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Controlled Coordinate Anionic Polymerization of Oxetane by Novel Initiating Systems: Onium Salts/Bulky Organoaluminum Diphenolates

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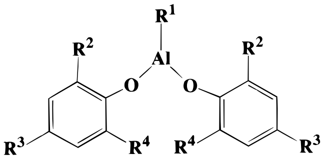
ABSTRACT: Onium salts such as quaternary ammonium and phosphonium halides in conjunction with sterically hindered methylaluminum diphenolates (**1**) brought about living coordinate anionic polymerization of oxetane, giving a narrow molecular weight distribution (MWD) polyether. In contrast, use of a simple trialkylaluminum such as trimethylaluminum in the place of **1** resulted in no polymerization. X-ray crystallographic studies demonstrated the formation of an ate complex (**2b**$_{Cl}$) from **1b** and Et_4NCl. **2** in the presence of **1** was capable of initiating the controlled polymerization of oxetane, whereas **2** alone was not. ^{1}H NMR studies on a mixture of **2b**$_{Cl}$ and **1b** indicated the occurrence of a rapid, reversible migration of the halide group from **2b**$_{Cl}$ to **1b**.

Introduction

In anionic polymerization, coordination and activation of monomer prior to nucleophilic attack of the growing species play an important role in controlled chain growth. We have clearly demonstrated this by sterically separated nucleophile/Lewis acid systems.[1,2] Namely, aluminum porphyrins as sterically crowded nucleophiles in conjunction with bulky methylaluminum diphenolates (**1**) as monomer activators bring about the coordinate anionic polymerization of methacrylic esters in a highly accelerated fashion.[3] Because of the steric suppression of a neutralization between the nucleophilic growing species and the Lewis acids, the polymerization proceeds cleanly without any side reactions, affording narrow molecular weight distribution (MWD) polymers. Use of Lewis acids with poor steric protection in place of **1** for the polymerization results in undesired termination during polymerization.[4] Therefore, coexisting and cooperation of well-defined nucleophilic and Lewis acidic species are important for realizing the rapidness and cleanness of the anionic chain growth.



1a: $R^1 = Me, R^2 = R^3 = {}^{tert}Bu, R^4 = H$
1b: $R^1 = Me, R^2 = R^4 = {}^{tert}Bu, R^3 = Me$
1c: $R^1 = Me, R^2 = R^3 = R^4 = {}^{tert}Bu$
1d: $R^1 = Et, R^2 = R^4 = {}^{tert}Bu, R^3 = Me$

As an extension of the above-mentioned "high-speed living anionic polymerization", we have recently succeeded in the living coordinate anionic polymerization of oxetane by using the system consisting of chloroaluminum porphyrin and **1**.[5] Oxetane has long been categorized in the monomer which is only cationically polymerizable, because of its high Lewis basicity and therefore low susceptibility to nucleophiles.[6,7] In the present paper, we report more simple and versatile initiating systems, consisting of quaternary onium halides and bulky organoaluminum diphenolates, for controlled coordinate anionic polymerization of oxetane, and also provide results of crystallographic and NMR studies on the initiating systems.

Results and Discussion

Polymerization of Oxetane Initiated with the Quaternary Onium Halide/Organoaluminum Diphenolate Systems. Polymerization of oxetane with quaternary onium halides proceeded smoothly at room temperature in the presence of bulky organoaluminum diphenolates (**1**), affording a narrow molecular weight distribution (MWD) polyether. For example, when 100 equiv of oxetane was added at room temperature under nitrogen to a CH_2Cl_2 solution of a mixture of ethyltriphenylphosphonium bromide ($EtPh_3PBr$)($[EtPh_3PBr]_0$ = 33 mM) and 3 equiv of **1c**, the polymerization proceeded to attain 100% monomer conversion in 9 h, giving a narrow MWD polymer with M_n and M_w/M_n, respectively, of 5200 and 1.12.[8] The molecular weight of the produced polymer increased proportionally to monomer conversion, retaining the low polydispersity, where the M_n values were in good agreement with those calculated from the assumption that every molecule of $EtPh_3PBr$ produces one polymer molecule. Upon increment of the mole ratio $[\mathbf{1c}]_0/[EtPh_3PBr]_0$ from 3 to 6, the rate of polymerization was enhanced, while the molecular weight of the polymer finally attained was virtually intact. In sharp contrast, no polymerization took place when the mole ratio of **1c** to $EtPh_3PBr$ was less than unity.

In order to confirm the living character of the polymerization initiated with the $EtPh_3PBr$/**1c** system, a sequential two-stage polymerization of oxetane was investigated (Figure 1). Thus, the first-stage polymerization of oxetane ($[oxetane]_0/[EtPh_3PBr]_0/[\mathbf{1c}]_0 = 50/1/3$) was allowed to proceed up to 100% monomer conversion, and then 150 equiv of oxetane with respect to $EtPh_3PBr$ was freshly added to the system, whereupon the second-stage polymerization ensued, and the M_n of the polymer increased from 2900 [$M_w/M_n = 1.09$] (I) to 10 000 (II), retaining the narrow MWD [$M_w/M_n = 1.21$]. As shown in Figure 2, the molecular weight of the polymer could be controlled by changing the initial mole ratio of oxetane to $EtPh_3PBr$. For example, at the mole

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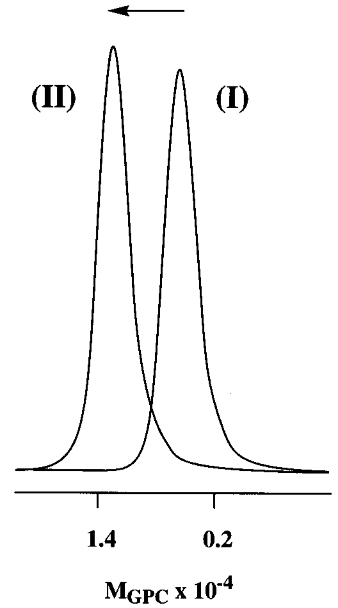


Figure 1. Two-stage polymerization of oxetane with the $EtPh_3PBr$/**1c** (1/6) system in CH_2Cl_2 at room temperature ($[EtPh_3PBr]_0 = 33$ mM). GPC profiles of the polymers formed at (I) the first stage ($[oxetane]_0/[EtPh_3PBr]_0 = 50$, 100% monomer conversion, $M_n = 2900$, $M_w/M_n = 1.09$) and (II) the second stage ($[oxetane]_0/[EtPh_3PBr]_0 = 150$, 100% monomer conversion, $M_n = 10\,000$, $M_w/M_n = 1.21$).

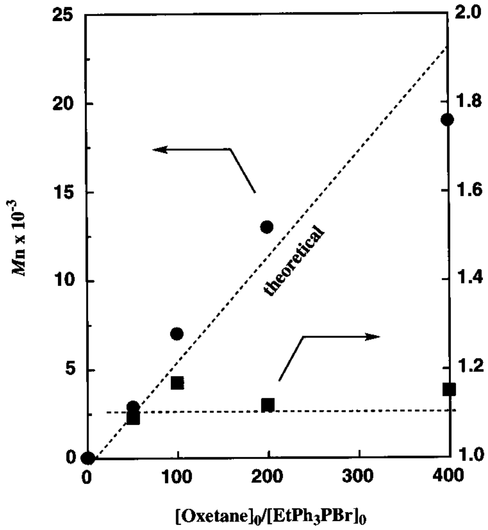


Figure 2. Polymerization of oxetane with the $EtPh_3PBr$/**1c** (1/6) system in CH_2Cl_2 at room temperature ($[EtPh_3PBr]_0 =$ 33 mM). Relationship between M_n of the polymer at 100% monomer conversion and the initial mole ratio $[oxetane]_0/[EtPh_3PBr]_0$.

ratio $[oxetane]_0/[EtPh_3PBr]_0$ of 400 in the presence of 6 equiv of **1c** with respect to $EtPh_3PBr$, a narrow MWD polyoxetane with M_n of 17 000 ($M_{n_{theory}} = 23\,000$) [$M_w/M_n = 1.15$] was obtained at 100% monomer conversion.

In addition to **1c**, **1a** and **1b** were also usable as the Lewis acid component for the above polymerization, whereas use of a simple trialkylaluminum such as Me_3Al coupled with $EtPh_3PBr$, in contrast, resulted in no polymerization under similar conditions. As for the onium salt component, benzyltriphenylphosphonium chloride ($BnPh_3PCl$) and ammonium salts such as tetraethylammonium chloride (Et_4NCl) and bromide (Et_4NBr) were also effective for the polymerization. In contrast, when a tetraphenylborate salt (Bu_4NPh_4B) was used in conjunction with **1a**, no polymerization took place.

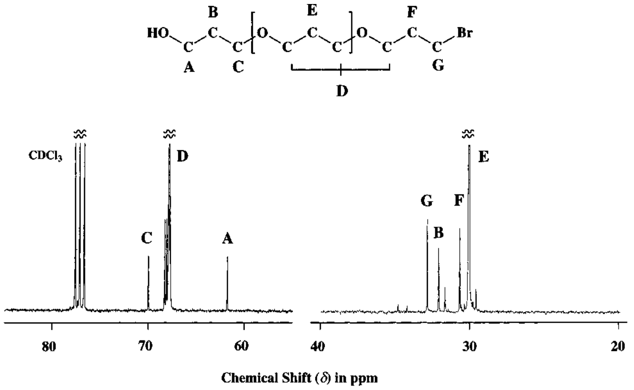
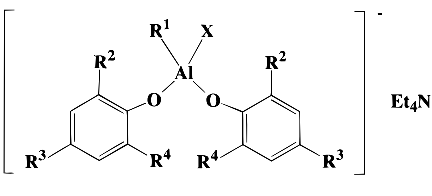


Figure 3. Polymerization of oxetane with the $EtPh_3PBr$/**1a** system in CH_2Cl_2 at room temperature ($[oxetane]_0/[EtPh_3PBr]_0/[\mathbf{1a}]_0 = 10/1/6$, $[EtPh_3PBr]_0 = 33$ mM). ^{13}C NMR spectrum in $CDCl_3$ at 22 °C of the polymer formed at 100% monomer conversion.

In GPC, the polyoxetanes formed with the quaternary onium halides/**1** systems were silent at 254 nm when monitored with a UV detector, indicating the absence of phenoxy groups originating from **1** in the polymer main chain. In order to investigate the polymer end group, the polymerization of oxetane was carried out with the $EtPh_3PBr$/**1a** system at a low mole ratio of oxetane to $EtPh_3PBr$ ($[oxetane]_0/[EtPh_3PBr]_0/[\mathbf{1a}]_0 = 10/1/3$), and a polyoxetane at 100% monomer conversion was isolated by column chromatography. The ^{13}C NMR spectrum in $CDCl_3$ of this polymer (Figure 3) showed signals **E** (δ 30.0) and **D** (δ 67.7) due to repeating oxypropylene units, and relatively weak signals **G** (δ 32.7) and **A** (δ 61.6) assignable respectively to $BrCH_2$ and $HOCH_2$, by reference to 1-bromobutane and 3-methoxypropan-1-ol.[9] The intensity of the signal **G** was almost comparable to that of **A**, and the sum of the intensities of the signals **B**, **E**, and **F** relative to that of **G** was in good agreement with the initial mole ratio of oxetane to $EtPh_3PBr$. The presence of the brominated and hydroxylated terminal units in the polymer main chain was also supported by ^1H NMR, where triplet signals due to $BrCH_2CH_2$ and $HOCH_2CH_2$ were observed at δ 3.50 and 3.70 ppm, respectively,[10] in addition to the signals due to repeating oxypropylene units (δ 1.79 and 3.45 ppm). Thus, in the polymerization with $EtPh_3PBr$ in the presence of **1a**, the bromide group in $EtPh_3PBr$ is quantitatively incorporated into the polymer terminal.

Reaction of Quaternary Onium Halides with Organoaluminum Diphenolates (1). As described in the introductory part, the key importance for the Lewis acid-assisted controlled anionic polymerization is the steric suppression of neutralization between nucleophilic and Lewis acidic components.[2] On the other hand, in the present case, we observed that quaternary onium halides react with **1** to give the corresponding "ate" complexes (**2**) quantitatively. For example, when



$\mathbf{2b_{Cl}}$: R^1 = Me, $R^2 = R^4 = {}^{tert}Bu$, R^3 = Me, X = Cl
$\mathbf{2b_{Br}}$: R^1 = Me, $R^2 = R^4 = {}^{tert}Bu$, R^3 = Me, X = Br
$\mathbf{2d_{Cl}}$: R^1 = Et, $R^2 = R^4 = {}^{tert}Bu$, R^3 = Me, X = Cl

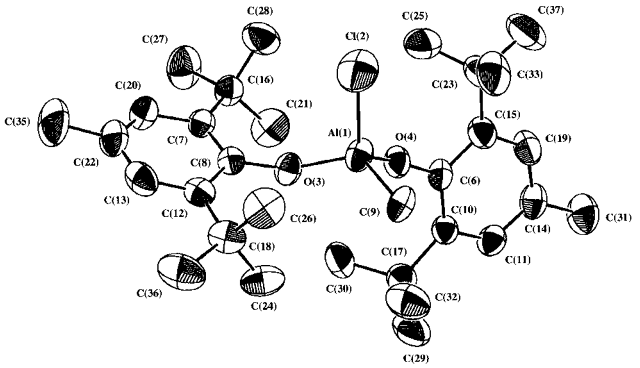


Figure 4. ORTEP view of **2b**$_{\mathrm{Cl}}$ (anionic moiety). Atoms shown with 50% probability ellipsoids. Selected bond lengths (Å): Al(1)–Cl(2) = 2.186(4); Al(1)–O(3) = 1.743(5); Al(1)–O(4) = 1.745(5); Al(1)–C(9) = 2.043(6). Selected bond angles (deg): Cl(2)–Al(1)–O(3) = 104.8(2); Cl(2)–Al(1)–O(4) = 117.0(2); Cl(2)–Al(1)–C(9) = 104.1(3); C(9)–Al(1)–O(3) = 120.9; C(9)–Al(1)–O(4) = 106.3(3); O(3)–Al(1)–O(4) = 104.5(3); Al(1)–O(3)–C(8) = 152.6(4); Al(1)–O(4)–C(6) = 158.9(5).

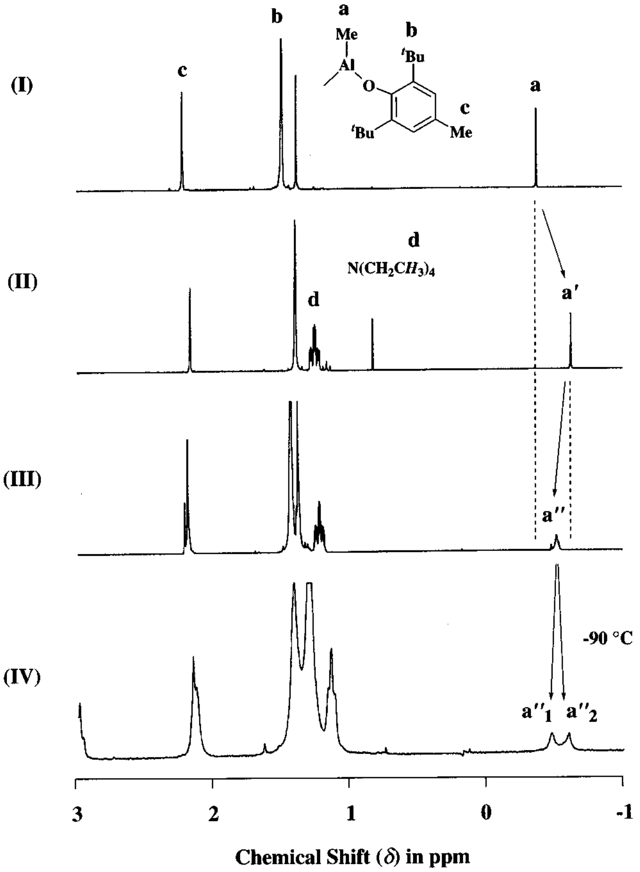
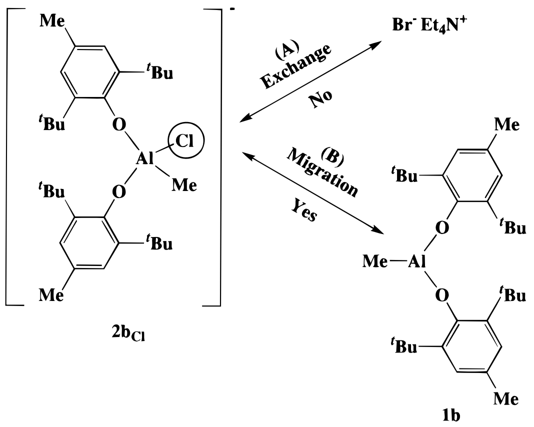


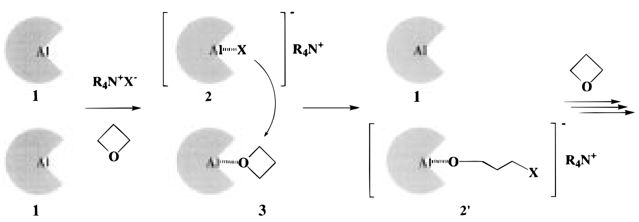
Figure 5. ^{1}H NMR spectra in CD$_2$Cl$_2$ at 22 °C of (I) **1b** and (II) **2b**$_{\mathrm{Cl}}$ and those of an equimolar mixture of **1b** and **2b**$_{\mathrm{Cl}}$ at (III) 22 °C and (IV) −90 °C.

toluene was added at room temperature to a tetrahydrofuran solution of an equimolar mixture of Et$_4$NCl and **1b**, colorless cubic crystals formed. The X-ray crystal structure analysis gave an ORTEP view of the product (**2b**$_{\mathrm{Cl}}$) which demonstrates that the chloride group is attached to the tetrahedral aluminum center at a distance of 2.19 Å (Figure 4). In the ^{1}H NMR spectrum of **2b**$_{\mathrm{Cl}}$ in CD$_2$Cl$_2$ at 22 °C (Figure 5 [II]), the signal due to Me–Al (a′, δ −0.62) was observed at an upfield region from that of **1b** (δ −0.38, a in Figure 5 [I]). Similar upfield shifts were observed for **1b** (Me–Al; δ $-0.38 \rightarrow -0.48$) and **1d** (MeCH_2–Al; δ $0.34 \rightarrow 0.15$) upon mixing with Et$_4$NBr and Et$_4$NCl, respectively.

Scheme 1



Scheme 2



Reactivities of Ate Complexes (2). The ate complex (**2b**$_{\mathrm{Cl}}$), obtained from Et$_4$NCl and **1b**, was not sensitive to air and could be handled without decomposition even under aerobic conditions. Addition of oxetane at room temperature to a CH$_2$Cl$_2$ solution of **2b**$_{\mathrm{Cl}}$ resulted in no polymerization, whereas, in the presence of a bulky Lewis acid such as **1b**, the polymerization did occur. For example, at the initial mole ratio [oxetane]$_0$/[**2b**$_{\mathrm{Cl}}$]$_0$ of 100/1 in the presence of 5 equiv of **1b** with respect to **2b**$_{\mathrm{Cl}}$, the polymerization attained 100% monomer conversion within 4 h, affording a narrow MWD polyether with M_n and M_w/M_n of 8000 and 1.23, respectively. The polymer thus formed carried a chlorinated terminal unit (δ 3.62, ClCH_2CH$_2$) originating from **2b**$_{\mathrm{Cl}}$, in addition to a hydroxylated one (δ 3.72, CH$_2$CH_2OH).[11]

Upon addition of 10 equiv of Et$_4$NBr to a CD$_2$Cl$_2$ solution of **2b**$_{\mathrm{Cl}}$, neither the chemical shift change as for the Me–Al signal (δ −0.62, a′ in Figure 5 [II]) nor the appearance of any new Me–Al signal due to the halogen-exchanged product (**2b**$_{\mathrm{Br}}$, δ −0.48) took place indicating a low ligand exchange activity of **2b**$_{\mathrm{Cl}}$ (Scheme 1A). In contrast, when an equimolar amount of **1b** was added to **2b**$_{\mathrm{Cl}}$, the signal due to Me–Al was broadened and shifted to the middle between those for **1b** and **2b**$_{\mathrm{Cl}}$ (δ −0.51, a″ in Figure 5 [III]). Upon cooling of this solution to −90 °C, the signal a″ split into two signals (a″$_1$ and a″$_2$) (Figure 5 [IV]), which are assignable to the Me–Al groups in **1b** and **2b**$_{\mathrm{Cl}}$, respectively. Thus, the broadening and upfield shift observed for the signal a″ in Figure 5 [III] is the consequence of a rapid, reversible halide migration from the ate complex (**2b**$_{\mathrm{Cl}}$) to the Lewis acid (**1b**) (Scheme 1B). A similar trend was observed for the ^{1}H NMR spectrum at 22 °C of a mixture of **2b**$_{\mathrm{Cl}}$ and **1d**, where a broadened signal due to Me–Al appeared at δ −0.44 ppm.

Taking into account also the fact that the polymerization of oxetane with the quaternary onium halide/**1** systems requires excess Lewis acid (**1**) with respect to the onium halide, the polymerization is likely to occur according to Scheme 2: At the initiation step, the halide group (X) in **2** reacts with the activated monomer (**3**) to generate, with a release of **1**, a halopropanolate growing species (**2′**), which in turn undergoes repeated nucleophilic reactions with the activated monomers (**3**) for chain growth.

Conclusion

We have demonstrated that quaternary onium salts coupled with bulky organoaluminum diphenolates (**1**) serve as the novel, versatile initiating systems for controlled coordinate anionic polymerization of oxetane to give a narrow MWD polyether. Upon mixing of onium salts with **1**, bulky "ate" complexes (**2**) are generated, which function as nucleophilic species for chain growth by the assistance of **1**. Thus, similarly to the Lewis acid-assisted "high-speed living anionic polymerization" with aluminum porphyrin initiators,[2] the coexistence and cooperation of nucleophilic and Lewis acidic species are the key importance for the present polymerization. Molecular design of a nucleophilic initiator with a "built-in" Lewis acidic monomer activation site is one of the subjects worthy of further investigation.

Experimental Part

Materials. Tetraethylammonium chloride (Et_4NCl) and bromide (Et_4NBr) were recrystallized from *N*,*N*-dimethylacetamide and ethanol, respectively. Benzyltriphenylphosphonium chloride ($BnPh_3PCl$) and ethyltriphenylphosphonium bromide ($EtPh_3PBr$) were recrystallized from dichloromethane/toluene and water, respectively. Tetrabutylammonium tetraphenylborate (Bu_4NPh_4B) was recrystallized from chloroform/hexane. Dichloromethane (CH_2Cl_2), washed successively with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and dried over $CaCl_2$, was distilled over CaH_2 in a nitrogen atmosphere. Deuterated dichloromethane (CD_2Cl_2) was distilled over Et_3Al in a nitrogen atmosphere. Tetrahydrofuran (THF), hexane, and toluene were distilled over sodium benzophenone ketyl in a nitrogen atmosphere. Deuterated chloroform ($CDCl_3$) was used as received. Oxetane was distilled over sodium wire in a nitrogen atmosphere. Phenols were recrystallized from hexane. Trimethylaluminum (Me_3Al) and triethylaluminum (Et_3Al) were fractionally distilled under reduced pressure in a nitrogen atmosphere.

Procedures. Preparation of Organoaluminum Diphenolates (1a−1d). Typically, to a 50-mL round-bottomed flask equipped with a three-way stopcock, containing 2,6-di-*tert*-butyl-4-methylphenol (12.5 mmol, 2.75 g) and a magnetic stirring bar under nitrogen, were successively added hexane (10 mL) and Me_3Al (6.25 mmol, 6 mL) at 0 °C in a nitrogen stream, and the mixture was stirred at room temperature for 2 h, whereupon white precipitates formed. The reaction mixture was once heated at 60 °C, and the resulting clear solution was allowed to cool to room temperature, affording white crystals. Then, the liquid phase was removed by a syringe from the flask in a nitrogen stream, and the residue was washed several times with hexane (2 mL) and dried under reduced pressure at room temperature, to leave **1b** as colorless crystals in 60% yield. ^1H NMR (CD_2Cl_2): δ −0.38 (s, Al−CH_3), 1.51 (s, $C(CH_3)_3$), 2.25 (s, CH_3), and 7.00 (s, C_6H_2).

Likewise, **1a**, **1c**, and **1d** were prepared from the corresponding trialkylaluminums and 2 equiv of phenols. ^1H NMR (CD_2Cl_2): **1a** δ −0.61 (s, Al−CH_3), 1.29 and 1.49 (s, $C(CH_3)_3$), and 6.98−7.70 (m, C_6H_3); **1c** δ −0.27 (s, Al−CH_3), 1.34 and 1.62 (s, $C(CH_3)_3$), and 7.29 (s, C_6H_2); **1d** δ 0.34 (q, Al−CH_2), 0.81, (t, CH_2CH_3), 1.53 (s, $C(CH_3)_3$), 2.25 (s, CH_3), and 7.02 (s, C_6H_2).

Preparation of Ate Complexes ($\mathbf{2b_{Cl}}$, $\mathbf{2b_{Br}}$, and $\mathbf{2d_{Cl}}$). Typically, to a 100-mL round-bottomed flask fitted with a three-way stopcock, containing Et_4NCl (2.5 mmol, 4.14 g) and a magnetic stirring bar under nitrogen, was added a THF solution (14 mL) of **1b** (2.5 mmol, 1.20 g) at room temperature in a nitrogen stream, and the reaction mixture was stirred at 60 °C until the solution became clear. Then, toluene (13.5 mL) was added to this hot solution, and the mixture was allowed to cool to room temperature, affording $\mathbf{2b_{Cl}}$ as white crystals in 83% yield. ^1H NMR (CD_2Cl_2): δ −0.62 (s, Al−CH_3), 1.26 (t, CH_2), 1.40 (s, $C(CH_3)_3$), 2.17 (s, $ArCH_3$), 3.15 (q, CH_3), and 6.89 (s, C_6H_2). Anal. Calcd for $C_{39}H_{59}AlClNO_2$: C, 72.47; H, 10.76; N, 2.17. Found: C, 72.18; H, 10.48; N, 2.35. Crystal data: orthorhombic; *Pcab*; $a = 19.306(2)$, $b = 22.959(3)$, $c = 18.238(3)$ Å; $D_{calcd} = 1.06$ g/cm^{-3}; $Z = 8$. A total of 6822 reflections (maximum 2θ of 120°) was collected on a Mac Science MXC18 diffractometer at room temperature using the $2\theta-\omega$ scan method. The structure was solved by the heavy atom method (DIRDIF 92) and refined with 4157 reflections ($|F_o| > 3\sigma$), GOF = 15.8, $R = 0.0799$, $R_w = 0.095$.

Likewise, $\mathbf{2b_{Br}}$ and $\mathbf{2d_{Cl}}$ were prepared from the corresponding organoaluminum diphenolates and onium salts. ^1H NMR (CD_2Cl_2): $\mathbf{2b_{Br}}$ δ −0.48 (s, Al−CH_3), 1.26 (t, N−CH_2), 1.42 (s, $C(CH_3)_3$), 2.18 (s, $ArCH_3$), 3.22 (q, CH_3), and 6.90 (s, C_6H_2); $\mathbf{2d_{Cl}}$ δ 0.15 (q, Al−CH_2), 0.95 (s, Al−CH_2CH_3), 1.21 (t, N−CH_2), 1.43 (s, $C(CH_3)_3$), 2.20 (s, $ArCH_3$), 3.04 (q, N−CH_2CH_3), and 6.93 (s, C_6H_2).

Polymerization. Typically, to a 50-mL round-bottomed flask attached to a three-way stopcock, containing a CH_2Cl_2 solution (2 mL) of $EtPh_3PBr$ (0.1 mmol) and a magnetic stirring bar under nitrogen, was added a CH_2Cl_2 solution (1 mL) of a mixture of **1** and oxetane (10 mmol, 0.64 mL) by a syringe in a nitrogen stream, and the mixture was stirred at room temperature. A portion of the polymerization mixture was periodically taken out from the flask and subjected to ^1H NMR ($CDCl_3$) and gel permeation chromatography (GPC) to determine the monomer conversion and average molecular weights (M_n, M_w) of the produced polymer, respectively. The monomer conversion was determined from the relative intensity of the signals at δ 4.78 and 3.45 ppm due to OCH_2 in oxetane and poly(oxetane), respectively.

For end-group analysis, oxetane was polymerized similarly to the above with the $EtPh_3PBr$/**1a** system ($[\text{oxetane}]_0/[EtPh_3PBr]_0/[\mathbf{1a}]_0 = 10/1/6$) up to 100% monomer conversion, and the reaction mixture, evaporated to dryness, was chromatographed on silica gel with ethyl acetate/hexane (4/1) as eluent. The fraction containing polymeric products was evaporated under reduced pressure at room temperature, to leave a colorless viscous liquid, which was subjected to ^1H and ^{13}C NMR analyses.

Measurements. Gel permeation chromatography (GPC) was performed at 40 °C on a TOSO 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), 2800 (1.05). ^1H and ^{13}C NMR measurements were performed using CD_2Cl_2 or $CDCl_3$ as solvent on a JEOL type GSX-270 spectrometer, where the chemical shifts were determined with respect to $CHCl_3$ (δ 7.28) or CH_2Cl_2 (δ 5.31) for ^1H and $CDCl_3$ (δ 77.2) for ^{13}C as internal standards.

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Supporting Information Available: Fractional coordinates and isotropic thermal factors for $\mathbf{2b_{Cl}}$ (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(8) Average molecular weights (M_n and M_w), estimated by GPC calibrated with polystyrene standards, were multiplied by a factor of 0.6 for polyoxetane samples (see ref 5).

(9) ^{13}C NMR ($CDCl_3$): (of $CH_3CH_2CH_2CH_2Br$) δ 13.1 (CH_3), 21.2 ($MeCH_2$), 33.6 (CH_2), and 34.7 (CH_2Br); (of $CH_3OCH_2CH_2CH_2OH$) δ 13.1 (CH_3O), 21.2 (OCH_2), 33.6 (CH_2), and 34.7 (CH_2OH) [prepared according to: Smith, L. I.; Sprung, J. A. *J. Am. Chem. Soc.* **1943**, *65*, 1276].

(10) ^{1}H NMR ($CDCl_3$): (of $CH_3CH_2CH_2CH_2Br$) δ 0.94 (CH_3), 1.45 ($MeCH_2$), 1.84 (CH_2), and 3.43 (CH_2Br); (of $CH_3OCH_2CH_2CH_2OH$) δ 3.36 (CH_3O), 3.58 (OCH_2), 1.84 (CH_2), 3.77 (CH_2O), and 2.44 (OH).

(11) By reference to $ClCH_2CH_2CH_2OH$: ^{1}H NMR ($CDCl_3$) δ 3.68 ($ClCH_2$), 2.01 (CH_2), and 3.80 (CH_2O).

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