

Notes

An Aluminum Complex Supported by a Fluorous Diamino-Dialkoxide Ligand for the Highly Productive Ring-Opening Polymerization of ϵ -Caprolactone

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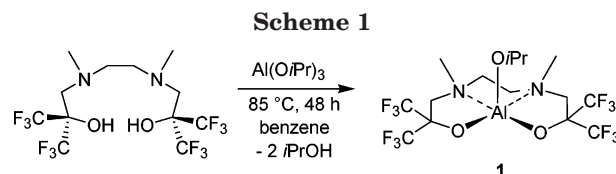
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Summary: The new discrete aluminum alkoxide complex $(iPrO)Al\{CH_2NMeCH_2C(CF_3)_2O\}_2$ (**1**) initiates the controlled ring-opening polymerization of caprolactone in dichloromethane at 20 °C with high activity (TOF = 250 h^{-1}) and productivity (TON up to 1000), leading to polymers with high molecular weight and narrow molecular weight distribution.

Introduction

Aluminum alkoxide complexes modified by ancillary ligands have been used with great success for the ring-opening polymerization (ROP) of cyclic esters such as ϵ -caprolactone (ϵ -CL)^{1–4} and lactide.^{5–8} This is an important process since the resulting polyesters are biodegradable and of practical application.^{9,10} A major interest of these so-called single-site aluminum catalysts



is the high degree of control they exhibit over polymerization, resulting in materials with controlled molecular weight and narrow molecular weight distribution. However, the use of a stoichiometric amount of metal complex per macromolecular chain remains a major limitation of initiating polymerization systems. Highly productive systems enabling the conversion of many (i.e., ≥ 500) equivalents of monomer units are therefore very desirable. However, such examples remain rather scarce.¹¹ We report here a rare example of a discrete aluminum initiator stabilized by a C_2 -symmetric fluorous diamino-dialkoxide ligand which shows a hitherto unknown high activity and productivity for the ROP of ϵ -CL at room temperature. Such a poor electron-donating dialkoxide ligand has recently been designed by some of us and coordinated to group 3 and 4 metals.¹²

Results and Discussion

The Al-OiPr complex $\{CH_2NMeCH_2C(CF_3)_2O\}_2Al(OiPr)$ (**1**) (Scheme 1) was synthesized in a straightforward way by reaction of the corresponding tetradentate diprotio fluorinated ligand with 1 equiv of $Al(OiPr)_3$ and was isolated in good yield (72%) as a colorless solid. In contrast, numerous attempts to cleanly generate the Al-Me analogous complex, via reaction of $\{CH_2NMeCH_2C(CF_3)_2OH\}_2$ with 1 equiv of $AlMe_3$ at RT or -78 °C, remained unsuccessful, although reaction clearly occurred, at both temperatures, as evidenced by vigorous methane evolution.

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Table 1. Polymerization of ϵ -Caprolactone Initiated by **1** and Other Aluminum-Based Isopropoxide Initiators^a

entry	complex	solvent	[CL]/[Al]	time ^c (h)	conv (%)	M_n^{calc} (g/mol)	$M_n^{\text{exp,d}}$ (g/mol)	M_w/M_n^d
1	1	CH ₂ Cl ₂	100	1	100	11 400	12 700	1.16
2	1	CH ₂ Cl ₂	200	1	85	19 400	18 400	1.10
3	1	CH ₂ Cl ₂	500	4	95	57 000	60 300	1.11
4 ^b	1	CH ₂ Cl ₂	500	4	61	34 700	27 900	1.24
5	1	toluene	500	3	94	53 500	45 400	1.58
6	1	CH ₂ Cl ₂	1000	12	98	114 100	141 400	1.23
7 ^b	1	CH ₂ Cl ₂	1000	12	30	34 200	21 700	1.16
8	1	CH ₂ Cl ₂	350 (+650)	2 +6	100 98	39 900 112 500	44 200 149 200	1.18 1.21
9	Al(OiPr) ₃	CH ₂ Cl ₂	500	18	80	45 600	49 790	1.21
10	Al(OiPr) ₃	toluene	500	1	90	51 300	41 800	1.66
11	A ^e	CH ₂ Cl ₂	500	48	0			
12	A ^e	toluene	500	48	84	47 900	46 300	1.14

^a [CL]₀ = 1.0 M, room temperature. ^b [CL]₀ = 2.7 M. ^c Reaction time was not necessarily optimized. ^d Number-average molecular weight (M_n), peak molecular weight (M_p), and molecular weight distribution determined by GPC in THF vs polystyrene standards. ^e A = [(3,5-*t*Bu₂-2-C₆H₃O)CH₂]₂NCH₂CH₂NMe₂Al(OiPr).

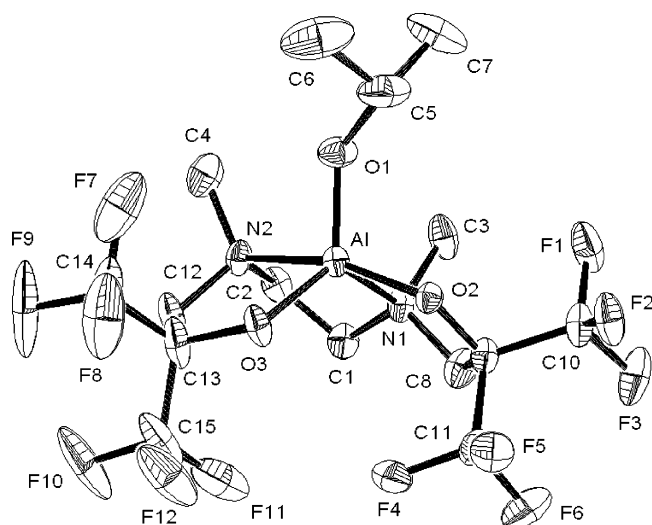


Figure 1. Molecular structure of **1**, with 30% thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Al–O(1), 1.699(3); Al–O(2), 1.806(3); Al–O(3), 1.762(3); Al–N(1), 2.017; Al–N(2), 2.196(4); C(5)–O(1)–Al, 131.8(3); C(9)–O(2)–Al, 120.7(3); C(13)–O(3)–Al, 125.2(3); N(1)–Al–N(2), 81.58(15); O(2)–Al–N(2), 161.28(15); O(3)–Al–N(2), 82.69(15); O(3)–Al–N(1), 122.41(17).

The Al complex **1** is air-stable for several days at RT, is sparingly soluble in CH₂Cl₂, and is nearly insoluble in hydrocarbon solvents such as toluene and benzene. Single crystals of **1**, obtained from CH₂Cl₂, allowed its molecular structure to be determined by X-ray crystallography (Figure 1). The Al center in **1** adopts a distorted trigonal bipyramidal coordination geometry with the OiPr oxygen (O(1)), N(1), and O(3) being in equatorial positions, while O(2) and N(2) occupy the axial ones. As expected for the observed geometry, the Al–N_{axial} bond distance (Al–N(2) = 2.196(4) Å) is significantly longer than the Al–N_{equa} (Al–N(1) = 2.017 Å). The Al–O bond distances of the Al–ligand moiety (Al–O(3) = 1.762(3) Å; Al–O(2) = 1.806(3) Å) are longer than those expected for a terminal Al–O alkoxide bond (typically 1.68–1.72 Å),¹³ which may result from constraints associated with the Al chelate. Accordingly, the

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Al–OiPr bond length (Al–O(1) = 1.699(3) Å) is shorter and lies within the expected range.² Overall, the structural features at the Al center of **1** can be related to those observed in a recently reported N₂O₂-tetradentate phenoxyamine aluminum methyl complex (a salan-AlMe derivative), which exhibits a similar geometry at the Al center.⁵ However, the significantly shorter Al–N_{axial} in **1** vs that in the salan-AlMe (2.196(4) vs 2.4532(19) Å) strongly suggests a quite electrophilic and Lewis acidic Al center in **1**.

The ¹H NMR spectrum of **1** (CD₂Cl₂, RT) contains singlet resonances for each of the CH₃-iPr, NCH₃, and NCH₂, but two sets of CH₂C(CF₃)₂ resonances. Also, the ¹⁹F NMR spectrum of **1** (CD₂Cl₂, RT) exhibits only two distinct quartets, indicating that the two CF₃ groups within each C(CF₃)₂ moiety are inequivalent. These data are consistent with the overall solid-state structure of **1** being retained in CD₂Cl₂ solution at RT, with a time-averaged C_s-symmetry due to fast motion in the Al–NCH₂CH₂N ring.

The Al–OiPr complex **1** is an effective initiator for the ROP of ϵ -CL. For solubility reasons, most of the polymerizations were conducted in dichloromethane, but the use of toluene was also investigated to evaluate the abilities of **1** in this common solvent;¹⁴ representative results are collected in Table 1. High polymerization activity was observed at room temperature in both dichloromethane and toluene.¹⁵ Kinetic monitoring by ¹H NMR of experiments conducted at high monomer-to-initiator ratios ([ϵ -CL]/[Al] \geq 500, *vide infra*) in CH₂Cl₂ indicated turnover frequencies (TOFs) in the range 200–250 h^{−1}, which remain constant up to 60–70% conversion; at higher conversions, a progressive decrease in activity is observed, concomitant with an increase of viscosity. These activity data compare favorably with most discrete aluminum initiators, in particular related bis(phenolate) salen and salan complexes, which are usually reported to be active from 50 °C¹ and/or afford TOFs 1 order of magnitude lower than **1** at

(14) Prior to monomer addition, a catalytic amount of **1** used for these polymerization tests was quantitatively dissolved in both CH₂Cl₂ and toluene under the studied conditions. In addition, the reaction mixture remained a solution during the entire time of the polymerization reaction.

(15) Note that the polymerization activity of **1** is completely inhibited by the presence of 5 equiv (vs **1**) of a carboxylic acid such as butyric acid and caproic acid, thus requiring the use of an extrapure ϵ -CL monomer to run polymerization tests with high [ϵ -CL]/[**1**] ratios.

room temperature.^{2,3} However, comparison with literature data may be hazardous due to possible differences in reaction conditions (temperature, monomer-to-initiator ratio, monomer concentration, solvent and monomer purity, etc.). To obtain truly comparable data, control experiments were carried out with Al(O*i*Pr)₃ and the Al-bis(phenoxy)bis(amine) complex [(3,5-*t*Bu₂-2-C₆H₃O)CH₂]₂NCH₂CH₂NMe₂Al(O*i*Pr) (**A**)² as initiators (entries 9–12). These results show that **1** indeed features a significantly higher activity than those two reference systems when polymerizations are carried out in dichloromethane. However, Al(O*i*Pr)₃ is more active than **1** in toluene (while **A** is inactive at this monomer-to-initiator ratio), but the level of control of these polymerizations is much lower, as indicated by the larger polydispersities (entries 5 and 10). A similarly highly active (TOF up to 300 h⁻¹, monomer-to-initiator ratios ([ϵ -CL]/[Al] < 300, 25 °C) salicylaldimine-aluminum-benzyl alcohol system has been very recently reported.⁴ However, this system was not shown to be active in the presence of larger amounts of monomer. By contrast, complex **1** proved to be a very productive system, enabling the quantitative conversion of up to 1000 equiv of ϵ -CL within a few hours at room temperature (time, conv: 40 min, 15%; 120 min, 40%; 180 min, 60%) (entry 6). More, all of the experimental molecular weights are in close agreement with calculated values and molecular weight distributions are narrow, both features being characteristic of a controlled polymerization. The productivity of the system and the controlled character of the polymerizations initiated by **1** were further evidenced by the sequential polymerization of 350 + 650 equiv of caprolactone (entry 8), for which complete conversion was observed together with minor broadening of the molecular weight distribution between the two stages. These interesting performances are observed provided a moderate concentration of ϵ -CL is used (e.g., [CL]₀ = 1.0 M); at a higher concentration ([CL]₀ = 2.7 M), lower conversions as well as experimental *M_n* values lower than the calculated values were observed, possibly reflecting transfer reactions (entries 4 and 7).

The high polymerization activity and productivity afforded by **1** suggest a high electrophilicity of the metal center. The high Lewis acidity of the Al center in **1**, although not independently assessed, is logically anticipated from the presence of strong electron-withdrawing CF₃ groups α to the ligand alkoxides. In this regard, Gibson et al. have shown that introduction of electron-withdrawing substituents on phenoxy platforms of ancillary ligands affords a more active aluminum initiator for the ROP of lactide.⁶ A similar activity–electronic effects trend has been recently reported by Nomura et al. in the ROP of ϵ -CL with salicylaldimine-aluminum complexes.⁴ On the other hand, Hillmyer and Tolman have observed an opposite trend for the ROP of ϵ -CL with five-coordinate aluminum alkoxide initiators supported by bis(phenoxy)-bis(amine) ligands and have proposed that the overall rate of polymerization depends on a subtle interplay between Lewis acidity and alkoxide (isopropoxide) nucleophilicity.² The latter is obviously necessary to achieve rapid initiation and obtain in turn narrow molecular weight distributions, as in the present case.

In conclusion, the original fluoros diamino-dialkoxide ligand we recently designed confers unique activity

and productivity to the Al-O*i*Pr derivative, which readily initiates the ROP of ϵ -CL, with a good level of control. Work is under progress in our laboratories to extend the scope of these highly electrophilic polymerization systems.

Experimental Section

General Procedures. All experiments were carried out under nitrogen or argon using standard Schlenk techniques or a glovebox. Benzene and toluene were distilled from Na/K alloy, dichloromethane was distilled from calcium hydride under nitrogen, and all were degassed by freeze–thaw–vacuum cycles prior to use. ϵ -Caprolactone (ϵ -CL, Acros) was distilled twice under argon over CaH₂. Al(O*i*Pr)₃ was purchased from ACROS and used as received. Complex [(3,5-*t*Bu₂-2-C₆H₃O)CH₂]₂NCH₂CH₂NMe₂Al(O*i*Pr) (**A**) was prepared as reported in the literature.² NMR spectra were recorded on Bruker AC-300 and AC-400 spectrometers. ¹H and ¹³C NMR chemical shifts were determined using residual solvent resonances and are reported vs TMS. Assignment of signals was made from ¹H–¹H COSY, ¹H–¹³C HMQC, and ¹H–¹³C HMBC 2D NMR experiments. ¹⁹F NMR chemical shifts are referenced to external CFCl₃. Elemental analyses were performed at the Institute of Chemistry of Rennes and are the average of two independent determinations. Molecular weights of PCL were determined by GPC at room temperature on a Waters apparatus equipped with five PL gel columns (Polymer Laboratories Ltd) and a Shimadzu RID 6A differential refractometer. THF was used as eluent at a flow rate of 1.0 mL·min⁻¹, and PSt standards were used for calibration.

Al Complex 1. In a glovebox, an equimolar amount of the tetradentate fluorinated ligand {CH₂NMeCH₂C(CF₃)₂OH}₂¹⁶ (439 mg, 0.980 mmol) and Al(O*i*Pr)₃ (200 mg, 0.980 mmol) were charged in a 5 mL ampule equipped with a secured Teflon valve, and the mixture was dissolved in benzene (3 mL). The resulting colorless solution was heated at 85 °C in an oil bath for 2 days and allowed to cool to room temperature, provoking the massive precipitation of a colorless solid. The suspension was then filtered through a glass frit and the obtained solid residue washed several times with toluene to afford, after further drying in vacuo, pure **1** as a colorless solid (375 mg, 72% yield). Anal. Calcd for C₁₅H₂₁AlF₁₂N₂O₃ (532.32): C, 33.85; H, 3.98; N, 5.26. Found: C, 33.68; H, 4.07; N, 5.22. ¹H NMR (300 MHz, CD₂Cl₂, 20 °C): δ 1.07 (d, ³J_{H–H} = 6.0 Hz, 6H, Me-*i*Pr), 2.69 (s, 6H, NMe), 2.95 (s, 4H, N(CH₂)₂N), 3.05 (d, ²J_{H–H} = 15.1 Hz, 2H, CHH'C(CF₃)₂), 3.23 (d, ²J_{H–H} = 15.1 Hz, 2H, CHH'C(CF₃)₂), 4.12 (septet, ³J_{H–H} = 6.0 Hz, 1H, CH-*i*Pr). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 20 °C): δ 26.7 (Me-*i*Pr), 46.9 (NMe), 56.8 (N-CH₂), 59.0 (N-CH₂), 63.0 (CH-*i*Pr), 75.8 (br, CCF₃), 123.6 (q, ¹J_{CF} = 289 Hz, CF₃), 123.7 (q, ¹J_{CF} = 290 Hz, CF₃). ¹⁹F NMR (282.4 MHz, CD₂Cl₂, 20 °C): δ -79.4 (q, ⁴J_{F–F} = 10 Hz, 6F, CF₃), -77.8 (q, ⁴J_{F–F} = 10 Hz, 6F, CF₃).

Crystal data for compound 1: C₁₅H₂₁AlF₁₂N₂O₃, *M_r* = 532.32, crystal size 0.08 × 0.07 × 0.05 mm, orthorhombic, space group *Pbca*, *a* = 13.352(2) Å, *b* = 19.546(3) Å, *c* = 16.723(2) Å, *V* = 4364.2(11) Å³, *Z* = 8, *D_c* = 1.620 g cm⁻³, *F*(000) = 2160, Mo K α radiation (λ = 0.71073 Å), *T* = 173(2) K, μ = 0.214 mm⁻¹. The 8899 reflections measured on a Nonius Kappa CCD system yielded 4933 independent reflections, *R*₁ (*I* > 2 σ (*I*)) = 0.0639, *wR*₂ (*I* > 2 σ (*I*)) = 0.1329. Crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC number 271252) and are also available as a cif file.

(16) This ligand was prepared from the reaction of the CF₃-substituted oxirane (CF₃)₂COC₂H₂ with *N,N'*-dimethylethylenediamine at room temperature; see: Chi, Y.; Hsu, P.-F.; Liu, C.-S.; Ching, W.-L.; Chou, T.-Y.; Carty, A. J.; Peng, S.-M.; Lee, G.-H.; Chuang, S.-H. *J. Mater. Chem.* **2002**, *12*, 3541.

Typical Polymerization Procedure. A Schlenk flask was charged with a solution of **1** in CH₂Cl₂. To this solution was rapidly added under stirring a solution of ϵ -caprolactone in the appropriate ratio in CH₂Cl₂. The reaction mixture was stirred at the desired temperature for the desired reaction time. After an aliquot of the crude solution was removed for analytical purposes, the reaction was quenched with acidic methanol (0.5 mL), and the polymer was precipitated with excess methanol. The polymer was then dried in vacuo to constant weight.

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Supporting Information Available: Crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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