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Accounts

The Control of Living Anionic Polymerization by Metalloporphyrins

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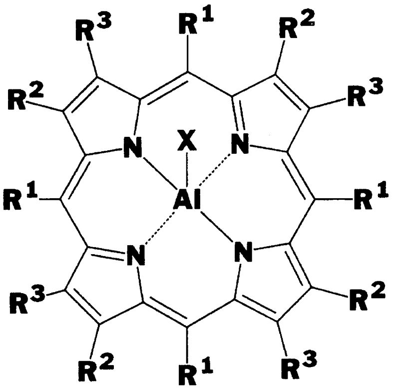
The living polymerization of methacrylic esters initiated with aluminium porphyrins was found to be dramatically accelerated upon the addition of organoaluminium or organoboron compounds as a Lewis acidic monomer activator (*high-speed living polymerization*). Under appropriate conditions, high-molecular-weight poly(methyl methacrylates) (M_n>500000) having a narrow molecular-weight distribution (M_w/M_n=1.1—1.2) were synthesized. The key concept of the *high-speed living polymerization* is the coexistence of nucleophilic growing species and a Lewis acid without a degradative direct reaction.

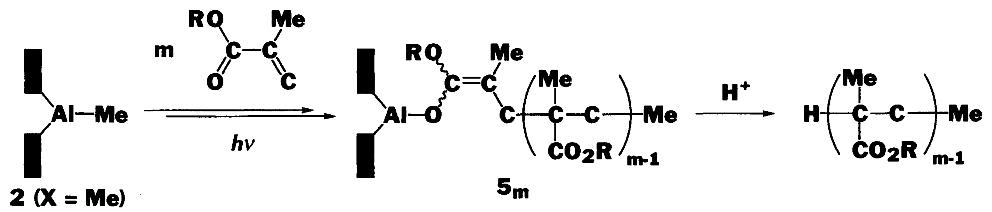
There has been increasing interest in high-performance and new functional polymer materials. The well-defined structure of biopolymers, such as protein and nucleic acid, in terms of the molecular weight (number of the repeating units, or degree of polymerization) and the sequence of different repeating units, is essential for their specific functions. In this respect, the synthesis of polymers with uniform molecular weight is of both fundamental and practical importance for the molecular design of controlled architectures of polymer materials with elaborate functions.

We have developed new initiators based on aluminium complexes of tetraphenylporphyrin (2) (Chart 1) which can be applied to various types of polymerization reactions, such as ring-opening polymerizations of epoxide[1] and lactone,[2] and addition polymerizations of acrylic monomers.[3,4] During the course of this study we recently discovered a new method, "high-speed living polymerization", by using aluminium porphyrin as a nucleophilic initiator in conjunction with an organoaluminium[5,6] or organoboron compound[7] as an electrophilic monomer activator (Lewis acid). This is the first successful example of a clean anionic polymerization assisted by an externally added Lewis acid, which enables us to synthesize uniform molecular-weight polymers within only a few seconds.[5] The basic concept of high-speed living polymerization involves the coordinative activation of a monomer by a Lewis acid. Although such a methodology has been utilized in the field of organic synthesis, an undesired direct reaction between nucleophile and electrophile always occurs in competition with the main reaction. Therefore, of primary importance for the application of this concept to living polymerization is how to suppress undesired side reactions. To date, three differ-



1 : R^1 = H, R^2 = Me, R^3 = Et
2 : R^1 = Ph, R^2 = R^3 = H
3 : R^1 = (2',4',6'-Me_3)Ph, R^2 = R^3 = H
4 : R^1 = (3',5'-^{t}Bu_2)Ph, R^2 = R^3 = H

Chart 1. Structures of aluminium porphyrins.



Scheme 1.

ent approaches have been developed in order to realize the coexistence of the nucleophilic growing species (**5**) and a Lewis acid without degradative neutralization leading to the termination of polymerization. The first one is to carry out the polymerization reaction thermostated at a low temperature. The second is to make use of sterically crowded Lewis acids in order to introduce a steric repulsion between nucleophile and the Lewis acid. As already reported, the polymerization of methacrylic esters with aluminium porphyrins proceeds via (porphyrinato)aluminium enolates (**5**) (Scheme 1), which are one of the most sterically crowded enolates because of the presence of a bulky aluminium porphyrin counter species. Therefore, the aluminium enolate species (**5**) can coexist with a Lewis acid when the steric bulk around the Lewis acidic center is sufficiently large. An alternative method of this approach focuses attention on the steric bulk of the nucleophile component (**5**) by using strategically designed aluminium porphyrins and methacrylates with a bulky ester group in order to utilize sterically fine-tuned initiators/growing species having sufficiently bulky substituents at the porphyrin periphery or in axial enolate species. This allows us to use sterically less-hindered, more common Lewis acids as accelerators. The third approach is to make use of Lewis acids with a sufficiently low ligand-exchange activity, where the steric protection of the initiator and Lewis acid is not necessary.

The present paper describes the results of the polymerization of methacrylic esters with various aluminium porphyrin/Lewis acid systems for the purpose of understanding both the scope and limitation of the novel methodology, high-speed living polymerization.

Results and Discussion

1. High-Speed Living Polymerization at Low Temperature. For investigating the acceleration effect of organoaluminium Lewis acids on the polymerization of methyl methacrylate (MMA) with aluminium porphyrins (**5**), trimethylaluminium (Me_3Al) was chosen first, since Me_3Al is one of the commonly used Lewis acids, and, by itself, has no ability to bring about the polymerization of MMA under ordinary conditions.[6)] For example, the polymerization of MMA (100 mmol) initiated with methyl(tetraphenylporphyrinato)aluminium ((TPP)AlMe (**2**, X=Me); 0.1 mmol) in CH_2Cl_2 (4 mL) proceeded rather sluggishly via **5** (R=Me), resulting in a 9% conversion in 2 h under irradiation with xenon arc light (λ>420 nm). When 3 molar amount of Me_3Al with respect to **5** (R=Me) were added to the polymerization mixture, although heat evolution was observed at a very early stage, it subsided within only 1—2 min. It is also noted here that the addition of Me_3Al were accompanied by a rapid color change of the system from dark-reddish purple due to **5** (R=Me) to bluish purple, characteristic of (TPP)AlMe (**2**, X=Me). The monomer conversion after 5 min was only 30%, and no longer increased upon a prolonged reaction for 2 h.

At a lower temperature, in contrast, Me_3Al was able to accelerate the polymerization of MMA. At −40 °C, for example, after 3 molar amount of Me_3Al were added to the polymerization system ($[MMA]_0/[\mathbf{2}\ (X=Me)]_0=$ 100, 11% conversion) 91% conversion was attained in the following 1 h. Furthermore, the polymer formed had a narrow molecular-weight distribution (MWD), as indicated by the ratio of the weight-average molecular weight to a number-average molecular weight (M_w/M_n) of 1.17; the M_n value (9700)[8] 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 the color of the system.

Thus, the polymerization temperature is one of the important factors to achieve a clean and rapid polymerization initiated with aluminium porphyrin (**2**) in the presence of trialkylaluminiums.

2. High-Speed Living Polymerization by a Steric Effect. 2.1. Use of Bulky Lewis Acids. By selecting an appropriate trialkylaluminium, the acceleration of the polymerization of MMA can be accomplished even at room temperature.[6)] For this purpose, the size of the alkyl groups in trialkylaluminiums was significant, as was clearly demonstrated by using $^{i}Bu_3Al$ in place of Me_3Al for the polymerization of MMA ($[MMA]_0/[\mathbf{5}\ (R=Me;\ m=12)]_0/[^{i}Bu_3Al]_0=$ 200/1.0/3.0), which gave an essentially similar result as that observed for polymerization using Me_3Al, although the finally attained monomer conversion was higher (64%). During polymerization in the presence of $^{i}Bu_3Al$, a color change of the system from the dark-reddish purple characteristic of **5** to the greenish purple typical of the isobutylaluminium porphyrin family was observed. The M_n of the polymer formed at this conversion (20200) was much higher than that expected from the ratio of MMA reacted to **2** (X=Me) (12800), and the MWD was broad ($M_w/M_n=1.41$). On the contrary, when Ph_3Al (3 molar amount with respect to **5** (R=Me)) was added at room temperature to the system ($[MMA]_0/[\mathbf{2}]_0=200$, 3% conversion), a fairly rapid polymerization took place with heat evolution, and the monomer was completely consumed within 90 min. The M_n of the produced polymer (22300) was close the expected value of 20000 and the MWD was satisfactorily narrow ($M_w/M_n=1.18$). In this case, the system retained the original color characteristic of **5** (R=Me) throughout the polymerization.

The upper part of Table 1 provides a list of the sterically crowded Lewis acids that are effective for the high-speed living polymerization of MMA initiated with aluminium porphyrins. An example of the high-speed living polymerization of MMA is as follows: To (TPP)-AlMe (**2**, X=Me; 0.2 mmol) was added MMA (43.4 mmol); the mixture was then irradiated with visible light at 35 °C in order to initiate the polymerization so as to convert **2** (X=Me) into **5** (R=Me). After 2.5-h irradiation, the conversion of MMA at this stage was only 6.1% ($M_n=1600$ [$M_{n\ \mathrm{theory}}=1300$], $M_w/M_n=1.13$). On the other hand, when 3 molar amount of methylaluminium bis(2,4-di-*t*-butylphenolate) (Table 1, **6b**) with respect to **5** (R=Me) were added at room temperature to the above-mentioned reaction mixture under diffuse light, the polymerization proceeded with considerable heat evolution, and was completed within only 3 s. This corresponds to at least 46200-times acceleration, where 68 MMA molecules on the average were consumed every second per molecule of the growing enolate species (**5**). The GPC profile of this accelerated polymerization is shown in Fig. 1, where the elution pattern (**a**) of the polymer formed before the addition of **6b** clearly shifted toward a higher molecular weight region to provide a unimodal, sharp chromatogram (**b**). The M_n and M_w/M_n values of the polymer, calculated based on polystyrene standards, were 25500 and 1.07, respectively. It should be noted here that the observed M_n value was close to the expected one when every molecule of **5** (R=Me) generated before the addition of **6b** participated in the subsequent high-speed polymerization. In contrast, **6b** alone did not bring about the polymerization of MMA under similar conditions.

The living character of polymerization was demonstrated by the following two-stage polymerization: In the first stage, 50 molar amount of MMA were polymerized with the **5** (R=Me)/**6f** (1.0/3.0) system up to 100% conversion; after a 4-h interval at 25 °C in the absence of MMA, 200 molar amount of MMA were again added to the polymerization mixture, whereupon a second-stage polymerization ensued along with heat evolution. The GPC profile of this two-stage polymerization showed a clear increase in the molecular-weight of the polymer from 7000 (first stage) to 47600 (second stage), retaining the narrow molecular weight distribution (M_w/M_n: from 1.12 to 1.05).

2.2. Use of Sterically Crowded Growing Species. The steric bulk of the growing species was also important for realizing a nucleophile-Lewis acid separation.[9] As we have already mentioned in the above section, the polymerization of MMA initiated with methyl(tetraphenylporphyrinato)aluminium (**2**, Fig. 2(B)) was accelerated during the early stage after the addition of $^i\mathrm{Bu}_3\mathrm{Al}$, but soon terminated, since $^i\mathrm{Bu}_3\mathrm{Al}$ reacted rather easily with the growing enolate species (**5**, R=Me). When a sterically less crowded initiator, such as methylaluminium etioporphyrin I (**1**, Fig. 2(A)), was used under otherwise identical conditions, the polymerization stopped immediately after the addition of $^i\mathrm{Bu}_3\mathrm{Al}$. Thus, in these two

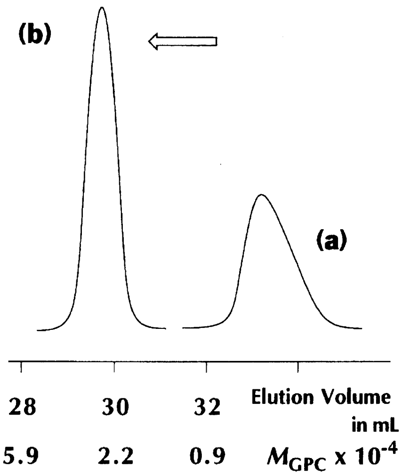


Fig. 1. Polymerization of methyl methacrylate (MMA) initiated with (TPP)AlMe (**2**, X=Me)-methylaluminium bis(2,4-di-*t*-butylphenolate) (**6b**) systems, $[MMA]_0/[\mathbf{2}\ (X=Me)]_0/[\mathbf{6b}]_0=216/1.0/3.0$, $[\mathbf{2}\ (X=Me)]_0=16.2$ mM, CH_2Cl_2 as solvent: GPC profiles of poly(methyl methacrylate)s obtained (**a**) in 2.5 h under irradiation with visible light at 35 °C in the absence of **6b**; 6.1% monomer conversion, $M_n=1600$ ($M_w/M_n=1.13$) and (**b**) in 3 s at room temperature after addition of **6b**; 100% monomer conversion, $M_n=25500$ ($M_w/M_n=1.07$).

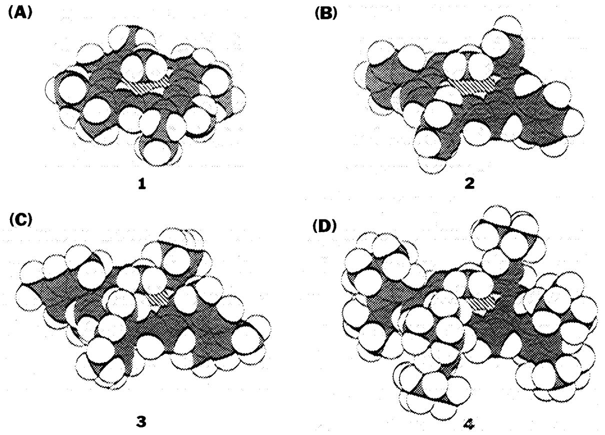
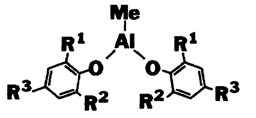
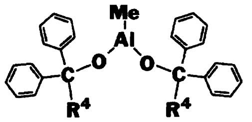


Fig. 2. Space- filling representations of methyl-(porphyrinato)aluminiums (**1**—**4**).

Table 1. Organoaluminium-Based Lewis Acids for High-Speed Living Polymerization of Methyl Methacrylate (MMA) Initiated with Aluminium Porphyrins (**2**)

R_3Al		
Effective (Living)		
R=Ph	**6a**: $R^1={}^tBu$, $R^2=R^3=H$	**7a**: $R^4=Ph$
	6b: $R^1=R^3={}^tBu$, $R^2=H$	
	6c: $R^1={}^tBu$, $R^2=H$, $R^3=OMe$	
	6d: $R^1=Ph$, $R^2=R^3=H$	
	6e: $R^1=R^2={}^tBu$, $R^3=Me$	
	6f: $R^1=R^2=R^3={}^tBu$	
	6g: $R^1=R^2=Cl$, $R^3=H$	
Ineffective (Termination)		
R=Me	**6h**: $R^1=R^2=H$, $R^3={}^tBu$	**7a**: $R^4=H$
Et	**6i**: $R^1=R^2=H$, $R^3=OMe$	
${}^iBu$		

cases, an undesired reaction took place between the nucleophilic growing species (**5**) and ${}^iBu_3Al$, leading to the termination of chain growth. On the contrary, when methyl(tetramesitylporphyrinato)aluminium (**3**, Fig. 2(C)), a sterically more crowded initiator than **2**, was used ($[initiator]_0/[MMA]_0/[{}^iBu_3Al]_0=1/200/3$), the polymerization proceeded from 8 to 61% monomer conversion in 10 min after the addition of ${}^iBu_3Al$, and reached complete monomer consumption within 30 min. In this case, the color of the system characteristic of **5** (R=Me) was retained throughout the polymerization. The M_n of the produced polymer (21400) was very close to the expected value (20000) and M_w/M_n was 1.06, indicating the living character of polymerization. Thus, the methyl groups at the ortho positions of the peripheral phenyl rings in **3** were considered to serve as a steric barrier for the access of ${}^iBu_3Al$ to the nucleophilic center. Nevertheless, the barrier seems not to be sufficient when less bulky Me_3Al and Et_3Al were used as Lewis acids. In connection with this observation, when methylaluminium tetraphenylporphyrin carrying *t*-butyl groups at the meta positions (**4**, Fig. 2(D)) was used in place of **3**, polymerization in the presence of ${}^iBu_3Al$ was terminated at 53% monomer conversion, giving a polymer with a broader MWD ($M_w/M_n=1.35$). Thus, even bulky *t*-butyl groups, when introduced at the meta positions of the phenyl rings of **4**, are not able to form an effective barrier to suppress any undesired reaction.

The enolate species (**5**), derived from methacrylates with bulkier ester groups than MMA, are sterically protected against the access of ${}^iBu_3Al$ under the above-mentioned conditions, even when the porphyrin moiety was ortho-non-substituted tetraphenylporphyrin. An example is the polymerization of ethyl methacrylate (EMA) using **2** (X=Me) as an initiator ($[initiator]_0/[EMA]_0=1/200$), where the growing species have an EtO group in the terminal enolate unit **5** (R=Et). After the addition of ${}^iBu_3Al$ to the system ($[\mathbf{5}\ (R=Et)]/[{}^iBu_3Al]_0=1/3$), polymerization proceeded to 100% monomer conversion in 10 min. The M_n of the produced polymer (26500) was close to the expected value (22800), and the MWD was narrow ($M_w/M_n=1.19$). A similar result was obtained for the polymerization of isopropyl methacrylate (PMA) with the **2**–${}^iBu_3Al$ system, which quantitatively gave a narrow MWD poly(methacrylate) with a predicted M_n.

From these results, not only the steric bulk of the Lewis acid (monomer activator), but also that of the nucleophilic growing species (**5**), are important for realizing the Lewis acid-assisted, controlled anionic polymerization; the basic concept involving a sterically separated nucleophile-electrophile model is thus clearly supported.

3. High-Speed Living Polymerization by Lewis Acids with Low Ligand-Exchange Activity. Since organoboron compounds are much more reluctant than organoaluminium compounds to undergo a ligand-exchange reaction with nucleophiles, they can be used as Lewis-acid accelerators without any steric protection of the nucleophilic and Lewis acidic centers.[7] For example, when $(C_6H_5)_3B$ was added at room temperature to the polymerization mixture of MMA with **5** (R=Me) ($[MMA]_0/[\mathbf{2}\ (X=Me)]_0=200$, 3-h irradiation, 9.3% conversion) at a mole ratio of $(C_6H_5)_3B$ to **5** (R=Me) of 1.0, a modest heat evolution occurs, and the polymerization proceeded up to 74.9% conversion in 2 h (Fig. 3: ●). This corresponds to an acceleration of the polymerization process by a factor of 12. Although the thus-observed acceleration effect was lower than those of, e.g., methylaluminium bis(ortho-substituted phenolates) as Lewis acids, it was almost comparable to that of $(C_6H_5)_3Al$. The GPC curve of the polymer formed

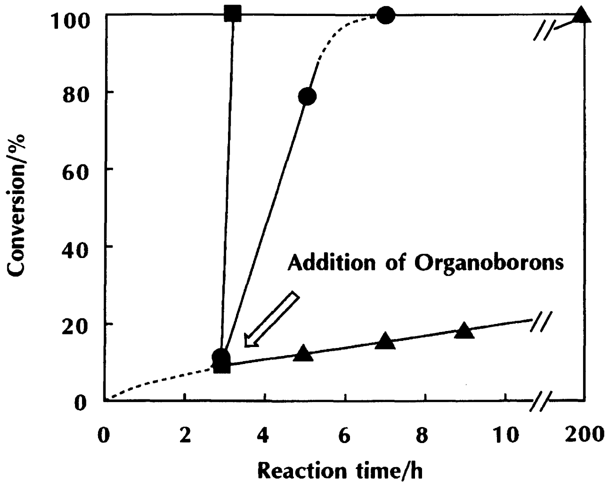


Fig. 3. Polymerization of methyl methacrylate (MMA) initiated with (TPP)AlMe (**2**, X = Me); [MMA]$_0$/[**2** (X=Me)]$_0$=200, [**2** (X=Me)]$_0$=16.2 mM, C_6H_6 as solvent, room temperature. Effects of triphenylboron (●), tris(pentafluorophenyl)boron (■), and tributylboron (▲) on the rate of polymerization; [organoboron]$_0$/[**5** (R=Me)]$_0$=1.0.

at 100% conversion in Fig. 3 (●) was unimodal and very sharp, where the M_w/M_n ratio was 1.04 and the average degree of polymerization (D_p) of the polymer (220) was very close to the initial monomer-to-initiator mole ratio of 200.

Sequential two-stage polymerization of MMA using $(C_6H_5)_3B$ as a Lewis acid clearly demonstrated the living character of polymerization. After the first-stage polymerization of MMA in the presence of $(C_6H_5)_3B$ ([MMA]$_0$/[**2** (X = Me)]$_0$/[$(C_6H_5)_3B$]$_0$ = 75/1.0/1.0, $(C_6H_5)_3B$ added after photoinitiation), a 48-h interval is created at 25 °C; then, 200 molar amount of MMA were again charged to the system. The GPC profile of this two-stage polymerization showed a clear increase in M_n of the polymer from 8400 to 29000 from the first to the second stages, respectively, retaining a narrow molecular-weight distribution (M_w/M_n: 1.06 and 1.07). These results clearly showed a very long lifetime of the growing enolate species (**5**), even in the presence of $(C_6H_5)_3/B$.

Tris(pentafluorophenyl)boron ($(C_6F_5)_3B$), a triarylboron bearing electron-withdrawing perfluorinated phenyl rings, was a much more powerful accelerator than was $(C_6H_5)_3B$ for the polymerization of MMA initiated with (TPP)AlMe (**2**, X=Me). For example, when $(C_6F_5)_3B$ was added at room temperature to the polymerization system ([MMA]$_0$/[**2** (X=Me)]$_0$=200, 3-h irradiation, 8.8% conversion) at an equimolar ratio of $(C_6F_5)_3B$ to the growing species (**5**), the polymerization took place rapidly with considerable heat evolution, attained 100% monomer conversion within only 13 min (Fig. 3, ■). This polymerization was estimated to be 150-times faster than that in the absence of $(C_6F_5)_3B$, and 12.5-times faster than that with $(C_6H_5)_3B$ as a Lewis acid under similar conditions. The M_n of the produced polymer (20400) is close to the expected value of 20000, and the molecular-weight distribution is narrow (M_w/M_n=1.16).

Unlike triarylborons, a trialkylboron, such as tributylboron (Bu_3B), neither accelerates nor terminates the polymerization under similar conditions ([Bu_3B]$_0$/[**2**]$_0$= 1.0) (Fig. 3, ▲). Even at a mole ratio of Bu_3B to the growing species (**5**) of 20.0, the polymerization still requires 183 h for completion. On the other hand, the molecular-weight distribution of the produced polymer is narrow (M_w/M_n = 1.08), and the M_n value (21300 (GPC)) is close to the theoretical one (20000). This is in sharp contrast with trialkylaluminiums, which rapidly react with the growing species (**5**) to terminate the polymerization. Thus, no termination in the presence of Bu_3B indicates the essential difference in the susceptibility between the boron–carbon and aluminium–carbon bonds toward nucleophiles. In sharp contrast with the above-mentioned organoboron compounds, a BF_3–ether complex and BCl_3, more commonly used Lewis acids, rapidly terminate the polymerization.

4. "One-Shot" High-Speed Living Polymerization. Unlike (TPP)AlMe (**2**, X=Me), a thiolate complex of the aluminium porphyrin, such as (TPP)AlSPr (**2**, X = SPr), is capable of initiating the living polymerization of methacrylic esters without irradiation by visible light. Thus, one-shot high-speed living polymerization of MMA without a photoinitiation step is possible by the direct addition of a mixture of MMA and a Lewis acid (**6e**) to the initiator solution.[10] For example, when 100 molar amount of MMA containing 1.5 mol% of **6e** were added at room temperature to a C_6H_6 solution (10 mL) of (TPP)AlSPr (**2**, X=SPr; 0.25 mmol), the color of the solution immediately turned from reddish brown to reddish purple, which is characteristic of a (porphyrinato)aluminium enolate species (**5**). The polymerization took place rapidly with heat evolution, and is completed within only 90 s, affording a polymer with M_n and M_w/M_n (estimated by GPC) of 11200 and 1.13, respectively. An excellent agreement between the thus estimated M_n value and that expected from the monomer-to-initiator mole ratio (10000) indicated the participation of all the molecules of (TPP)AlSPr in initiating the high-speed polymerization. When MMA was added again after the 1st-stage polymerization was completed, 2nd-stage polymerization ensued (living polymerization).

From an end-group analysis of the polymer by ^1H and ^{13}C NMR, the polymerization of MMA with the (porphyrinato)aluminium thiolate–Lewis acid (**6e**) system was initiated by a nucleophilic attack of the thiolate group of the initiator to the monomer, leading to the formation of an alkylthio moiety at the polymer terminal.

5. Synthesis of Monodisperse, High-Molecular-Weight Polymers. The synthesis of monodis-

Table 2. Polymerization of Methacrylic Esters via (Porphyrinato)aluminium Enolates (**5**) in the Presence of Methylaluminium Bis(2-*t*-butyl-4-methoxyphenolate) (**6c**).[a)]

Run	Monomer	Time/s	Conversion[b)]/%	M_n[c)]	($M_{n\,\mathrm{theory}}$)	M_w/M_n[c)]
1	EMA	30	100	27700	(23000)	1.09
2	^{i}PMA	30	100	30900	(25600)	1.10
3	^{n}BMA	30	100	34900	(28400)	1.07
4	^{i}BMA	30	100	36300	(28400)	1.07
5	^{t}BMA	90	11	—	—	—
6	BnMA	90	100	32900	(35200)	1.08
7	C_{12}MA	90	64	30600	(32600)	1.09

a) In CH_2Cl_2 under nitrogen, [Monomer]$_0$/[**2** (X=Me)]$_0$/[**6c**]$_0$=200/1.0/0.5, [**2** (X=Me)]$_0$=16.2 mol m^{-3}. b) Determined by ^{1}H NMR analysis of the reaction mixture. c) Estimated by GPC based on polystyrene standards.

perse, ultrahigh-molecular-weight polymers is one of the challenging subjects of both fundamental and practical interest. The aluminium porphyrin (**2**)–Lewis acid systems can be used for this purpose by taking advantage of their strikingly high activities.[11)] A typical example is given below. To a CH_2Cl_2 solution (12.0 mL) of (TPP)AlMe (**2**, X=Me; 0.30 mmol) in a 200-mL round-bottomed flask carrying a side ampule (20 mL) (Fig. 4) was added MMA (30 mmol) with a syringe; the mixture was irradiated with xenon arc light ($\lambda > 420$ nm) at 35 °C for 4 h, where **2** (X=Me) was completely converted to the aluminium enolate species (**5**). Then, the irradiation was stopped, and the flask was tilted to the ampule side in order to minimize the amount of **5** (R=Me) remaining in the flask to provide a high MMA-to-**5** mole ratio in the next-stage polymerization. After most of the initiator solution had been transferred to the side ampule, a CH_2Cl_2 solution of a mixture of 3590 molar amount of MMA and 85 molar amount of **6e** (2.5 mol% with respect to MMA) was added to the remaining solution with a syringe; the polymerization was conducted at 0 °C. Complete consumption of MMA was attained within 20 min, affording a polymer with M_n and M_w/M_n, respectively, of 5.6×10^5 and 1.1. Similarly, PMMA with M_n exceeding a million ($M_n=1.02\times10^6$, $M_w/M_n=1.2$) was synthesized by polymerizing 8300 molar amount of MMA with **5** (R=Me) in the presence of **6e** (4.2 mol%) under similar conditions.

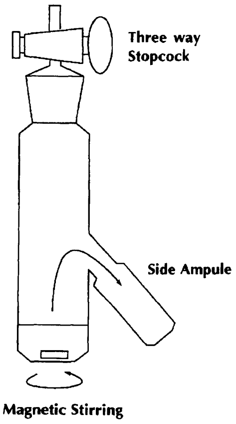


Fig. 4. The polymerization flask designed for the synthesis of high molecular weight ($M_n > 500000$) poly(methyl methacrylate)s by the high speed living polymerization with the (porphyrinato)aluminium enolate (**5**)–Lewis acid (**6e**) systems.

6. Monomers for High Speed Living Polymerization. As shown in Table 2, a variety of methacrylic esters such as ethyl, isopropyl, butyl, isobutyl, benzyl, and dodecyl methacrylates were found to undergo high-speed living polymerization with the aluminium porphyrin (**2**)/Lewis acid (**6b** or **6d**) (1/3) systems, giving the corresponding polymers with narrow molecular-weight distributions (M_w/M_n: 1.1—1.2). On the contrary, the high-speed polymerization of *t*-butyl methacrylate was not successful, probably due to the essential difficulty in a coordinative interaction at the sterically crowded carbonyl group with the bulky Lewis acidic center (Run 5).

In addition to methacrylic esters, a conjugate vinyl monomer, such as methacrylonitrile (MAN), was rapidly polymerized with the (porphyrinato)aluminium enolate (**5**)–Lewis acid (**6e**) system, where the sequential two-stage high-speed polymerization of MMA and MAN afforded the corresponding block copolymer of a narrow molecular-weight distribution.[12)] For example, when 100 molar amount of MAN with respect to **5** (R=Me) were added to the living polymer of MMA prepared with **2** (X=Me) in the presence of **6e** ([MMA]$_0$/[**2**]$_0$/[**6e**]$_0$=100/1/10, 100% conversion), a rapid polymerization of MAN took place to attain a 100% conversion within 3 h, affording the corresponding block copolymer with a narrow MWD ($M_w/M_n=1.18$), where the M_n value (20200) was close to that expected from the initial monomer-to-initiator mole ratio (16700).

The system of aluminium porphyrin (**2**) coupled with a bulky Lewis acid (**6d**) brought about the high-speed living ring-opening polymerization of 1,2-epoxypropane (propylene oxide, PO). The polymerization of PO via (porphyrinato)aluminium alkoxide (**2**, X=OR) as a growing species was dramatically accelerated (ca. 500 times) upon the addition of a Lewis acid (**6d**).[13] The molecular weight of the polyether formed increased linearly with the amount of propylene oxide reacted, while the molecular-weight distribution was invariably narrow. Furthermore, the high-speed immortal polymerization of PO was realized with the aluminium porphyrin (**2**)–alcohol–Lewis acid (**6e**) system.[14] The immortal polymerization of PO with the (TPP)AlCl (**2**, X=Cl)–2-propanol (1/9) system at room temperature proceeded rather slowly in CH_2Cl_2 to attain a 31% conversion in 2 h. On the other hand, when 3 molar amount of **6e** with respect to **2** were added to the system, a rapid polymerization took place, and a 52% monomer conversion was attained only after 1 min, affording a polymer with an M_w/M_n of 1.10, the ratio of the number of the polymer molecules to that of **2** (N_p/N_{TPP}) being 10. By taking advantage of this, narrow MWD poly(propylene oxide)s with an N_p/N_{TPP} of 55 to 1100 were synthesized by increasing the ratio of 2-propanol to **2** from 49 to 1000 in the presence of 0.1—3.3 mol% of **6e** with respect to the monomer.

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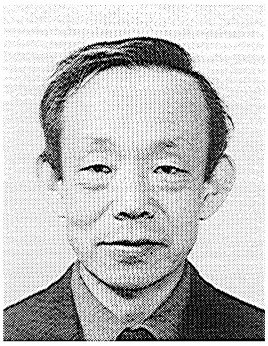

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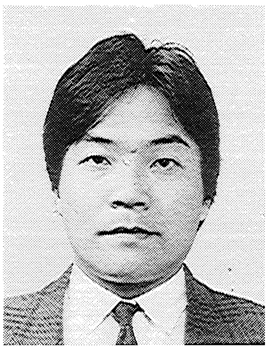

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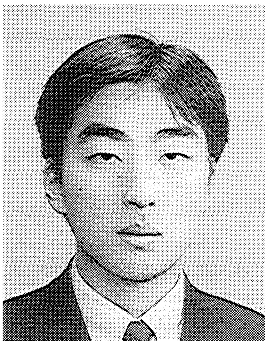

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