Lewis Acid-Assisted Anionic Ring-Opening Polymerization of Epoxide by the Aluminum Complexes of Porphyrin, Phthalocyanine, Tetraazaannulene, and Schiff Base as Initiators

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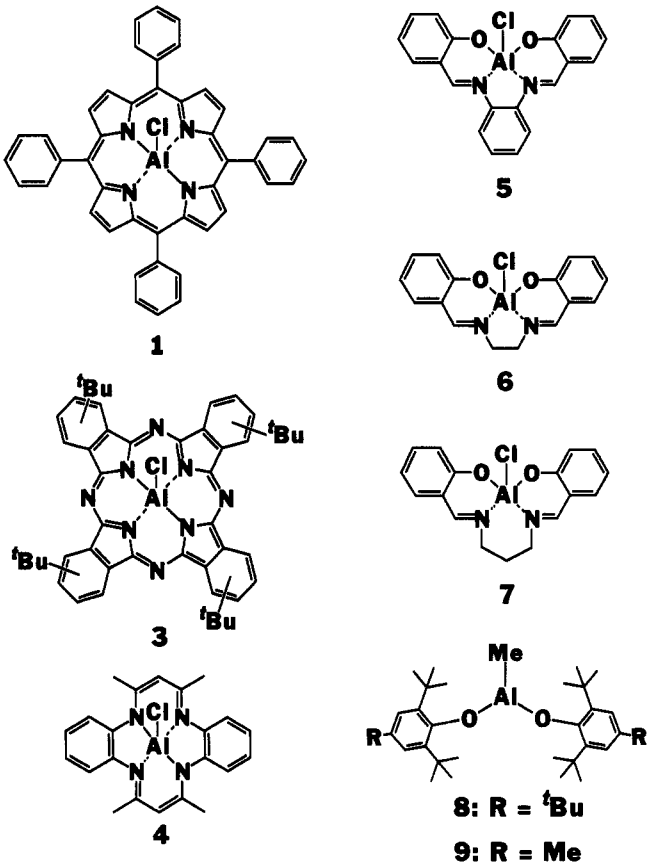
ABSTRACT: Polymerization of 1,2-epoxypropane (PO) with aluminum porphyrin (2) was substantially accelerated (460 times) by the addition of an organoaluminum compound such as methylaluminum bis-(2,4,6-tri-*tert*-butylphenolate) (8). The molecular weight of the produced polyether increased linearly with the amount of PO reacted, while the molecular weight distribution (MWD) was invariably narrow throughout the polymerization. Sequential polymerizations of PO and 1,2-epoxybutane (BO) with the aluminum porphyrin–8 system afforded the corresponding block copolymer with a narrow MWD. In the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (9) as Lewis acid, aluminum complexes of phthalocyanine (3), tetraazaannulene (4), and Schiff bases (5–7) with very low reactivities brought about the polymerization of 1,2-epoxypropane fairly rapidly at room temperature.

Introduction

Aluminum porphyrins are excellent initiators for the living polymerizations of a wide variety of monomers such as epoxides,[1] lactones,[2] alkyl methacrylates,[3] and alkyl acrylates,[4] affording the corresponding polymers of controlled molecular weights with a narrow molecular weight distribution (MWD). In the course of this study, we have found the polymerization of methyl methacrylate with aluminum porphyrin, proceeding via an enolate aluminum porphyrin as the growing species,[3] is dramatically accelerated by the addition of a bulky Lewis acid such as methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (8), where the polymerization is completed within seconds under appropriate conditions to give a polymer with a narrow MWD.[5] The basic concept of this high-speed living polymerization involves the coordinative activation of monomer by the bulky Lewis acid which does not react directly with the growing species on bulky aluminum porphyrin (Figure 1).

Anionic living ring-opening polymerization of an epoxide such as 1,2-epoxypropane (propylene oxide, PO) proceeds via an alcoholate aluminum porphyrin (2) as the growing species (Scheme 1).[1] In the present paper, we wish to report results of the successful extension of the above method to the Lewis acid-assisted anionic living ring-opening polymerization of PO with aluminum porphyrin. Furthermore, in order to generalize the basic concept of the high-speed living polymerization, aluminum complexes of phthalocyanine (3), tetraazaannulene (4), and Schiff bases (5–7) were also employed as initiators.



Results and Discussion

Ring-Opening Polymerization of Epoxide Initiated with Aluminum Porphyrin (1) in the Presence of an Organoaluminum Compound (8). Polymerization of 1,2-epoxypropane (propylene oxide, PO), carried out at room temperature by using chloroaluminum porphyrin (1; (TPP)AlCl, 0.20 mmol) as initiator in CH_2Cl_2 (8.0 mL) at the initial mole ratio $[PO]_0/[1]_0$ of 200, proceeded rather slowly to attain 19.8% conversion in 7 h, giving a polymer with M_n and M_w/M_n of 3300 and 1.05, respectively (Figure 2a). On the other hand, when a CH_2Cl_2 solution (0.3 mL) of methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (8) (0.1 mmol; 0.25 mol % with respect to PO) was added to the reaction mixture, a rapid polymerization took place with vigorous heat evolution to attain 85.5% conversion within only 3 min. The extent of acceleration was estimated to be 460 times. The GPC profile of the polymer thus formed (Figure 2b) showed a unimodal, sharp chromatogram, from which the M_w/M_n ratio was estimated, based on polystyrene standards, to be 1.21. Absence of

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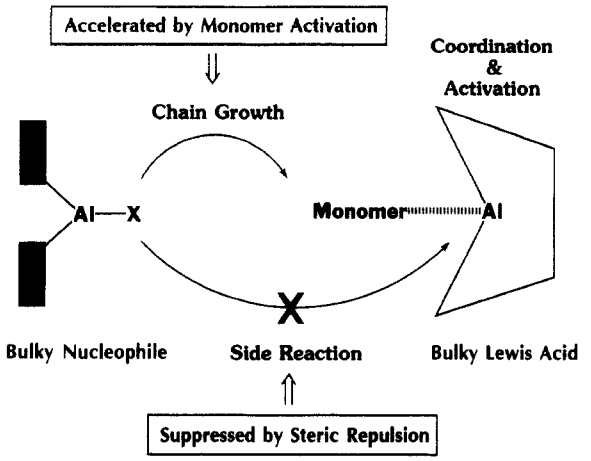


Figure 1. "High-speed living polymerization" by aluminum porphyrin as nucleophile in conjunction with organoaluminum compound as Lewis acid. Schematic representation of the basic concept.

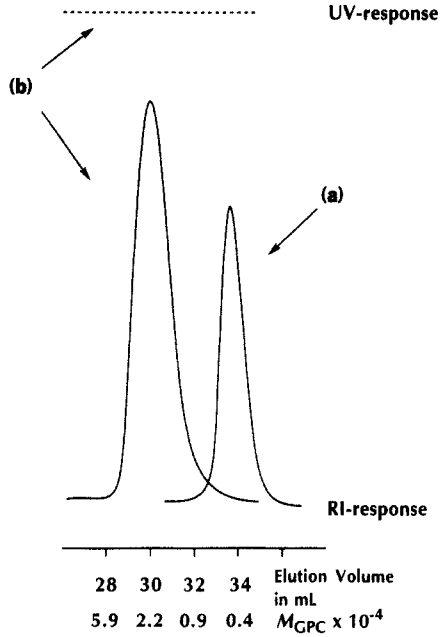
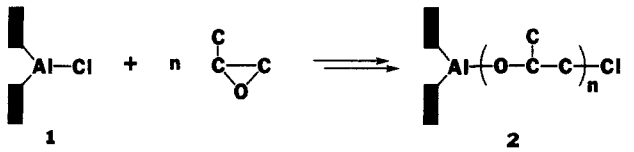


Figure 2. Polymerization of 1,2-epoxypropane (PO) by the chloroaluminum porphyrin(1)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (8) system, $[PO]_0/[8]_0/[1]_0$ = 200/0.5/1.0, $[1]_0$ = 18.5 mM, CH_2Cl_2 as solvent, room temperature. GPC profiles of poly(1,2-epoxypropanes) formed (a) in 7 h in the absence of 8, 19.8% conv, and (b) in 3 min after the addition of 8, 85.5% conversion.

Scheme 1



the peak a in the chromatogram, b indicates that every molecule of the growing polymer **2** formed before addition of 8 took part in the subsequent rapid polymerization in the presence of 8. The M_n of the produced polymer was estimated to be 11 900, which is close to the expected value (9900), taking the monomer-to-initiator mole ratio and conversion into consideration. Polymerization of PO using an alcoholate aluminum porphyrin ((TPP)Al$(PO)_{10}$Cl, **2**) as initiator also proceeded rapidly in the presence of 8: As soon as 200 equiv of PO were added to a CH_2Cl_2 solution of (TPP)Al$(PO)_{10}$Cl (**2**, n = 10) containing only 0.1 mol % of methylaluminum diphenolate (8) with respect to PO, the polymerization started and attained 52.5, 73.6,

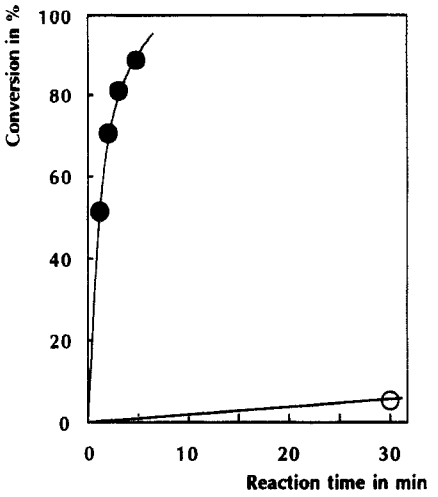


Figure 3. Polymerization of 1,2-epoxypropane (PO) by the alcoholate aluminum porphyrin (**2**, n = 10)/methylaluminum bis-(2,4,6-tri-*tert*-butylphenolate) (8) system, $[PO]_0/[8]_0/[2]_0$ = 200/0.2/1.0, $[2]_0$ = 18.5 mM, CH_2Cl_2 as solvent, room temperature. Time–conversion curve.

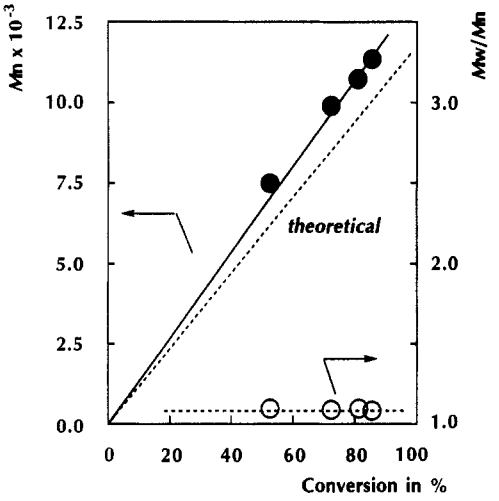


Figure 4. Polymerization of 1,2-epoxypropane (PO) by the alcoholate aluminum porphyrin (**2**, n = 10)/methylaluminum bis-(2,4,6-tri-*tert*-butylphenolate) (8) system. Relationship between M_n(●) (M_w/M_n (○)) of the polymer and conversion (reaction conditions, see Figure 3).

and 81.1% conversion in 1, 2, and 3 min, respectively (Figure 3). The M_n value of the polymer increased linearly with conversion, retaining the ratio M_w/M_n at 1.1 (Figure 4). An excellent agreement between the observed and expected M_ns of the polymer (Figure 4) again indicates the quantitative initiation and propagation from every molecule of the starting alcoholate aluminum porphyrin (**2**).

The rate of polymerization by the **2** (n = 10)/8 system is dependent on the concentration of 8 (Figure 5): When the initial mole ratio of 8 to PO was increased from 0.025 to 2.5 mol %, the polymerization was much more accelerated to attain 94.1% conversion in only 3 min. If the added 8 initiates the polymerization, the number of the polymer molecules produced should increase with an increment of the amount of 8 and the M_n value should be decreased. However, irrespective of the mole ratio of 8 to PO (0.025–2.5 mol %), the observed M_n values at 100% conversion were all close to the theoretical M_n (11 600), as indicated by the ratio of the number of the polymer molecules and **2** (N_pN_{TPP})[6] being almost constant at unity (Figure 6), and the produced polymers were all of narrow MWD. As shown in Figure 7, the M_n of the polymer could be controlled by changing the monomer-to-initiator ratio in the presence of 0.2 equiv of 8 with respect to **2** (n = 10),

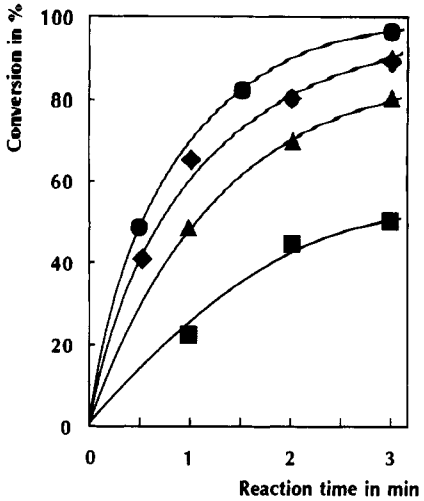


Figure 5. Polymerization of 1,2-epoxypropane (PO) by the alcoholate aluminum porphyrin (**2**, $n = 10$)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**8**) system, $[PO]_0/[2]_0 = 200$, $[2]_0 = 18.5$ mM, CH_2Cl_2 as solvent, room temperature, initial ratios of **8** to PO (mol %) = 0.025 (■), 0.1 (▲), 0.5 (◆), and 2.5 (●). Effect of the amount of Lewis acid (**8**) on the rate of polymerization.

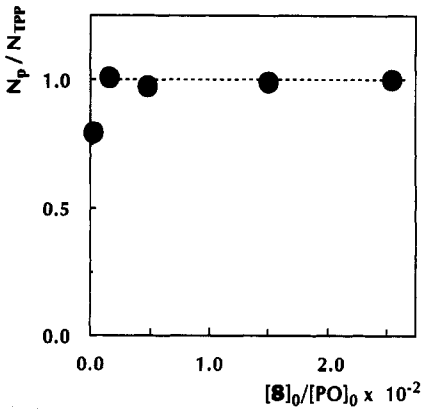


Figure 6. Polymerization of 1,2-epoxypropane (PO) by the alcoholate aluminum porphyrin (**2**, $n = 10$)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**8**) system, $[PO]_0/[2]_0 = 200$, $[2]_0 = 18.5$ mM, CH_2Cl_2 as solvent, room temperature. Relationship between the ratio of the numbers of the molecules of polymer (N_p) to **2** (N_{TPP}) and the initial mole ratio of **8** to PO.

where the observed M_ns of the polymers obtained at 100% conversion were in good agreement with the estimated value from $[PO]_0/[2]_0$. These results indicate that the added **8** does not initiate but only accelerates the polymerization. In this regard, as exemplified by the GPC profile (Figure 2b), all the polymers produced by the **2**/**8** system were peakless when monitored at 276 nm (2,4,6-tri-*tert*-butylphenol, λ_{max} 276 nm; anisole 269 nm),[7] indicating no incoporation of the phenolate unit of **8** into the polymer terminal. **8** alone did not bring about the polymerization of PO under similar conditions.

The living nature of the polymerization of PO by the alcoholate aluminum porphyrin (**2**)/organoaluminum (**8**) system was clearly demonstrated by a successful block copolymerization from PO to 1,2-epoxybutane (BO): At the first stage, polymerization of PO in CH_2Cl_2 by the **2**/**8** system ($[PO]_0/[8]_0/[2]_0 = 50/1.0/0.2$) was completed within 15 min at room temperature to give a polymer with M_n and M_w/M_n, respectively, of 4600, and 1.04 (Figure 8 (peak I)). When BO (200 equiv) was added to the polymerization mixture, the second-stage polymerization of BO took place rapidly to attain 75.2% conversion in 60 min. The GPC chromatogram of the polymer obtained at 75.2% conversion was observed to shift toward the higher molecular weight region (Figure 8 (peak II); M_n = 11 300, M_w/M_n = 1.18) from that of the prepolymer of PO (peak I), retaining the narrow MWD.

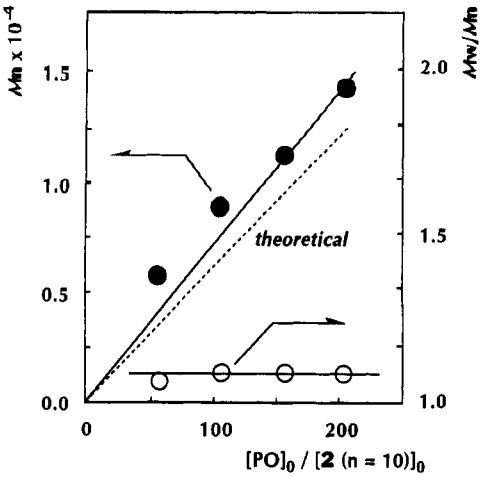


Figure 7. Polymerization of 1,2-epoxypropane (PO) by the alcoholate aluminum porphyrin (**2**, $n = 10$)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**8**) (1.0/0.2) system in CH_2Cl_2 at room temperature. Relationship between M_n (●) (M_w/M_n (○)) of the polymer formed at 100% conversion and the initial monomer-to-initiator mole ratio ($[PO]_0/[2]_0$).

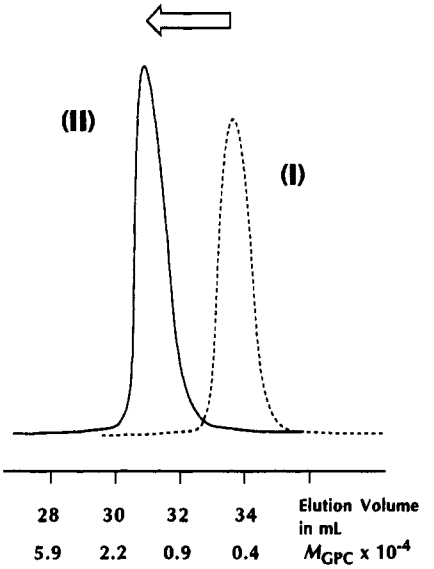


Figure 8. Block copolymerization of 1,2-epoxypropane (PO) and 1,2-epoxybutane (BO) in CH_2Cl_2 at room temperature by the alcoholate aluminum porphyrin (**2**, $n = 10$)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**8**) (1.0/0.5) system. GPC profiles of (I) the prepolymer of PO ($[PO]_0/[2]_0 = 50$, 100% conversion (M_n = 4600, M_w/M_n = 1.04) and (II) the block copolymer of PO and BO ($[BO]_0/[2]_0 = 200$, 75.2% conversion (M_n = 11 300, M_w/M_n = 1.18).

Thus, the concept of the Lewis acid-assisted "high-speed living polymerization", established by the polymerization of methacrylic esters, was successfully applied to the ring-opening polymerization of epoxides.

Ring-Opening Polymerization of Epoxide with Various Aluminum Complexes (3–7) as Initiators in the Presence of a Lewis Acid (9). The key point of the "high-speed living polymerization" (Figure 1) is the steric suppression of an undesired reaction between the nucleophilic growing species (**2**) and the Lewis acid, for which not only the steric bulk of the Lewis acid but also that of the porphyrin ligand in **2** is considered important. Thus, the Lewis acid-promoted ring-opening polymerization of PO was attempted by using aluminum complexes bearing other chelating ligands (**3**–**7**) as initiators in the presence of **9** as Lewis acid. As reported by Spassky et al.,[8] aluminum complexes of Schiff bases as initiators exhibit much lower activities than aluminum porphyrins for the

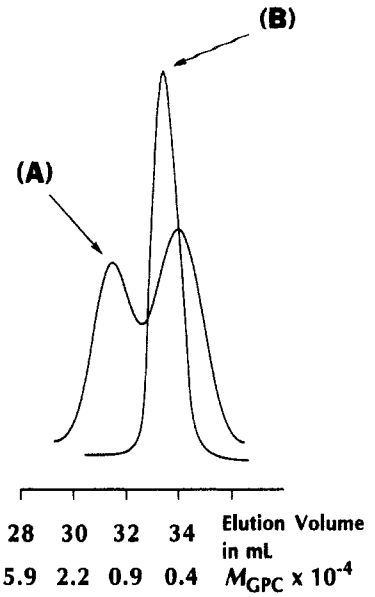


Figure 9. Polymerization of 1,2-epoxypropane (PO) by (Salphen)AlCl (**5**) and the (Salphen)AlCl (**5**)/methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**9**) system. GPC profiles of poly(1,2-epoxypropanes) obtained with (A) **5** ($[PO]_0/[5]_0$ = 500, $[5]_0$ = 28.6 mM, without solvent, 80 °C, 6 days, 100% conversion (M_n = 6700, M_w/M_n = 2.31), and (B) the **5**/**9** system ($[PO]_0/[9]_0/[5]_0$ = 200/1.0/1.0, $[5]_0$ = 71.4 mM, without solvent, room temperature, 7 days in the absence of **9** and 70 min after the addition of **9**, 43.3% conversion (M_n = 4200, M_w/M_n = 1.18).

ring-opening polymerization of epoxides. In fact, the polymerization of PO (50 equiv) by using a Schiff base complex (Salphen)AlCl (**5**) as initiator proceeded extremely slowly at room temperature to attain only 4% conversion in 8 days. Even at 80 °C, the polymerization was slow and required 6 days for completion, affording a polymer with broad and bimodal MWD (Figure 9A).

In the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**9**), the polymerization of PO with **5** took place smoothly even at room temperature, affording a polymer with a narrow MWD: An example is shown by the polymerization of PO (200 equiv) with **5** without solvent at room temperature. The polymerization proceeded up to 5.1% conversion in 7 days without **9**, while the monomer conversion reached 29.5 and 43.3% in 15 and 70 min, respectively, after the addition of **9** ($[9]_0/[5]_0$ = 1.0). This corresponds to approximately 3200 times acceleration compared with the polymerization in the absence of **9**. As estimated by GPC (Figure 9B), the M_w/M_n ratio of the polymer produced at 43.3% conversion was 1.18, and the M_n was 4200, which is close to that expected (5000) when every molecule of **5** forms one polymer molecule (Table 1, run 3). In the presence of **9**, (Salen)AlCl (**6**) and (Salpn)AlCl (**7**) were also capable of bringing about the polymerization of PO at room temperature under appropriate conditions, where the degrees of acceleration are estimated to be 1300 and 1200 times, respectively (Table 1, runs 4 and 5).

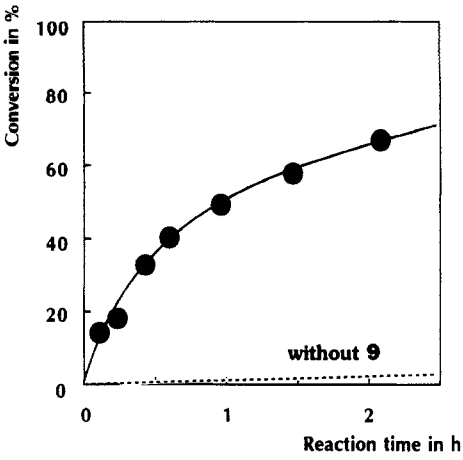


Figure 10. Polymerization of 1,2-epoxypropane (PO) by the (Me_4DBTAA)AlCl (**4**)/methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**9**) system, $[PO]_0/[9]_0/[4]_0$ = 200/1.0/1.0, $[2]_0$ = 71.4 mM, without solvent, room temperature. Time–conversion curve.

A similar Lewis acid-promoted anionic chain growth was realized in the ring-opening polymerization of PO initiated with the aluminum complexes of phthalocyanine (**3**) and tetraazaannulene (**4**). Although a phthalocyanine complex, (Bu_4Pc)AlCl (**3**), is structurally analogous to (TPP)AlCl (**1**), the polymerization of PO (200 equiv) with (Bu_4Pc)AlCl (**3**) alone hardly took place at room temperature, and the monomer conversion after 3 days was less than 1%. On the other hand, addition of **9** to the above mixture gave rise to the polymerization of PO, where 51.0% conversion was attained in 3 days (Table 1, run 1). The polymerization of 200 equiv of PO with a tetraazaannulene complex, (Me_4DBTAA)AlCl (**4**), without solvent at room temperature proceeded to only 29.9% conversion in 4 days in the absence of **9**, but the chain growth progressed considerably up to 74.0% conversion in only 90 s upon addition of **9** to this system. The extent of acceleration was estimated to be 5200 times (Table 1, run 2). As shown in Figure 10, a rapid polymerization proceeded from the beginning when PO (200 equiv) was added to a mixture of **4** and **9** (1/1), where the M_n value of the produced polymer increased linearly with monomer consumption (Figure 11), while the M_w/M_n ratio was almost constant at 1.4–1.5.

Tacticities of Poly(propylene oxides). ^{13}C NMR studies indicated that the stereoregularity of the produced polymer is affected by the structure of the initiator but not by the presence of Lewis acid. Figure 12 shows the ^{13}C NMR spectrum in $CDCl_3$ at 22 °C of the polymer obtained by the 1/8 system ($[PO]_0/[1]_0/[8]_0$ = 200/1.0/0.5, 85.5% conversion; M_n = 11 900, M_w/M_n = 1.21), where the signals a, b, and c are due to the methyl, methylene, and methine carbons, respectively. The simplicity of signal a indicates that the polymer chain consists exclusively of head-to-tail linkages, as typically observed for anionic polymerization of PO. Two methylene carbon signals

Table 1. Polymerization of 1,2-Epoxypropane (PO) with Aluminum Complexes (3–7) in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (9)[a]

	before addition of 9			after addition of 9				
run	initiator	time/days	conv[b]/%	time/min	conv[b]/%	M_n[c]	($M_{n_{calc}}$)	M_w/M_n[c]
1	**3**	3	<1	3 days	50.9	1800	(5900)	1.14
2	**4**	4	29.9	1.5	73.9	5800	(8600)	1.40
3	**5**	7	5.1	70	43.3	4200	(5000)	1.18
4	**6**	7	10.9	75	44.8	2900	(5200)	1.06
5	**7**	2	2.3	30	22.1	1800	(2600)	1.12

[a] Without solvent under nitrogen, $[PO]_0/[initiator]_0/[9]_0$ = 200/1.0/1.0, $[initiator]_0$ = 71.4 mM. [b] Determined by ^1H NMR analysis of the reaction mixture. [c] Estimated by GPC on the basis of polystyrene standards.

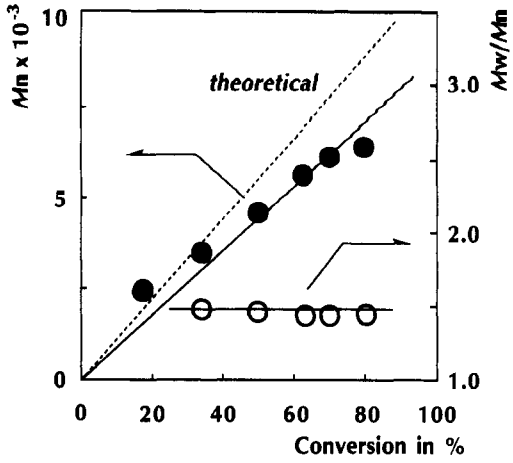


Figure 11. Polymerization of 1,2-epoxypropane (PO) by the (Me_4DBTAA)AlCl (4)/methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (9) system (reaction conditions, see Figure 10). Relationship between M_n(●) (M_w/M_n(○)) of the polymer and conversion.

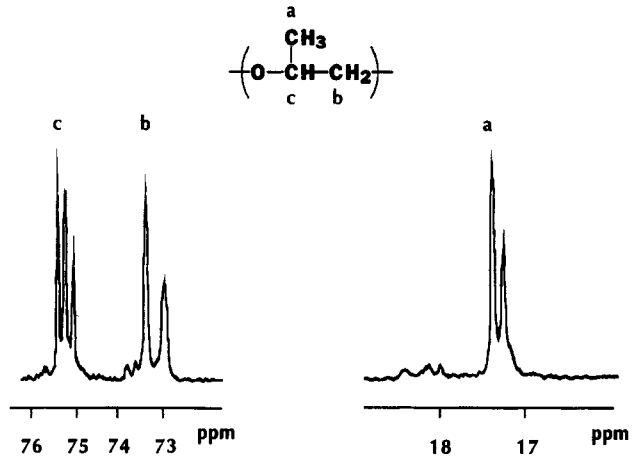


Figure 12. Polymerization of 1,2-epoxypropane (PO) by the (TPP)AlCl (1)/methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (8) system (reaction conditions, see Figure 2). ^{13}C NMR spectrum in $CDCl_3$ of poly(1,2-epoxypropane) obtained at 85.5% conversion (M_n = 11 900, M_w/M_n = 1.21).

observed at δ 73.3 and 72.9 ppm (b) are due to meso (m) and racemic (r) diads respectively, and three methine signals observed at δ 75.5, 75.3, and 75.1 ppm (c) are due to isotactic (I), heterotactic (H), and syndiotactic (S) triads, respectively.[9] The intensity ratios of the related signals indicate that the polymer obtained with the 1/8 system is rich in meso diad (73%) and isotactic triad (59%) sequences (Table 2, run 1). As shown in run 2, the tacticity of this polymer is amost the same as that observed for the polymer prepared with 1 alone in the absence of 8.[1] The intensity ratios of I to m in these two cases satisfy the statistics for the "chain end control mechanism" ($I = m^2$),[10] where the tacticity is determined by the stereoselection of the antipodes of monomer at the asymmetric growing end of polymer.

In the polymerizations of PO with (Me_4DBTAA)AlCl (4) and (Salphen)AlCl (5) as initiators, virtually atactic polymers were formed both in the absence and presence of a Lewis acid (9) (Table 2, runs 3–5).

Conclusion

The Lewis acid-assisted "high-speed" living anionic polymerization of epoxide was realized by using aluminum porphyrin as nucleophilic initiator in conjunction with bulky Lewis acids as monomer activators. Owing to this monomer activation method, aluminum complexes of Schiff bases, tetraazaannulene, and phthalocyanine (3–7) with much lower reactivates became new candidates as initiator.

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 that precipitated upon standing overnight at room temperature from the reaction mixture was recrystallized from $CHCl_3$/MeOH (1/2 in v/v) to give $TPPH_2$ in 20% yield.[11] For the synthesis of tetra-*tert*-butylphthalocyanine (Bu_4PcH_2), a mixture of 4-*tert*-butylphthalonitrile and $NaOCH_2CH_2CH(CH_3)_2$ in the presence of a catalytic amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was refluxed in $(CH_3)_2CHCH_2CH_2OH$ for 5 h.[12] After the reaction mixture was evaporated to dryness, the residue was washed with MeOH and subjected to column chromatography on silica gel (Wakogel C-300, 200–300 mesh) with CH_2Cl_2/hexane (1/2 in v/v) as eluent. The blue fraction was collected and recrystallized from $CHCl_3$/MeOH (1/3 in v/v) to give Bu_4PcH_2 as a blue powder in 42% yield. The nickel complex of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclodecine ((Me_4-DBTAA)Ni) was synthesized by refluxing a MeOH solution of *o*-phenylenediamine with acetylacetone in the presence of Ni-$(OAc)_4\cdot 4H_2O$ for 48 h. (Me_4DBTAA)Ni thus obtained was collected by filtration, suspended in EtOH, and demetallated with dry HCl gas.[13] The precipitates were recrystallized from $CHCl_3$MeOH (1/2 v/v) (45%) to give $Me_4DBTAAH_2$ as an orange powder in 45% yield. Schiff bases such as *N*,*N*′-Bis(2-hydroxybenzlidene)-1,2-phenylenediamine (SalphenH_2), *N*,*N*′-bis(2-hydroxybenzylidene)ethylenediamine (SalenH_2), and *N*,*N*′-bis(2-hydroxybenzylidene)-1,3-propylenediamine (SalpnH_2) were synthesized from the corresponding diamines and salicylaldehyde in EtOH in almost quantitative yield.[14]

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. 1,2-Epoxypropane (propylene oxide, PO) and 1,2-epoxybutane (1,2-butene oxide, BO) were refluxed over a mixture of KOH and CaH_2 and fractionally distilled under a nitrogen atmosphere. 2,4,6-Tri-*tert*-butylphenol and 2,6-di-*tert*-butyl-4-methylphenol were recrystallized from hexane.

Trimethylaluminum (Me_3Al) and chlorodiethylaluminum (Et_2-AlCl) were fractionally distilled under reduced pressure in a nitrogen atmosphere.

Preparation of Aluminum Complexes. Chloro(5,10,15,-20-tetraphenylporphinato)aluminum ((TPP)AlCl, 1) (Scheme 2). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1.0 mmol) under dry nitrogen were successively added CH_2Cl_2 (40 mL) and Et_2-AlCl (1.2 equiv, 0.16 mL) by means of hypodermic syringes in a nitrogen stream, and the mixture was stirred for 2 h. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave 1 as a purple powder.[15]

(TPP)Al-Alcoholate (2) (Scheme 1). To a 100-mL round-bottomed flask equipped with a three-way stopcock and containing (TPP)AlCl (1) (1 mmol) were added successively CH_2Cl_2 (20 mL) and PO (10 mmol, 0.70 mL), via syringes in a nitrogen stream. After being stirred overnight at room temperature, the reaction mixture was evaporated under reduced pressure, leaving (TPP)Al$(PO)_{10}$Cl (2, n = 10) as a reddish purple viscuous liquid.[1,2c]

Other Aluminum Complexes [(Bu_4Pc)AlCl (3), (Me_4-DBTAA)AlCl (4), (Salphen)AlCl (5), (Salen)AlCl (6), and (Salpn)AlCl (7)]. According to the literature methods with slight modification, aluminum complexes of phthalocyanine (3),[16] tetraazaannulene (4),[17] and Schiff bases (5–7)[8] were prepared by the reaction of the corresponding free bases with Et_2AlCl.

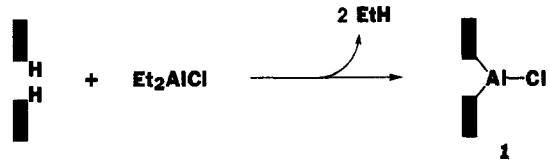
Preparation of Methylaluminum Diphenolates. Methylaluminum Bis(2,4,6-tri-*tert*-butylphenolate) (8) (Scheme 3). To a 50-mL round-bottomed flask equipped with a three-way stopcock, were successively added at 0 °C 2,4,6-tri-*tert*-butylphenol (4.0 mmol, 1.1 g), CH_2Cl_2 (6.7 mL), and Me_3Al (2.0 mmol, 0.19 mL), and the mixture was stirred at room temperature for 1 h,[18] affording a CH_2Cl_2 solution of 8. Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (9) was synthesized similarly to 8.

Table 2. Tacticities of Poly(1,2-epoxypropanes) Prepared by the Polymerization with Aluminum Complexes (1, 4, and 5) as Initiators in the Presence and Absence of Methylaluminum Diphenolates (8 and 9)[a]

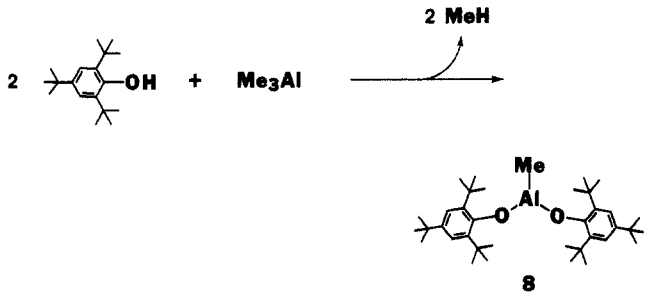
			diad[b]		triad[c]		
run	initiator	Lewis acid	m	r	I	H	S
1	1	8	0.73	0.27	0.59	0.32	0.09
2	1		0.74	0.26	0.57	0.35	0.08
3	4	9	0.48	0.52	0.26	0.46	0.28
4	4		0.49	0.51	0.27	0.48	0.25
5	5	9	0.57	0.43	0.28	0.42	0.32
6	5		0.56	0.44	0.32	0.38	0.30

[a] Determined by ^{13}C NMR in $CDCl_3$ at 22 °C. [b] m and r represent the fractions of meso and racemic diad sequences, respectively. [c] I, H, and S represent the fractions of isotactic, heterotactic, and syndiotactic triad sequences, respectively.

Scheme 2



Scheme 3



Polymerization. Polymerizations of 1,2-Epoxypropane (PO) Initiated with (TPP)AlCl (1) in the Presence of Methylaluminum Bis(2,4,6-tri-*tert*-butylphenolate) (8). A typical example of the polymerization of 1,2-epoxypropane (propylene oxide, PO) with (TPP)AlCl (1) is given: To a 50-mL round-bottomed flask attached to a three-way stopcock containing a CH_2Cl_2 solution (4.0 mL) of 1 (0.20 mmol) in a nitrogen atmosphere was added PO (40 mmol, 2.8 mL) by a syringe in a nitrogen stream. After the mixture was stirred for 7 h at room temperature under nitrogen, methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (8) (0.5 equiv with respect to 1) was added. 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 average molecular weights of the produced polymer, respectively.

Polymerization of PO by the (TPP)Al$(PO)_{10}$Cl (2, n = 10)/8 system was carried out similarly to the above. Polymerizations with other aluminum complexes (3–7)/9 systems were carried out without solvent.

Block Copolymerization of 1,2-Epoxypropane (PO) and 1,2-Epoxybutane (BO) by (TPP)Al$(PO)_{10}$Cl (2, n = 10) in the Presence of Methylaluminum Bis(2,4,6-tri-*tert*-butylphenolate) (8). To a 50-mL round-bottomed flask attached to a three-way stopcock containing a CH_2Cl_2 solution (2.0 mL) of (TPP)Al$(PO)_{10}$Cl (2, n = 10) (0.10 mmol) was added a CH_2Cl_2 solution (0.07 mL) of 8 (0.02 mmol) and PO (5.0 mmol, 0.35 mL) successively by syringe at room temperature in a nitrogen stream. After 15 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, BO (40 mmol) was added to the above reaction mixture, and the polymerization was continued under similar conditions.

Measurements. GPC was performed at 40 °C on a TOSOH Model 8020 high-speed liquid chromatograph equipped with a differential refractometer detector and a variable-wavelength UV–vis detector, using tetrahydrofuran as eluent at 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 NMR measurements were performed using $CDCl_3$ as solvent on a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) as an internal standard.

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(6) N_p/N_{TPP} = {molecular weight of PO (58) × $[PO]_0/[2]_0$ × (conversion/100)}/M_n.
(7) The aluminum porphyrin residue eluted separately from the polymer fraction (elution volume, 40 mL), because of possible hydrolysis of the growing alcoholate terminal of **2** during the course of GPC measurement.
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