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Communications to the Editor

Controlled Synthesis of High Molecular Weight Poly(methyl methacrylate) Based on Lewis Acid-Assisted High-Speed Living Polymerization Initiated with Aluminum Porphyrin

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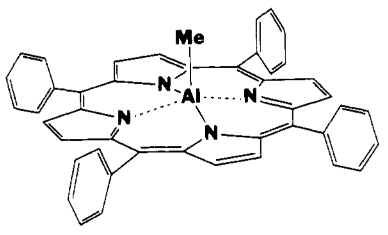
The synthesis of monodisperse, ultrahigh molecular weight polymers is one of the challenging subjects of both fundamental and practical interests. For the synthesis of poly(methacrylic ester) with a narrow molecular weight distribution, some excellent initiators have been reported, which include biphenyl sodium,[1] ketene silyl acetal-based GTP initiators,[2] ^{t}BuMgBr coupled with $MgBr_2$ or R_3Al,[3,4] metalloporphyrins of aluminum,[5] (1,1-diphenylhexyl)lithium/LiCl,[6] and some lanthanide complexes[7] as representative examples. However, to our knowledge, only a limited success has been reported in the controlled synthesis of poly(methacrylic ester) with M_n exceeding half a million.[7]

In the present paper, we report a novel method for the controlled synthesis of high molecular weight poly(methyl methacrylate) (M_n 10^5–10^6) with a narrow molecular weight distribution. This is accomplished based on our recent discovery of the Lewis acid-assisted high-speed living polymerization of methyl methacrylate using aluminum porphyrin initiators.[8] We have already reported that the polymerization of methacrylic esters initiated with alkylaluminum porphyrins takes place with living character via an enolatealuminum porphyrin as the growing species, affording the polymer with a narrow molecular weight distribution.[5] However, the polymerization proceeds rather slowly and is not applicable to the synthesis of a high molecular weight polymer. In the course of this study, we have very recently found a dramatic acceleration effect of sterically crowded organoaluminum phenolates, where the polymerization with the monomer-to-initiator mole ratio of, e.g., 200, is completed within a few seconds at room temperature.[8]



(TPP)AlMe (1)

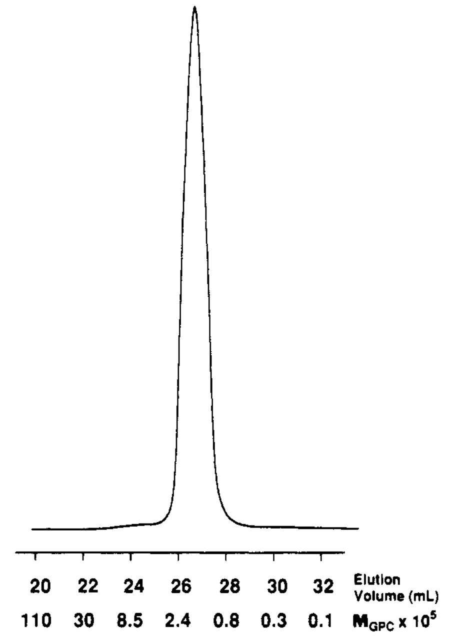
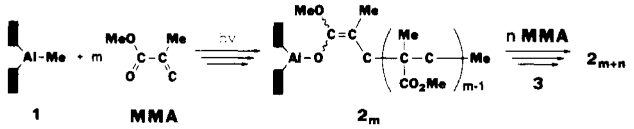
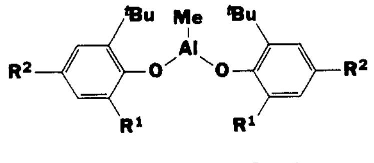


Figure 1. Polymerization of methyl methacrylate (MMA) with the enolate–aluminum porphyrin (2)–methylaluminum bis(2,4-di-*tert*-butylphenolate) (3a) system in CH_2Cl_2 at -40 °C with a $[MMA]_0/[3a]_0/[2]_0$ of 2160/6/1 (run 2, Table I). GPC profile of the polymer obtained at 100% conversion (15 min).

Scheme I



A typical example of the synthesis of a high molecular weight polymer is given below: To a 100-mL round-bottomed flask fitted with a three-way stopcock, containing a CH_2Cl_2 solution (12.0 mL) of (TPP)AlMe[9] (1; 0.30 mmol) and a Teflon-coated stirring bar under nitrogen was added methyl methacrylate (MMA)[10] (30 mmol) by means of a hypodermic syringe, and the mixture was irradiated with a xenon arc light (λ > 420 nm) at 35 °C for 4 h, where 1 was completely converted to the aluminum enolate species (2) but the conversion of MMA was only 11% (Scheme I). Then, the irradiation was stopped, and a part of this reaction mixture was removed from the flask by a syringe in order to minimize the amount of 2 remaining in the flask in order to provide a high MMA to 2 mole ratio in the next-stage polymerization. To this flask containing 2 (0.02 mmol)[11] and MMA (1.8 mmol) in CH_2Cl_2 (0.8 mL) was added at -40 °C a CH_2Cl_2 (13.0 mL) solution of a mixture of MMA (41.2 mmol) and methylaluminum bis(2,4-di-*tert*-butylphenolate) (3a; 0.12 mmol)[12] by a syringe,



3a: R^1 = H, R^2 = ^{t}Bu
3b: R^1 = ^{t}Bu, R^2 = Me

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Table I
Polymerization of Methyl Methacrylate with the Enolate–Aluminum Porphyrin (2)/Methylaluminum Bis(phenolate) (3) Systems[a]

run	3	$[\mathrm{MMA}]_0/[\mathbf{3}]_0/[\mathbf{2}]_0$	temp/°C	time/min	conv[b]/%	M_n[c]	M_w/M_n[c]
1	**a**	930/3/1	−40	5	100	96 000	1.1
2	**a**	2160/6/1	−40	15	100	176 000	1.1
3	**a**	3170/8/1	−40	10	100	372 000	1.2
4	**b**	3590/85/1	0	20	100	560 000	1.1
5	**b**	8300/350/1	0	35	100	1 017 000	1.2

[a] Polymerization was carried out in CH_2Cl_2 under nitrogen. [b] Determined by ^{1}H NMR analysis of the reaction mixture. [c] Estimated by GPC based on polystyrene standards (see ref 14).

whereupon the high-speed polymerization of MMA started to attain 100% conversion within only 15 min under diffuse light.[13] The polymer (PMMA) thus obtained was of a narrow molecular weight distribution ($M_w/M_n = 1.13$) with a number-average molecular weight (M_n), as estimated by GPC (Figure 1) based on polystyrene standards,[14] of 176 000, which is in fair agreement with the value (216 000) expected by assuming the formation of one polymer molecule from every molecule of **2**. By changing the mole ratio of MMA to **2**, PMMAs with M_n of 96 000–372 000 (M_w/M_n = 1.1–1.2) could be synthesized (runs 1–3, Table I).

On the basis of this new method, PMMAs with much higher molecular weights (M_n > half a million) could be synthesized, where freshly distilled MMA and CH_2Cl_2[15] and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**3b**) recrystallized just before use[16] were employed, and the polymerization procedure was partly modified as follows: A CH_2Cl_2 solution of **2** was prepared similarly to that above in a 200-mL round-bottomed flask carrying a side ampule (20 mL), which allows us to minimize the amount of the initiator (**2**) remaining in the flask simply by tilting the flask to the ampule side without injecting a syringe to the solution. After most of the initiator solution was transferred to the side ampule, a CH_2Cl_2 solution of a mixture of MMA and **3b** was added to the remaining solution[17] by a syringe, and the polymerization was conducted at 0 °C. In this way, PMMAs with M_n = 560 000 (M_w/M_n = 1.1) and 1 017 000 (M_w/M_n = 1.2) were actually synthesized (runs 4 and 5, Table I).

In runs 1–3 using **3a** and runs 4 and 5 using **3b**, the amounts of Lewis acids used were, respectively, 0.25–0.3 and 2.5–5 mol % to those of MMA. It was noted that the amount of Lewis acid is important for achieving a satisfactory high speed of polymerization and low dispersity of molecular weight of produced PMMA and should be optimized depending on the structure of the Lewis acid used as well as the amounts of the solvent and MMA charged.

Thus, the controlled synthesis of poly(methyl methacrylate) having a very high molecular weight with a narrow molecular weight distribution was achieved based on the high-speed polymerization with the aluminum porphyrin (**2**)–bulky organoaluminum (**3**) systems, by virtue of (1) the prohibited attack of the nucleophile (**2**) onto the Lewis acidic center of **3** due to the steric repulsion and (2) very rapid, efficient attack of **2** to the activated MMA by coordination with **3**.[8] Further studies are in progress to apply this novel concept to develop high-speed, controlled polymerization of various monomers.

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(9) (TPP)AlMe (1) was prepared in CH_2Cl_2 at room temperature under nitrogen by the reaction of 5,10,15,20-tetraphenylporphine ($TPPH_2$) and trimethylaluminum (Me_3Al; 1.2 equiv), and the reaction mixture after 1 h was evaporated under reduced pressure to remove the excess Me_3Al that remained unreacted. See: Hirai, Y.; Murayama, H.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1988**, *110*, 7287.

(10) MMA and CH_2Cl_2 were refluxed over CaH_2 and distilled in a nitrogen atmosphere.

(11) Determined by gravimetry of the remaining solution.

(12) **3a** was prepared by the reaction of Me_3Al and 2 equiv of 2,4-di-*tert*-butylphenol in CH_2Cl_2 under nitrogen and used without further purification (see ref 8).

(13) The polymerization was quenched by adding a small volume of MeOH to the polymerization system.

(14) For the estimation of M_n and M_w/M_n of the polymers, GPC was performed at 40 °C using tetrahydrofuran as the eluent with a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained by using standard polystyrenes: 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).

(15) MMA and CH_2Cl_2 were distilled in the presence of Et_3Al under nitrogen just before use.

(16) **3b** can be purified by recrystallization in hexane more easily than **3a**. The preparation and recrystallization of **3b** have been reported in: Maruoka, K.; Araki, Y.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 2650.

(17) For determination of the MMA to **2** mole ratio, the polymerization mixture, obtained after evaporation of the volatile fraction, was subjected to UV–vis analysis ($CHCl_3$, 20 °C) to measure the amount of (TPP)AlOMe (λ_{max} = 419 nm, $\epsilon = 4.6 \times 10^5$ L mol^{-1} cm^{-1}), formed from $\mathbf{2}_{m+n}$ (Scheme I) upon addition of MeOH to the system (see ref 13).