2820 Macromolecules 1994, 27, 2820-2825

High-Speed "Immortal" Polymerization of Epoxides Initiated with Aluminum Porphyrin. Acceleration of Propagation and Chain-Transfer Reactions by a Lewis Acid

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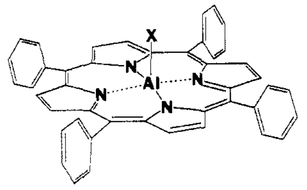
Received November 1, 1993; Revised Manuscript Received February 28, 1994®

ABSTRACT: Immortal polymerization of epoxides with (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1a**) as the initiator coupled with alcohol or phenol as the protic chain-transfer agent (ROH) was dramatically accelerated by a sterically crowded organoaluminum compound such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**), affording polymers of controlled molecular weights with narrow distribution. The number of the polymer molecules (N_{p}) is equal to the sum of the numbers of molecules of **1a** (N_{TPP}) and ROH (N_{ROH}). By taking advantage of this acceleration method, the turnover number ($N_{\mathrm{p}}/N_{\mathrm{TPP}}$) of the immortal polymerization was increased up to 1000 under selected conditions.

Introduction

Synthesis of macromolecules of controlled molecular weight with narrow distribution may be realized by "living" polymerization.[1] Living polymerization is defined as polymerization consisting only of initiation and propagation reactions with no termination and chain-transfer reactions.[2] When the initiation takes place faster than the propagation reaction and the propagation reaction proceeds uniformly with respect to all growing polymer molecules, a polymer with a narrow molecular weight distribution (MWD) is formed with the number of the polymer molecules equal to that of the initiator molecules. Aluminum porphyrin (1) is an excellent initiator for living addition and ring-opening polymerizations of various monomers.[3-5] The polymerization proceeds by repeated insertions of a monomer into the aluminum atom–axial ligand bond (Al–X) of the initiator (1). For example, the ring-opening polymerization of epoxides initiated with (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, **1a**) proceeds via a (porphinato)aluminum alcoholate (1, X = OR) as the growing species, which is formed by the insertion of an epoxide into the Al–Cl bond of the initiator (Scheme 1).[3d]

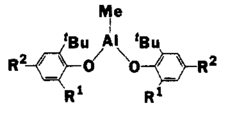


1, (TPP)AlX

1a: X = Cl

1b: X = CH$_3$

1c: X = OCH(CH$_3$)$_2$



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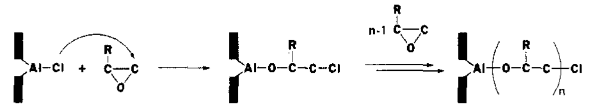
2a: R^1 = ^{t}Bu, R^2 = Me

2b: R^1 = H, R^2 = OMe

In 1985, we proposed "immortal" polymerization as a conceptually new methodology for the efficient synthesis of narrow MWD polymers.[6] Immortal polymerization involves a rapid, reversible chain-transfer (exchange) reaction (Figure 1). Since the chain-transfer reaction takes place much more rapidly than the propagation reaction, a polymer with a narrow MWD is formed, with the number of the polymer molecules (N_{p}) exceeding that of the initiator molecules (N_{TPP}). This concept has been established in the ring-opening polymerization of epoxides with aluminum porphyrin initiators. In the presence of a chain-transfer agent such as alcohol (R′OH), the growing species, an alcoholate aluminum porphyrin (**3$_n$**), reacts with R′OH reversibly (Scheme 2), so that the polymerization takes place from all the molecules of 1 (X = Cl) and R′OH ($N_{\mathrm{p}} = N_{\mathrm{TPP}} + N_{\mathrm{R'OH}}$). In this case, the exchange reaction (Scheme 2) has been estimated to occur 10 times faster than the propagation reaction (Scheme 1).[6b] Immortal polymerization of epoxide is therefore a highly efficient synthetic method for narrow MWD polyethers. However, unfortunately the polymerization slows down considerably when a high mole ratio of chain-transfer agent to initiator is used.

Scheme 1



1 (X = Cl) 3$_1$ 3$_n$

Recently, we found that the living polymerization of methacrylic esters initiated with aluminum porphyrin is dramatically accelerated by the addition of a sterically crowded Lewis acid such as **2a**, affording polymers with narrow MWD ("high-speed" living polymerization).[7] The polymerization proceeds by repeated nucleophilic attacks of the growing species (enolate aluminum porphyrin) to the activated monomer upon coordination with the Lewis acid. In this case, an undesired reaction such as degradative attack of the nucleophile to the Lewis acid, leading to termination, is suppressed due to the large steric barrier between the bulky porphyrin ligand and the bulky substituents of the Lewis acid. Similarly, the ring-opening polymerization of epoxides with aluminum porphyrin initiators affords narrow MWD polyethers with $M_{\mathrm{n}} > 10^4$.[8]

In the present study, the Lewis acid-assisted high-speed polymerization was applied to the immortal polymerization of epoxides in order to accelerate the polymerization and to achieve a much higher turnover number ($N_{\mathrm{p}}/N_{\mathrm{TPP}}$) of the reaction. The effect of the Lewis acid on the rate of the chain-transfer reaction was also studied.

Results and Discussion

Immortal Polymerization of Propylene Oxide (PO) Initiated with the Chloroaluminum Porphyrin

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® Abstract published in *Advance ACS Abstracts*, April 1, 1994.

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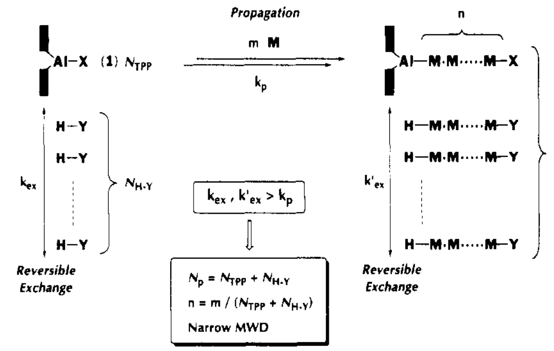
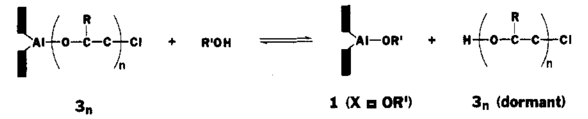


Figure 1. Schematic representation of "immortal" polymerization. H–Y: protic chain-transfer agent. M: monomer. k_{ex}, k'_{ex}: rate constants of chain-transfer (exchange) reactions. k_p: rate constant of the propagation reaction. N_{TPP}, $N_{H\text{-}Y}$, and N_p: numbers of molecules of (TPP)AlX (1), H–Y, and polymer, respectively.

Scheme 2



((TPP)AlCl, 1a)/2-Propanol (2-PrOH) System in the Presence of an Organoaluminum Compound (2a). Polymerization of propylene oxide (PO, 1,2-epoxypropane) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) was carried out by the addition of a mixture of PO and 2-PrOH to a CH_2Cl_2 solution of a mixture of **1a** and **2a** at room temperature in a nitrogen atmosphere (Figure 2). For example, when a mixture of 200 equiv of PO and 9 equiv of 2-PrOH was added to the solution of **1a** ($[\mathbf{1a}]_0$ = 100 mM) containing 0.3 equiv of **2a** (0.15 mol % with respect to PO), the color of the solution immediately turned from dark reddish purple to bright reddish purple, characteristic of the alcoholate aluminum porphyrin family. The polymerization proceeded very rapidly with heat evolution to attain 57% monomer conversion in 3 min (▲). In contrast, the polymerization without **2a** under similar conditions proceeded rather slowly to attain only 13% conversion (●). The acceleration was larger on increasing the amount of **2a** with respect to **1a**. For example, the polymerization at the initial mole ratio $[\mathbf{2a}]_0/[\mathbf{1a}]_0$ of 3.0 (1.5 mol % with respect to PO) proceeded to 70% conversion in only 30 sec (■) and gave at 100% conversion a narrow MWD polymer with M_n and M_w/M_n, respectively, of 1100 and 1.13. As shown in Figure 3, irrespective of the mole ratio of **2a** to **1a**, the MWDs of the produced polymers were narrow, and the N_p/N_{TPP} values, calculated from the M_ns of the polymers at 100% conversion, were close to the initial mole ratio ($[\mathbf{1a}]_0$ + $[\text{2-PrOH}]_0)/[\mathbf{1a}]_0$ of 10.

Polymerization of 1000 equiv of PO initiated with **1a** containing 49 equiv of 2-PrOH was carried out without solvent by the addition of a mixture of PO and 2-PrOH to a flask containing **1a** and **2a** at room temperature. The reaction proceeded rapidly when 0.1 mol % of **2a** with respect to PO was present; 86% monomer conversion was attained in 1.5 h (Table 1, run 1), and a polymer with M_n and M_w/M_n, respectively, of 1100 and 1.06 was obtained at 96% conversion (Figure 4). The ratio N_p/N_{TPP} was estimated here to be 53, which was again close to the theoretical value of 50. In sharp contrast, the polymerization without **2a** under similar conditions proceeded very slowly and required 380 h to reach 84% monomer conversion (Table 1, run 2).

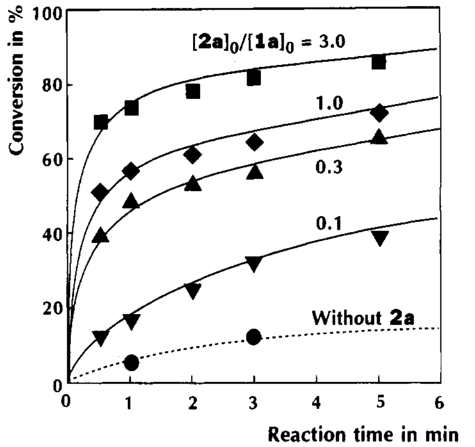


Figure 2. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) ($[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{1a}]_0$ = 9/200/1) in CH_2Cl_2 at room temperature. Effect of the concentration of **2a** on the rate of polymerization.

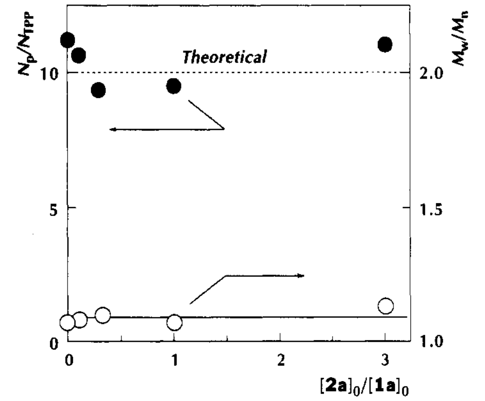


Figure 3. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) ($[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{1a}]_0$ = 9/200/1) in CH_2Cl_2 at room temperature. Relationship between N_p/N_{TPP} (●) (M_w/M_n (○)) at 100% conversion and the initial mole ratio $[\mathbf{2a}]_0/[\mathbf{1a}]_0$ (N_p and N_{TPP}: numbers of molecules of the produced polymer and initiator (**1a**), respectively).

When the initial mole ratio $[\text{PO}]_0/([\mathbf{1a}]_0 + [\text{2-PrOH}]_0)$ was increased from 10 to 40, M_n of the polymer formed at 100% conversion was increased linearly (Figure 5, broken line) as expected, assuming that the number of the produced polymer molecules is equal to the sum of the molecules of **1a** and 2-PrOH (N_p/N_{TPP} = 50). The M_w/M_n ratios of the produced polymers remained almost constant at 1.1.

The Lewis acid (**2a**) alone does not initiate the polymerization under similar conditions. For example, when a mixture of 2-PrOH, PO, and **2a** ($[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{2a}]_0$ = 49/1000/1) was stirred for 2.5 h in the absence of **1a**, no polymerization took place at room temperature. On the other hand, when **1a** (1 equiv with respect to **2a**) was added to this mixture, the polymerization immediately started to attain 66% monomer conversion in 3 h. Thus, the immortal polymerization of PO was successfully accelerated by a bulky Lewis acid such as **2a**, with all the advantages of immortal polymerization retained.

Immortal Polymerization of PO at Higher Ratios of 2-PrOH to (TPP)AlCl (1a) in the Presence of an Organoaluminum Compound (2a). The above observations prompted us to attempt the immortal polymerization of PO at the mole ratio $[\text{2-PrOH}]_0/[\mathbf{1a}]_0$ higher than 49. For example, when 2000 equiv of PO was added

Table 1. High-Speed Immortal Polymerization of Propylene Oxide (PO) with the (TPP)AlCl (1a)/2-Propanol (2-PrOH) System in the Presence of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (2a)[a]

run	$[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{1a}]_0$	$[\mathbf{2a}]_0/[\text{PO}]_0/\%$	time/h	conv/%	M_n[b]	M_w/M_n[b]	N_p/N_{TPP}[c]
1	49/100/1	0.1	1.5	86	900	1.10	55
2	49/1000/1	0	380	84	1100	1.08	45
3	99/2000/1	2.0	9	80	800	1.10	120
4	299/6000/1	3.3	19	81	800	1.11	340
5	999/20 000/1	1.5	250	62	600	1.13	1150
6[d]	999/20 000/1	1.5	120	61	600	1.14	1100
7	999/20 000/1	0	1900	10			

[a] Without solvent, under N_2 at room temperature. [b] Estimated by GPC based on poly(propylene glycol) standards. [c] Number of polymer molecules (N_p)/number of molecules of **1a** (N_{TPP}) = $58.08([\text{PO}]_0/[\mathbf{1a}]_0)(\text{conv}/100)M_n^{-1}$. [d] At 60 °C.

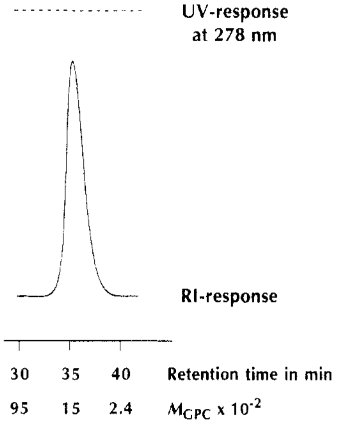


Figure 4. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) ($[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{2a}]_0/[\mathbf{1a}]_0$ = 49/1000/1/1) without solvent at room temperature. GPC profile of the polymer formed at 96% conversion (M_n = 1100, M_w/M_n = 1.06).

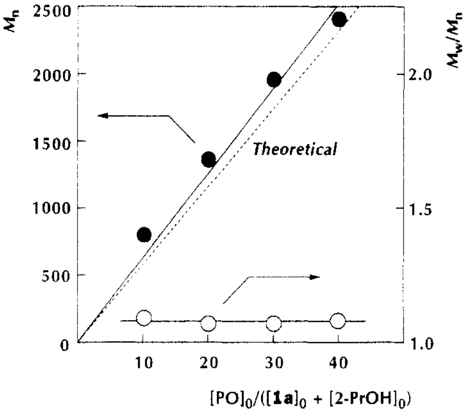


Figure 5. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) (1/49) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) without solvent at room temperature. Relationship between M_n (●) (M_w/M_n (○)) of the produced polymer and the initial mole ratio $[\text{PO}]_0/([\mathbf{1a}]_0 + [\text{2-PrOH}]_0)$ at 100% conversion.

to **1a** in the presence of 99 equiv of 2-PrOH without solvent at room temperature, a polymer with M_w/M_n of 1.10 and N_p/N_{TPP} of 120 (M_n = 800) was formed in 9 h (80% conversion) when 2.0 mol % of **2a** with respect to PO was present (Table 1, run 3). Similarly, at the ratio $[\text{2-PrOH}]_0/[\text{PO}]_0/[\mathbf{1a}]_0$ of 299/6000/1, a polymer with M_w/M_n of 1.11 and N_p/N_{TPP} of 340 (M_n = 800) was formed in 19 h (81% conversion) when 3.3 mol % of **2a** with respect to PO was present (run 4). Finally, we attempted the immortal polymerization of PO with **1a** by employing 999 equiv of 2-PrOH and 20 000 equiv of PO. In the absence of **2a** at room temperature without solvent, the polymerization proceeded extremely slowly to attain only 10% monomer conversion even in 1900 h (run 7). On the other hand, when 1.5 mol % of **2a** with respect to PO was present under similar conditions, 62% monomer conversion was attained in 250 h, affording a polymer with M_w/M_n of 1.13 and N_p/N_{TPP} of 1150 (M_n = 600) (run 5). This result corresponds to more than 12 000 repetitions of the ring-opening reaction per molecule of aluminum porphyrin initiator. At an elevated temperature such as 60 °C, the polymerization proceeded more rapidly to reach 61% monomer conversion in 120 h, affording a polymer with M_w/M_n of 1.14 and N_p/N_{TPP} of 1100 (M_n = 600) (run 6).

High-Speed Immortal Polymerization by Different Combinations of Epoxide, Chain-Transfer Agent, and Lewis Acid. **2a** is one of the best candidates as a Lewis acid accelerator for the immortal polymerization of PO initiated with the **1a**/2-PrOH system. For example, with methylaluminum bis(2-*tert*-butyl-4-methoxyphenolate) (**2b**) or aluminum tri(2-propanolate) (Al(O-2-Pr)_3) instead of **2a** as a Lewis acid (Table 2, runs 2 and 3), the polymerization of PO was less accelerated than the case with **2a** (run 1).

Other protic chain-transfer agents are available for the immortal polymerization of PO initiated with **1a** in the presence of **2a**. For example, when the polymerization of PO was carried out with methanol (MeOH) as a chain-transfer agent ($[\text{MeOH}]_0/[\text{PO}]_0/[\mathbf{1a}]_0$ = 49/1000/1) in the presence of 0.1 mol % of **2a** with respect to PO, 82% monomer conversion was attained in 1.5 h, affording a polymer with M_w/M_n of 1.07 and N_p/N_{TPP} of 46 (run 4). Use of benzyl alcohol (PhCH_2OH) as a chain-transfer agent for the immortal polymerization of PO under similar conditions resulted in the formation of a polymer with M_w/M_n of 1.08 and N_p/N_{TPP} of 47 (run 5).[9] Furthermore, use of a phenolic chain-transfer agent such as 4-*tert*-butylphenol (4-^{t}BuPhOH) instead of alcohol also resulted in the immortal polymerization of PO, giving a polymer with M_w/M_n and N_p/N_{TPP} of 1.07 and 50, respectively, at 66% conversion (run 6). The GPC chromatogram of the obtained polymer at 98% conversion is shown in Figure 6.

In the polymerization of 1000 equiv of epichlorohydrin (ECH, 1-chloro-2,3-epoxypropane) initiated with the **1a**/2-PrOH (1/49) system in the presence of 0.1 mol % of **2a** with respect to ECH, 66% of ECH was consumed in 24 h, and a narrow MWD polymer (M_w/M_n = 1.09) with N_p/N_{TPP} of 54 was formed (run 7).

End-Group Analyses of Polymers. The polymer obtained by the polymerization of 1000 equiv of PO initiated with the **1a**/2-PrOH (1/49) system in the presence of 0.1 mol % of **2a** with respect to PO was isolated by column chromatography and subjected to ^{13}C NMR analysis in CDCl_3 (Figure 7). Signals due to CH_3 (a), CH_2 (e), and CH (f) were observed at δ 17, 73, and 75, respectively. The weak signals at δ 21.8 and 47.3 are assignable to the terminal $CH(CH_3)_2$ (b)[10] and CH_2Cl (c)[3d] groups, respectively, while a set of two signals at δ 65.2 and 66.8 are due to the CHOH (d) group in the other

Table 2. High-Speed Immortal Polymerization of Epoxides with the (TPP)AlCl (1a)/Protic Compounds (ROH) System in the Presence of Lewis Acids[a]

run	Lewis acid (mol % to epoxide)	ROH	epoxide	time/h	conv/%	M_n[b]	M_w/M_n[b]	N_p/N_{TPP}[c]
1	**2a** (0.1)	2-PrOH	PO	1.5	86	900	1.10	55
2	**2b** (1.0)	2-PrOH	PO	1.5	79	800	1.11	58
3	Al(O-2-Pr)$_3$ (1.0)	2-PrOH	PO	7	74	600	1.12	75
4	**2a** (0.1)	MeOH	PO	1.5	82	1000	1.07	46
5	**2a** (0.1)	PhCH$_2$OH	PO	16	61	800	1.08	47
6	**2a** (0.1)	4-^{t}BuPhOH	PO	20	66	800	1.07	50
7	**2a** (0.1)	2-PrOH	ECH	24	66	1100	1.09	54

[a] Without solvent, under N$_2$ at room temperature, [ROH]$_0$/[epoxide]$_0$/[**1a**]$_0$ = 49/1000/1. [b] Estimated by GPC based on poly(propylene glycol) standards. [c] Number of polymer molecules (N_p)/number of molecules of **1a** (N_{TPP}) = 1000(molecular weight of epoxide)(conv/100)M_n^{-1}.

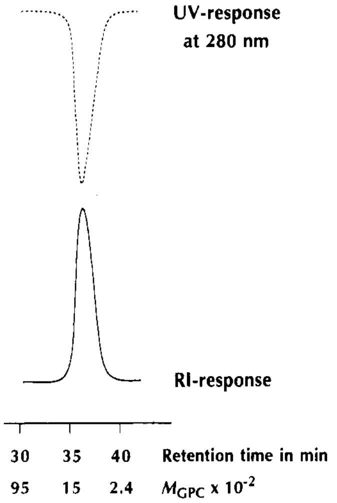


Figure 6. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/4-*tert*-butylphenol (4-^{t}BuPhOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) ([4-^{t}BuPhOH]$_0$/[PO]$_0$/[**2a**]$_0$/[**1a**]$_0$ = 49/1000/1/1) without solvent at room temperature. GPC profile of the polymer formed at 98% conversion (M_n = 1200, M_w/M_n = 1.05).

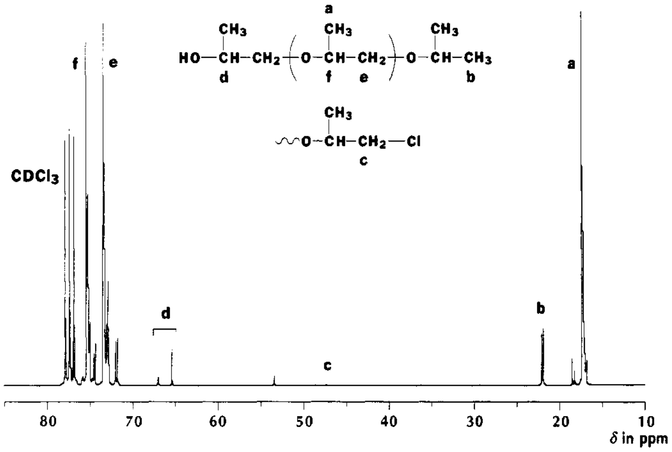


Figure 7. Polymerization of propylene oxide (PO) initiated with the (TPP)AlCl (**1a**)/2-propanol (2-PrOH) system in the presence of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**) ([2-PrOH]$_0$/[PO]$_0$/[**2a**]$_0$/[**1a**]$_0$ = 49/1000/1/1) without solvent at room temperature. ^{13}C NMR spectrum in CDCl$_3$ of the polymer formed at 96% conversion (M_n = 1100, M_w/M_n = 1.06).

terminal unit.[3b,11] The relative intensity of the signals a to d indicated a number-average degree of polymerization of 19.0, which is in excellent agreement with that observed by GPC (18.7) and the theoretical value (19.2) based on the initial mole ratio [PO]$_0$/([**1a**]$_0$ + [2-PrOH]$_0$) and conversion (96%). Furthermore, no signal was detected due to (CH$_3$)$_3$C in the terminal aryl ether unit originating from **2a**.[12] In conformity with these observations, no UV response was observed for the polymer in the GPC chromatogram monitored at 278 nm (Figure 4, broken line).[13] Thus, the polymerization of PO initiated with the **1a**/2-PrOH system in the presence of **2a** proceeds exclusively from **1a** and 2-PrOH, where the Lewis acid (**2a**) simply functions as the accelerator for the polymerization. Although the proton transfer from the monomer methyl group to the growing species, giving a terminal unsaturated polymer, is a chain-transfer reaction typical of the anionic polymerization of PO,[14] this side reaction is absent in the present case, as evidenced by the absence of the signals assignable to CH$_2$═CHCH$_2$–[15] in the ^{13}C NMR spectrum of the produced polymer (Figure 7).

On the other hand, the polymer obtained with 4-^{t}BuPhOH as a protic compound exhibited a clear UV response when monitored at 280 nm (Figure 6, broken line).[13] In the ^{13}C NMR spectrum of the polymer, the signals assignable to the aryl ether unit originating from 4-^{t}BuPhOH[16] were observed, while those assignable to the terminal unit originating from **2a**[12] were hardly detected. Thus, in addition to alcohols, phenols can be used as chain-transfer agents for the **2a**-assisted high-speed immortal polymerization of PO.

By contrast, the polymer prepared with the **1a**/2-PrOH/**2b** system (Table 2, run 2) showed a weak signal at δ 30 assignable to the (*C*H$_3$)$_3$C group in the aryl ether unit from **2b** and accordingly exhibited a clear UV response in the GPC chromatogram monitored at 278 nm.[13] Thus, not only 2-PrOH but also 2-*tert*-butyl-4-methoxyphenol, possibly generated by the ligand exchange reaction of **2b** with 2-PrOH, participates in the chain-transfer reaction. In the case of the immortal polymerization with Al(O-2-Pr)$_3$ as the Lewis acid (run 3), the observed N_p/N_{TPP} ratio (75) is much higher than the theoretical one (50), indicating the ligand exchange reaction of Al(O-2-Pr)$_3$ with $\mathbf{3}_n$[17] and/or $\mathbf{3}_n$ **(dormant)**.

NMR Study. Effect of the Lewis Acid on the Rate of the Chain-Transfer Reaction. In immortal polymerization, chain transfer takes place much more rapidly than propagation, leading to the uniformity of the molecular weight of the polymer. The successful high-speed immortal polymerization assisted by a Lewis acid, mentioned above, suggests that not only the propagation step (Scheme 1) but also the chain-transfer process (Scheme 2) is accelerated by the Lewis acid.

In order to examine the effect of the Lewis acid on the rate of the chain-transfer reaction, the ^{1}H NMR saturation transfer method[18] was applied to the model system, a mixture of 2-propanolate aluminum porphyrin ((TPP)AlOCH(CH$_3$)$_2$, **1c**) and 2-PrOH (1/13) in the absence (Figure 8) and presence (Figure 9) of the Lewis acid (**2a**, 3 equiv) in C$_6$D$_6$ at 21 °C.

In Figure 8A, the signals due to the C*H*$_3$ groups of **1c** and 2-PrOH are observed at δ –1.40 (a) and 1.20 (b), respectively. Although signal b was irradiated to saturate the C*H*$_3$ protons of 2-PrOH, signal a was only slightly decreased in intensity (Figure 8B), with the ratio of the

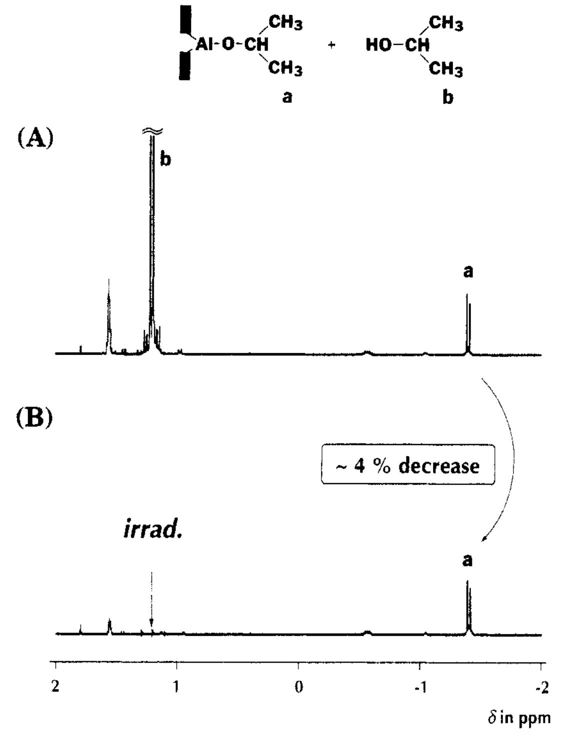


Figure 8. ^{1}H NMR spectra of a mixture of 1c and 2-PrOH (1/13) in C_6D_6 at 21 °C: (A) without irradiation and (B) with irradiation of signal b ([1c] = 25 mM).

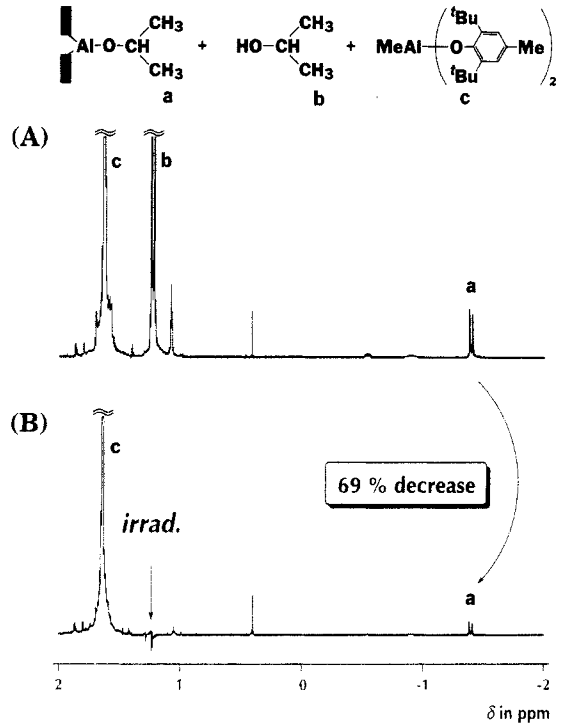


Figure 9. ^{1}H NMR spectra of a mixture of 1c, 2-PrOH, and 2a (1/13/3) in C_6D_6 at 21 °C: (A) without irradiation and (B) with irradiation of signal b ([1c] = 25 mM).

intensities with and without irradiation (I_{irrad}/I_0) approximately 0.96. When the Lewis acid (**2a**) is present, the alcoholate aluminum porphyrin (**1c**) can survive without degradative nucleophilic attack to the Lewis acid, as evidenced by the fact that the relative intensity of the signal a (6H) to that of the porphyrin pyrrole β protons (δ 9.33, 8H) satisfied the required ratio. More interestingly, upon irradiation of signal b, the intensity of signal a fell to 31% of the original intensity (I_{irrad}/I_0 = 0.31) (Figure 9). Therefore, it is concluded that the alcoholate–alcohol exchange reaction at the axial position of the aluminum porphyrin (Scheme 2) is accelerated by the Lewis acid. Here, the ratio I_{irrad}/I_0 is given by the following equation, where k_{ex} and T_1 represent the rate constant of the exchange reaction and the spin–lattice relaxation time of the CH_3 protons of **1c**, respectively:

$$I_{irrad}/I_0 = 1/(1 + k_{ex}T_1)$$

Thus, from the above two I_{irrad}/I_0 ratios observed in the absence and presence of **2a**, the exchange reaction is approximately accelerated 50-fold by **2a** under the experimental conditions. In the presence of **2a**, the alcohol should become more acidic upon coordination to the Lewis acid, leading to an acceleration of the exchange reaction with **1c**.

Conclusion

Owing to the effect of a bulky Lewis acid such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2a**), *high-speed immortal polymerization* of epoxides initiated with (TPP)AlCl (**1a**) in the presence of protic chain-transfer agents was achieved. The ratio of the number of polymer to initiator molecules (N_p/N_{TPP}: turnover number of the reaction) was dramatically increased to 1000, with all the advantages of the immortal polymerization retained. Equally interesting is the Lewis acid-promoted chain-transfer reaction (alcohol–alcoholate exchange), which accounts for the narrow MWD of the polymer produced under the accelerated conditions.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol (1/2, v/v).[19]

Dichloromethane (CH_2Cl_2) was washed successively with concentrated sulfuric acid, water, and aqueous sodium bicarbonate, dried over calcium chloride, and distilled over calcium hydride in a nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) was distilled over calcium hydride in a nitrogen atmosphere. Benzene (C_6H_6), deuterated benzene (C_6D_6), and hexane were distilled over sodium benzophenone ketyl in a nitrogen atmosphere. 2-Propanol (2-PrOH) and methanol (MeOH) were distilled over magnesium treated with iodine in a nitrogen atmosphere. Benzyl alcohol ($PhCH_2OH$) was distilled over potassium hydroxide in a nitrogen atmosphere. 4-*tert*-Butylphenol (4-^{t}BuPhOH), 2,6-di-*tert*-butyl-4-methylphenol, and 2-*tert*-butyl-4-methoxyphenol were recrystallized from hexane. Propylene oxide (PO) was distilled over a mixture of potassium hydroxide and calcium hydride in a nitrogen atmosphere. Epichlorohydrin (ECH) was distilled over calcium hydride in a nitrogen atmosphere.

Trimethylaluminum (Me_3Al), diethylaluminum chloride (Et_2AlCl), and aluminum tri(2-propanolate) ($Al(O\text{-}2\text{-}Pr)_3$) were fractionally distilled in a nitrogen atmosphere.

Preparation of (5,10,15,20-Tetraphenylporphinato)aluminum Chloride ((TPP)AlCl (1a)). To a round-bottomed flask (100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) under dry nitrogen were successively added by means of hypodermic syringes in a nitrogen stream CH_2Cl_2 (20 mL) and Et_2AlCl (1.2 equiv, 0.16 mL), and the mixture was stirred for 2 h. Then, volatile fractions were removed from the reaction mixture under reduced pressure to leave **1a** as a purple powder.[3c]

Preparation of the (5,10,15,20-Tetraphenylporphinato)aluminum 2-Propanolate (1c)/2-PrOH System for NMR Studies. (TPP)AlMe (**1b**) was prepared in a manner similar to that above by the reaction of $TPPH_2$ (0.1 mmol) and 1.2 equiv of Me_3Al (0.012 mL) in CH_2Cl_2 (4 mL) at room temperature in a nitrogen atmosphere. After 1 h, volatile fractions were removed from the reaction mixture under reduced pressure to leave **1b** as a purple powder.[20] C_6D_6 (4 mL) was added to dissolve **1b**, and 11 equiv of 2-PrOH (0.084 mL) was then added to this solution. The mixture was stirred for 1 week at room temperature, affording a C_6D_6 solution of a mixture of **1c** and 2-PrOH (1/10).

Preparation of Methylaluminum Bis(2,6-di-*tert*-butyl-4-methylphenolate) (2a) and Methylaluminum Bis(2-*tert*-butyl-4-methoxyphenolate) (2b). To a round-bottomed flask (50 mL) equipped with a three-way stop-cock containing 2,6-di-*tert*-butyl-4-methylphenol (25 mmol, 5.52 g) were successively added hexane (20 mL) and Me_3Al (12.5 mmol, 1.2 mL) at 0 °C. Upon stirring at room temperature, the reaction mixture gradually became turbid with evolution of methane. After 1 h, the temperature was raised to 60 °C, and the resulting solution was cooled to room temperature, affording **2a** as white crystals (4.0 g, 67% yield), which were dried under reduced pressure at room temperature.[21] **2b** was prepared in a manner similar to that above by the reaction of Me_3Al with 2-*tert*-butyl-4-methoxyphenol (2 equiv) in C_6H_6 in a nitrogen atmosphere.

Polymerization. Typically, to a round-bottomed flask (50 mL) attached to a three-way stopcock containing a CH_2Cl_2 solution of **1a** (0.25 mmol) was added a C_6H_6 solution of **2a** (0.25 mmol), and volatile fractions were removed from the mixture under reduced pressure. After CH_2Cl_2 (2.5 mL) and a mixture of PO (50 mmol, 3.5 mL) and 2-PrOH (2.25 mmol, 0.17 mL) were successively added to this flask by a syringe in a nitrogen stream, the reaction mixture was stirred magnetically for a prescribed time. Then, an aliquot of the polymerization mixture was taken out from the flask 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_n, M_w) of the produced polymer, respectively. The polymerization without solvent was carried out in a manner similar to that above by the addition of a mixture of PO and 2-PrOH to a flask containing **1a** and a Lewis acid. The polymerization at 60 °C was carried out in a sealed ampule.

Isolation of Polymers. After the polymerization mixture was evaporated under reduced pressure at room temperature, hexane was added to the residue, and the resulting suspension was filtered to remove the insoluble fractions (initiator residues). A pale purple viscous liquid was obtained by evaporation of the filtrate, and the residue was chromatographed on silica gel with acetone/hexane (1/3) as eluent to give quantitatively a polymer as a colorless liquid.

Measurements. ^1H and ^{13}C NMR measurements were performed using C_6D_6 or $CDCl_3$ as the 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 7.4) for ^1H and $CDCl_3$ (δ 77.1) for ^{13}C as internal standards. Proton homonuclear decoupling was employed for the ^1H NMR saturation transfer experiments by applying an irradiation power of 47.75 dB and a pulse repetition time of 6 s. ^{13}C NMR spectra were measured without NOE by applying a pulse repetition time of 15 s. Gel permeation chromatography (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 the eluent at a flow rate of 1.0 $mL \cdot min^{-1}$. The molecular weight calibration curve was obtained by using standard poly(propylene glycols) (Lion Fat & Oil Co., Ltd.); M_n, 2000, 1000, and 700 ($M_w/M_n \sim 1$).

Acknowledgment. The present work was partly supported by Grand-in-Aid No. 04204006 for Scientific Research on Priority Area, the Ministry of Education, Science and Culture, Japan. T.A. thanks Toray Science Foundation and Kanagawa Academy of Science and Technology for financial support. We also thank Dr. Hiroshi Sugimoto for his active collaboration.

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