Notes

Lewis Acid-Promoted Living Anionic Polymerization of Alkyl Methacrylates Initiated with Aluminum Porphyrins. Importance of Steric Balance between a Nucleophile and a Lewis Acid

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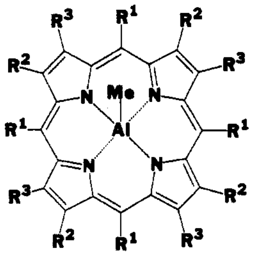
Introduction

We have reported the Lewis acid-assisted, high-speed living anionic polymerization of methacrylic esters via (porphinato)aluminum enolates (**5**$_m$) as the nucleophilic growing species (Scheme 1),[1] where the basic concept involves activation of monomer through coordination to a Lewis acid (Figure 1). A key importance in the methodology is how to suppress the undesired reaction between the nucleophile (**5**$_m$) and Lewis acid, leading to termination of polymerization. One of our approaches was to make use of sterically crowded Lewis acids such as methylaluminum bis(*ortho*-substituted phenolates). In the polymerization of methyl methacrylate initiated with methylaluminum tetraphenylporphine (**2**), these bulky Lewis acids serve as very effective accelerators without damaging the living character of polymerization, while *ortho*-nonsubstituted analogs and simple organoaluminum compounds such as trimethylaluminum cause termination.[2] The present paper focuses attention on the steric bulk of the nucleophile component (**5**$_m$), by using strategically designed aluminum porphyins and some other methacrylates, for the purpose of understanding the scope and limitation of this method (Figure 1).

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine was synthesized by Adler's method.[3] Tetramesitylporphine [5,10,15,20-tetrakis-(2′,4′,6′-trimethylphenyl)porphine] and 5,10,15,20-tetrakis(3′,5′-di-*tert*-butylphenyl)porphine were synthesized by Lindsey's method.[4] Etioporphyrin I (2,7,12,17-tetraethyl-3,8,13,18-tetramethylporphine) was synthesized from *tert*-butyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate, according to the literature method.[5] These free bases were converted into the corresponding methylaluminum porphyrins (**1**–**4**) by reaction with trimethylaluminum.[2] Purification of monomers, solvents, and trialkylaluminum compounds was carried out according to the established methods.[2]

Polymerization. A typical example is given below for the polymerization of methyl methacrylate (MMA) initiated with **2** in the presence of triisobutylaluminum (i-Bu$_3$Al): To a 50-mL round-bottomed flask attached to a three-way stopcock, containing a CH$_2$Cl$_2$ solution (10 mL) of **2** (0.25 mmol), was added MMA (50 mmol, 5.4 mL) by a syringe in a nitrogen stream. The mixture was illuminated at 35 °C by a xenon arc light (300 W) through a filter to cut out light of wavelength shorter than 420 nm. After 2.5-h irradiation, i-Bu$_3$Al was added (3 equiv with respect to **2**) at room temperature under diffuse light. An aliquot of the reaction mixture was periodically taken out by a syringe in a nitrogen stream and subjected to ^{1}H NMR and GPC analyses to determine the monomer conversion and average molecular weights of the produced polymer, respectively.



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

Polymerizations of MMA with other methylaluminum porphyrin–i-Bu$_3$Al systems and of ethyl methacrylate and isopropyl methacrylate with the **2**–i-Bu$_3$Al system were carried out similarly to the above.

Measurements. GPC was performed at 40 °C on a Tosoh Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector, using THF as eluent. The molecular weight calibration curve was obtained by using standard polystyrenes. ^{1}H NMR measurements were performed in CDCl$_3$ at 22 °C using a JEOL type GSX-270 spectrometer.

Results and Discussion

Polymerization of methyl methacrylate (MMA) was carried out by using as initiators methylaluminum porphyrins with different porphyrin ligands (**1**–**4**) under irradiation ($\lambda > 420$ nm) at 35 °C. After 2.5 h (monomer conversion: 6–9%) the irradiation was stopped, and triisobutylaluminum (i-Bu$_3$Al) was added at room temperature to the system ([initiator]$_0$/[MMA]$_0$/[i-Bu$_3$Al]$_0$ = 1/200/3). As we have already reported,[2] the polymerization of MMA initiated with methylaluminum tetraphenylporphine (**2**; Figure 2B) was accelerated at the early stage after the addition of i-Bu$_3$Al but soon terminated with a color change of the system from dark reddish purple characteristic of **5**$_m$ to the greenish purple typical of the alkylaluminum porphyrin family. The monomer conversion was increased from 9 to 63% in 10 min after the addition of i-Bu$_3$Al, but it was no longer increased upon prolonged reaction for 30 min (run 2, Table 1). The M_n of the polymer formed (20 200), as estimated by GPC, was higher than that expected from the ratio of the reacted MMA to **2** (12 800), and the MWD was broad (M_w/M_n = 1.41). When a sterically less crowded initiator such as methylaluminum etioporphyrin I (**1**; Figure 2A) was used under otherwise identical conditions, the polymerization stopped immediately after the addition of i-Bu$_3$Al (run 1). Thus, in these two cases, the undesired reaction (Scheme 2) takes place between the nucleophilic growing species (**5**$_m$) and i-Bu$_3$Al, leading to termination of chain growth. On the contrary, when methylaluminum tetramesitylpor-

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Table 1. Polymerization of Alkyl Methacrylates Initiated with Methylaluminum Porphyrins (1–4) in the Presence of Trialkylaluminums (R'_3Al)[a]

run	initiator	R'_3Al	monomer	time[b]/min	conv[c]/%	M_n[d]	($M_{n,calc}$)[e]	M_w/M_n[d]
1	**1**	i-Bu_3Al	MMA	0	9			
				10	11			
				30	12			
2[f]	**2**	i-Bu_3Al	MMA	0	6			
				10	63			
				30	64	20 200	(12 800)	1.41
3	**3**	Me_3Al	MMA	0	8			
				10	9			
				30	9			
4	**3**	Et_3Al	MMA	0	8			
				10	28			
				30	28			
5	**3**	i-Bu_3Al	MMA	0	8			
				10	61			
				30	100	21 400	(20 000)	1.06
6	**4**	i-Bu_3Al	MMA	0	7			
				10	53			
				30	53	11 100	(10 600)	1.35
7	**1**	i-Bu_3Al	EMA	0	5			
				10	100	26 400	(22 800)	1.19
8	**1**	i-Bu_3Al	PMA	0	12			
				10	100	27 400	(25 600)	1.18

[a] In CH_2Cl_2 under nitrogen, $[\text{initiator}]_0/[\text{monomer}]_0/[R'_3Al]_0 = 1/200/3$, $[\text{initiator}]_0 = 16.2$ mM. [b] After addition of R'_3Al. [c] Determined by ^1H NMR analysis of the reaction mixture. [d] Estimated by GPC based on polystyrene standards. [e] $M_{n,calc}$ = molecular weight of monomer × ($[\text{monomer}]_0/[\text{initiator}]_0$) × (conversion)/100. [f] Data from ref 2.

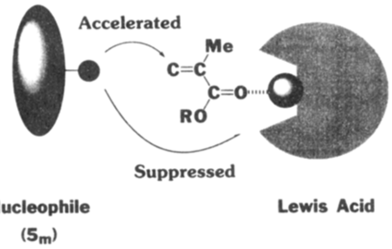


Figure 1. Basic concept of the Lewis acid-assisted, high-speed living anionic polymerization.

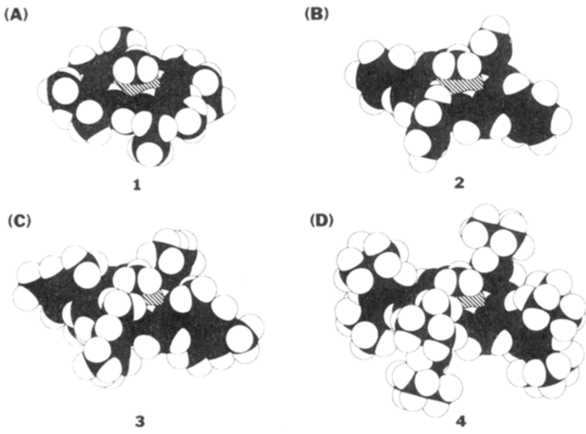
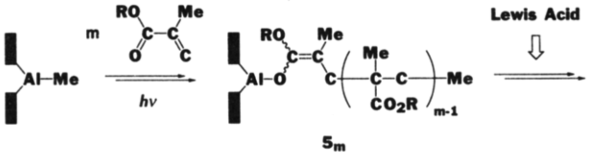


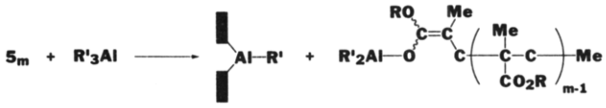
Figure 2. Space-filling representations of methylaluminum porphyrins (1–4).

Scheme 1



phine (**3**; Figure 2C), a sterically more crowded initiator than **2**, was used, the polymerization proceeded from 8 to 61% monomer conversion in 10 min after the addition of i-Bu_3Al and reached complete monomer consumption within 30 min (run 5). In this case, the color of the system characteristic of $\mathbf{5_m}$ was retained throughout the polymerization. The M_n of the produced polymer (21 400) was very close to the expected value (20 000) and the 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** are considered to serve as the steric barrier for the access of i-Bu_3Al to the nucleophilic center. Nevertheless, the barrier seems not sufficient when less bulky trimethylaluminum (Me_3Al) and triethylaluminum (Et_3Al) are used as Lewis acids (runs 3 and 4). In connection with this observation, when methylaluminum tetraphenylporphyrin carrying *tert*-butyl groups at the *meta* positions (**4**; Figure 2D) was used in place of **3**, the polymerization in the presence of i-Bu_3Al was terminated at 53% monomer conversion, giving a polymer with broader MWD (M_w/M_n = 1.35) (run 6). Thus, even bulky *tert*-butyl groups, when introduced at the *meta* positions of the phenyl rings of **2**, are not able to form the effective barrier to suppress the undesired reaction (Scheme 2).

Scheme 2



The enolate species ($\mathbf{5_m}$), derived from methacrylates with bulkier ester groups than MMA, are sterically protected against the access of i-Bu_3Al under the above-mentioned conditions, even when the porphyrin moiety is *ortho*-nonsubstituted tetraphenylporphine. An example is shown by the polymerization of ethyl methacrylate (EMA) using **2** as initiator ($[\text{initiator}]_0/[\text{EMA}]_0/[\text{i-}Bu_3Al]_0 = 1/200/3$), where the polymerization proceeded to 100% monomer conversion in 10 min after the addition of i-Bu_3Al to the system. The M_n of the produced polymer (26 500) was close the expected value (22 800), and the MWD was narrow (M_w/M_n = 1.19) (run 7). A similar result was obtained for the polymerization of isopropyl methacrylate (PMA) with the **2**–i-Bu_3Al system, which quantitatively gave a narrow MWD polymethacrylate with a predicted M_n (run 8).

In conclusion, not only the steric bulk of the Lewis acid (monomer activator) but also that of the nucleophilic growing species ($\mathbf{5}_{\mathbf{m}}$) is important for realizing the Lewis acid-assisted, controlled anionic polymerization, and our basic concept involving a sterically separated nucleophile–electrophile model is clearly supported.

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References and Notes

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