much higher M_n (21 700) than expected (10 000).

Conclusion

Owing to the high nucleophilicity of the thiolatealuminum porphyrins ((TPP)AlSPr (**1c**) and (TPP)AlSPh (**1d**)), the "one-shot" high-speed living polymerization of methyl methacrylate with no need for irradiation with visible light was realized (Scheme X). The poor result with lithium thiolate as initiator clearly indicates the unique reactivity of the aluminum thiolate species surrounded by a large, macrocyclic porphyrin ligand. In addition, particular notice should be taken of the new synthetic method of aluminum porphyrins utilizing the halogen exchange reaction of chloroaluminum porphyrin (**1b**) with lithium thiolates, which is simple, does not require irradiation (Scheme VII), and is thus more convenient than the previous method that requires light (Scheme VI).

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(22) The polymerization under irradiation with visible light was also examined with $[MMA]_0/[\mathbf{1c}]_0 = 200$ in CH_2Cl_2 at 35 °C, and a polymer with M_n and M_w/M_n, respectively, of 21 000 and 1.11 was obtained quantitatively in 18 h.

(23) The assignments were made based on the ^{13}C NMR spectra for $(CH_3CH_2CH_2)_2S$ (δ 34.3 (SCH_2), 23.3 (CH_2Me), and 13.6 (CH_3)) and for $CH_3CH_2CH_2SH$ (δ 27.4 (SCH_2), 26.6 (CH_2Me), and 12.9 (CH_3)) in C_6D_6.

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(26) The selection of the wavelength for UV detection was based on the λ_{max} of thioanisole in THF.

(27) Even when PMMA prepared with **1a** was mixed with benzenethiol prior to GPC analysis, no UV response was observed for the polymer fraction, where benzenethiol eluted very late and the peak was perfectly separated from that of the polymer.