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Aluminum Complexes of Tridentate Amine Biphenolate Ligands Containing Distinct *N*-alkyls: Synthesis and Catalytic Ring-opening Polymerization

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A series of aluminum complexes of amine biphenolate ligands that contain distinct *N*-alkyl substituents have been prepared and employed for ring-opening polymerization (ROP) of ε-caprolactone (ε-CL). Alkane elimination of trimethylaluminum with H_2[R-ONO] ($[R\text{-ONO}]^{2-}$ = $[RN(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2(t\mathrm{Bu})_2)_2]^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**), *n*Pr (**1c**)) in toluene solutions at 25 °C produces colorless crystalline [R-ONO]AlMe (**2a-c**). X-ray diffraction studies of these organoaluminum complexes showed them to be four-coordinate species having a distorted tetrahedral coordination core. In the presence of benzyl alcohol, complexes **2a-c** are all active catalyst precursors for ROP of ε-CL. The ROP rates of ε-CL are clearly a function of the steric sizes of the *N*-alkyl substituents, following an increasing order **2a** < **2b** < **2c**. Interestingly, both **2b** and **2c** exhibit controlled ROP catalysis whereas **2a** gives low molecular weight oligomers under identical conditions. In ROP catalyzed with **2b** or **2c**, the ε-CL disappearance rates follow pseudo-first order kinetics, with the latter being about 2.86(2) times faster than the former. Complex **2b** outperforms **2c** in view of maintaining controlled ROP catalysis in reactions with extremely high monomer-to-catalyst ratios. The complex constitution-reactivity relationship is discussed.

Keywords: Aluminum; ONO ligand; Amine biphenolate; Ring-opening polymerization.

INTRODUCTION

The search for appropriate methods to prepare biocompatible and biodegradable polymeric materials[1-6] continues to constitute an active area of exploratory research. Ring-opening polymerization (ROP) of heterocyclic molecules, e.g., lactides or ε-caprolactone (ε-CL), etc., catalyzed by main-group[7-23] or transition metal complexes[24-31] is attractive due to their versatilities and accessibilities to produce these biorenewable materials in a controlled manner.[32-35] Recent advances have shown that living ROP may be effectively devised with judiciously tailored metal complexes that contain chelating N- or O-donor ligands.[36-44] For instance, metal complexes supported by chelating β-diketiminate[37,38] or phenolate-based[39-42] ligands are known as catalysts to produce polylactides or poly(ε-caprolactone)s (PCLs) with controlled number averaged molecular weight (*M*n) and polydispersity index (PDI) values. For steric and/or electronic tuning, the phenolate-based ligands may in some cases integrate extra central or peripheral donor(s).[45-58] Figure 1 depicts representative examples of amine bi-phenolate ligands with and without a peripheral donor. Notably, while several reports disclose the influences of *ortho*- and *para*-substituents (R^1 and R^2, respectively)[45,47,59] and additional *N*-tethered donors[46,59] on ROP catalysis, the effect of *N*-alkyl substituents (R^3) lacking of extra donors is not well established. This result is somewhat surprising but may have something to do with the lack of efficient methods to construct amine biphenolate ligands that contain *N*-substituted secondary or tertiary alkyls. Having this in mind, we have set out to explore the possibilities to prepare these novel ligands. To evaluate the effects of *N*-alkyl substituents on ROP catalysis, we chose to examine the activities of aluminum complexes of $[RN(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2(t\mathrm{Bu})_2)_2]^{2-}$ ($[R\text{-ONO}]^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**), *n*Pr (**1c**)) with ε-CL. Aluminum complexes were in-

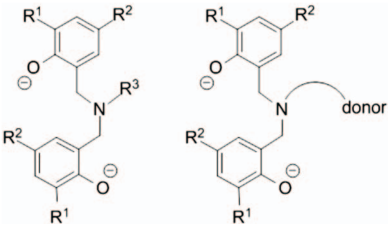

Fig. 1. Representative examples of amine biphenolate ligands.

Special Issue Dedicated to Prof. Yu Wang in Honor of Her 70th Birthday

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tentionally chosen on the basis of an elegant report by Chen et al. describing controlled ROP of ε-CL catalyzed by [*n*Pr-ONO]AlMe (**2c**)[42] that features a primary *N*-alkyl. We present herein the synthesis of H_2[**1a**] and H_2[**1b**] carrying a tertiary and secondary *N*-bound alkyl, respectively, and their corresponding aluminum complexes [*t*Bu-ONO]AlMe (**2a**) and [*i*Pr-ONO]AlMe (**2b**), along with their ROP catalysis with ε-CL. Kinetic studies employing **2b** and **2c** were also attempted to get insights regarding the effect of these *N*-alkyls on catalysis.

EXPERIMENTAL

General considerations. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. Compounds 2-(bromomethyl)-4,6-di-*tert*-butylphenol,[60] 2-(isopropylaminomethyl)-4,6-di-*tert*-butylphenol,[61] 2-(*tert*-butylaminomethyl)-4,6-di-*tert*-butylphenol,[62] H_2[**1c**],[59] and **2c**[42] were prepared according to literature procedures. All other chemicals were obtained from commercial vendors and used as received. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane. Coupling constants (*J*) and peak widths at half-height ($\Delta\nu_{1/2}$) are listed in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms for all new compounds is based on the DEPT ^{13}C NMR spectroscopy. ^{27}Al NMR spectra are referenced externally using $AlCl_3$ in D_2O at δ 0. Routine coupling constants are not listed. All NMR spectra were recorded at 22 °C in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer. GPC analyses were carried out at 45 °C on a JASCO instrument equipped with two Waters Styragel HR columns in series and a JASCO RI-2031 refractive index detector. HPLC grade THF was supplied at a constant flow rate of 1.0 mL/min with a JASCO PU-2080 Isocratic HPLC Pump. Molecular weights (*M*n and *M*w) were determined by interpolation from calibration plots established with polystyrene standards (*M*n range: 3790-189300).

Synthesis of H_2[1a]. An acetonitrile solution (10 mL) containing 2-(*tert*-butylaminomethyl)-4,6-di-*tert*-butylphenol (17.2 mmol) and K_2CO_3 (34.4 mmol, 2 equiv) was stirred at 25 °C for 30 min. To this was sequentially added NEt_3 (86 mmol, 5 equiv) and an acetonitrile solution (10 mL) of 2-(bromomethyl)-4,6-di-*tert*-butylphenol (22.4 mmol, 1.3 equiv). The reaction mixture was stirred at 25 °C overnight and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in Et_2O (30 mL) and deionized water (20 mL) was added. The ether solution was separated from the aqueous portion, from which the product was extracted two more times with diethyl ether. All ether solutions were combined and dried over $MgSO_4$. All volatiles were re-moved in vacuo. The residue was dissolved in acetonitrile (5 mL). The solution was cooled to −15 °C in a freezer to afford to product as an off-white solid. The yields were typically 70-75%. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.11 (s, 2, ArO*H*), 7.35 (d, 2, *J* = 1.9, Ar*H*), 6.95 (d, 2, *J* = 1.8, Ar*H*), 3.61 (s, 4, ArC*H₂*), 1.52 (s, 18, ArC*Me*₃), 1.32 (s, 18, ArC*Me*₃), 0.98 (s, 9, NC*Me*₃). ^{13}C NMR (C_6D_6, 75 Hz) δ 153.65 (*C*), 142.10 (*C*), 136.91 (*C*), 125.02 (*C*), 124.64 (*C*H), 123.57 (*C*H), 57.46 (N*C*Me₃), 53.56 (Ar*C*H₂N), 35.48 (Ar*C*Me₃), 34.73 (Ar*C*Me₃), 32.29 (ArC*Me₃*), 30.48 (ArC*Me₃*), 27.05 (NC*Me₃*). Anal. Calcd for $C_{34}H_{55}NO_2$: C, 80.09; H, 10.88; N, 2.75. Found: C, 80.23; H, 10.60; N, 2.64.

Synthesis of H_2[1b]. Procedures were similar to those of H_2[**1a**], producing the product as an off-white solid; yield 75%. ^{1}H NMR (C_6D_6, 500 MHz) δ 8.36 (s, 2, ArO*H*), 7.47 (d, 2, *J* = 2.5, Ar*H*), 6.96 (d, 2, *J* = 2.5, Ar*H*), 3.43 (s, 4, ArC*H₂*), 3.00 (sept, 1, *J* = 6.5, NC*H*Me₂), 1.62 (s, 18, ArC*Me₃*), 1.36 (s, 18, ArC*Me₃*), 0.75 (d, 6, *J* = 6.5, NCH*Me₂*). ^{13}C NMR (C_6D_6, 125 MHz) δ 153.25 (*C*), 141.76 (*C*), 136.55 (C), 125.27 (*C*H), 123.66 (*C*H), 122.20 (*C*), 52.35 (Ar*C*H₂N), 48.40 (N*C*HMe₂), 35.27 (Ar*C*Me₃), 34.36 (Ar*C*Me₃), 31.91 (ArC*Me₃*), 30.06 (ArC*Me₃*), 16.36 (NCH*Me₂*). Anal. Calcd for $C_{33}H_{53}NO_2$: C, 79.93; H, 10.78; N, 2.83. Found: C, 79.75; H, 10.81; N, 2.78.

Synthesis of 2a. Trimethylaluminum (0.2 mL, 2 M in toluene, 0.4 mmol) was added to a toluene solution (5 mL) of H_2[**1a**] (200 mg, 0.392 mmol) at 25 °C. After being stirred at 25 °C for 24 h, the reaction solution was evaporated to dryness under reduced pressure. The residue thus obtained was washed with pentane (2 mL) to give an off-white solid; yield 144 mg (67%). Colorless crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated pentane solution at −35 ºC. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.53 (d, 2, *J* = 2.3, Ar*H*), 6.70 (d, 2, *J* = 2.2, Ar*H*), 3.53 (d, 2, *J* = 13.7, ArC$H_A$$H_B$), 3.43 (d, 2, *J* = 13.8, ArC$H_A$$H_B$), 1.68 (s, 18, ArC*Me₃*), 1.37 (s, 18, ArC*Me₃*), 0.83 (s, 9, NC*Me₃*), −0.03 (s, 3, Al*Me*). ^{13}C NMR (C_6D_6, 125 Hz) δ 156.00 (*C*), 140.29 (*C*), 138.59 (*C*), 124.83 (*C*), 124.05 (*C*H), 123.68 (*C*H), 61.77 (Ar*C*H₂N), 55.10 (N*C*Me₃), 35.73 (Ar*C*Me₃), 34.71 (Ar*C*Me₃), 32.46 (ArC*Me₃*), 30.25 (ArC*Me₃*), 26.44 (NC*Me₃*), −9.31 (Al*Me*). Anal. Calcd for $C_{35}H_{56}NO_2Al$: C, 76.45; H, 10.27; N, 2.55. Found: C, 76.33; H, 10.32; N, 2.49.

Synthesis of 2b. Procedures were similar to those of **2a**, producing the product as an off-white solid; yield 61%. Colorless crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated pentane solution at −35 ºC. ^{1}H NMR (C_6D_6, 500 MHz) δ 7.56 (d, 2, *J* = 2.4, Ar*H*), 6.70 (d, 2, *J* = 2.3, Ar*H*), 3.40 (d, 2, *J* = 13.5, ArCH_AH_B), 3.19 (d, 2, *J* = 13.5, ArCH$_A$$H_B$), 2.66 (septet, 1, *J* = 6.6, NC*H*Me$_2$), 1.70 (s, 18, ArC*Me$_3$*), 1.40 (s, 18, ArC*Me$_3$*), 0.58 (d, 6, NCH*Me$_2$*), –0.20 (s, 3, Al*Me*). ^{13}C NMR (C_6D_6, 125 Hz) δ 156.12 (*C*), 140.21 (*C*), 138.82 (*C*), 125.04 (*C*), 124.71 (*C*H), 121.82 (*C*H), 53.75 (Ar*C*H$_2$N), 52.81 (N*C*HMe$_2$), 35.80 (Ar*C*Me$_3$), 34.70 (Ar*C*Me$_3$), 32.43 (ArC*Me$_3$*), 30.30 (ArC*Me$_3$*), 16.92 (NCH*Me$_2$*), −11.50 (Al*Me*). ^{27}Al NMR (toluene-d_8, 130 MHz) δ 150 ($\Delta\nu_{1/2}$ = 11186). Anal. Calcd for $C_{34}H_{54}NO_2Al$: C, 76.21; H, 10.16; N, 2.62. Found: C, 76.11; H, 10.33; N, 2.69.

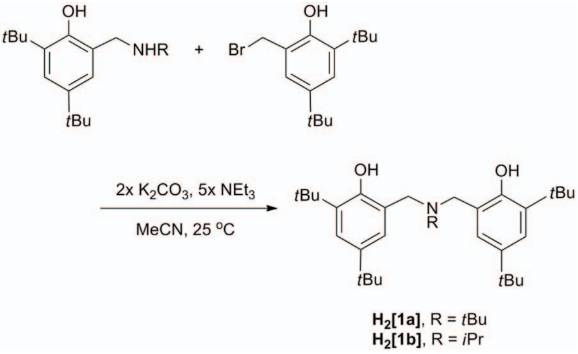
X-ray crystallography. Crystallographic data for all structurally characterized compounds are available in Supplementary material. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least squares procedures against F^2 using SHELXL-97.[63] All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The crystals of **2b** were of poor quality (R1 = 0.1079) but sufficient to establish the identity of this molecule. CCDC 889209–889214 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Synthesis and characterization of ligands

Ligand H$_2$[**1c**] was prepared following the known Mannich condensation method.[59] Attempts to synthesize H$_2$[**1a**] and H$_2$[**1b**] under similar conditions, however, led instead to the formation of the corresponding benzoxazines[64-66] on the basis of GC/MS analysis of reaction aliquots; neither H$_2$[**1a**] nor H$_2$[**1b**] was detected. In contrast, nucleophilic substitution reactions of 2-(bromomethyl)-4,6-di-*tert*-butylphenol[60] with 2-(alkylaminomethyl)-4,6-di-*tert*-butylphenol[61,62] in the presence of potassium carbonate and triethylamine in acetonitrile solutions at 25 °C afforded successfully in 12 hours the desired amine biphenol ligands in ca. 70% isolated yield (Scheme I). We note that the participation of both potassium carbonate and triethylamine in these reactions appears critical: no reaction occurred at all in the absence of potassium carbonate; little formation of the desired products (< 10% yield) was found if the reactions were performed without triethylamine, even under refluxed conditions for a prolonged period of time (e.g., 3 days).

Scheme I Ligand synthesis

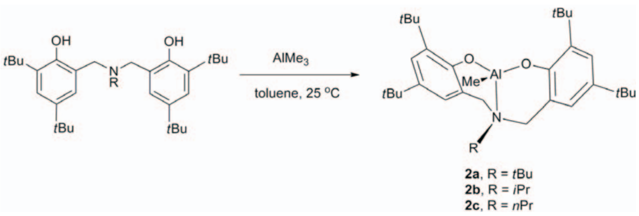


Compounds H$_2$[**1a**] and H$_2$[**1b**] were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, combustion analysis, and X-ray crystallography. As anticipated for pyramidal amine derivatives, these molecules are Cs-symmetric in solutions on the NMR timescale with two phenol moieties being chemically equivalent. The benzylic methylene protons show a singlet resonance at ca. 3.5 ppm and the phenol hydroxyl protons at ca. 8.2 ppm. Colorless crystals of H$_2$[**1a**], H$_2$[**1b**] and H$_2$[**1c**] suitable for X-ray diffraction analysis were grown from a concentrated acetonitrile solution at -15 °C. The molecular structures of these amine biphenol derivatives are depicted in Figures S1-S3 (see supplementary material). Compounds H$_2$[**1a**] and H$_2$[**1b**] are structurally similar in the solid state, containing both intramolecular and intermolecular hydrogen bonding involving hydroxyl with amine nitrogen and co-crystallized acetonitrile nitrogen, respectively. The *n*-propyl substituted H$_2$[**1c**], however, does not co-crystallize with acetonitrile, thereby having solely intramolecular hydrogen bonding. Neither bond distances nor angles are exceptional.

Synthesis and characterization of aluminum complexes

No reaction was found for Al(O*i*Pr)$_3$ with H$_2$[**1a**], H$_2$[**1b**] or H$_2$[**1c**] in C_6D_6 at 70 ºC for 2 days on the basis of ^{1}H NMR studies.[67] Addition of one equiv of trimethylaluminum to a toluene solution of H$_2$[**1a**], H$_2$[**1b**] or H$_2$[**1c**] at 25 °C affords colorless crystalline aluminum methyl complexes **2a**, **2b** and **2c**, respectively (Scheme II). Compounds **2a** and **2b** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, combustion analysis, and X-ray crystallography. Figures 2 and 3 depict the molecular structures of these complexes. Table 1 summarizes their selected

Scheme II Synthesis of aluminum complexes



bond distances and angles, in comparison with those of **2c**.[42] As depicted, these complexes are mononuclear, four-coordinate species whose coordination geometry is best described as distorted tetrahedral. Though the bond distances and angles about aluminum are all unexceptional and comparable with other pseudo-tetrahedral organoaluminum complexes ligated with phenolates or amines,[42,68-72] the Al-N bond length of **2a** is slightly longer than those of **2b** and **2c**, likely reflective of the steric discrepancy of these *N*-alkyl substituents. The solution NMR data of **2a** and **2b** are all consistent with a structure having Cs symmetry. In the ^{1}H NMR spectra, the benzylic methylene resonances appear as two doublets, contrasting sharply with what is found for H_2[**1a**] and H_2[**1b**] but clearly indicative of their diastereotopic nature as a consequence of amine coordination to aluminum. Variable temperature ^{1}H NMR studies of **2a**, **2b** and **2c** (in toluene-d_8) revealed that the two doublet resonances ascribed to the benzylic methylene protons do not coalesce even at 80 ºC, a result that is suggestive of the non-dissociative nature of the amine nitrogen donor in these organoaluminum complexes. These complexes are all thermally stable, remaining intact upon heating to 80 ºC for 24 hours as indicated by ^{1}H NMR studies (30 mM in toluene-d_8).

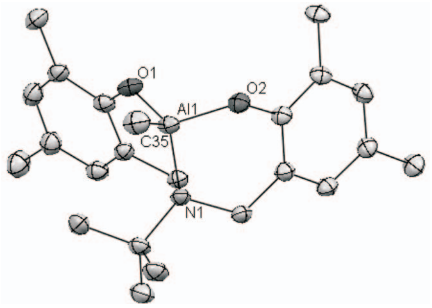


Fig. 2. Molecular structures of [*t*Bu-ONO]AlMe (**2a**) with thermal ellipsoids drawn at the 35% probability level. All methyl groups in aryl *tert*-butyl are omitted for clarity.

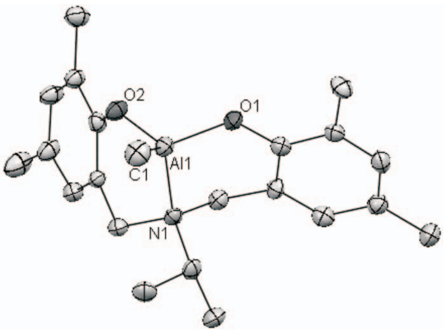


Fig. 3. Molecular structures of [*i*Pr-ONO]AlMe (**2b**) with thermal ellipsoids drawn at the 35% probability level. All methyl groups in aryl *tert*-butyl are omitted for clarity.

ROP catalysis

The polymerization activities of **2a**, **2b**, and **2c** with ε-CL were investigated. Table 2 summarizes the polymerization results. To establish parallel comparison with literature data, we chose to examine the activities of these aluminum complexes with conditions similar to those reported previously.[42] Both **2b** and **2c** complete ROP in 20 minutes with 100 equiv of ε-CL at 50 ºC in the presence of one equiv of benzyl alcohol, producing PCLs with extremely narrow molecular weight distributions (entries 1[73] and 4, respectively) whereas **2a** reacts much slower (entry 11, lower conversion with extended reaction time) to produce low molecular weight oligomers, highlighting the profound *N*-substituent effect of these complexes on ROP rates. Elevating the polymerization temperature to 80 ºC effectively increases the catalytic efficiency of **2a** but at the expense of an increased PDI value (entry 12), suggesting possibly the occurrence of undesired transesterification reactions. The *n*-propyl substituted **2c** appears to give well-defined PCLs at monomer-to-catalyst ratios up to 300.[42] With more monomer presence, the PDIs of PCLs increase appreciably (entry 2). In contrast, the isopropyl substituted **2b** polymerizes ε-CL in a much more controlled manner under similar conditions (entry 7). The PDI of PCLs prepared by **2b** is significantly lower than that by **2c** though the measured *M*n’s are virtually identical (entry 7 versus 2). More significantly, extremely low PDIs could also be obtained with extremely high monomer-to-catalyst ratios (entry 9) though a much more diluted solution is required to diminish inevitably increased viscosity due to the formation of high molecular weight polymers. Catalyst **2b** thus outperforms **2c** in production of well-defined polymers with a wider range of molecular weights.

Similar to **2c**,[42] complex **2b** is also a well-defined ROP catalyst for ε-CL. Notably, the *M*n values increase lin-

Table 1. Selected bond distances (Å) and angles (°) for [*t*Bu-ONO]AlMe (**2a**), [*i*Pr-ONO]AlMe (**2b**), and [*n*Pr-ONO]AlMe (**2c**)

Compound	**2a**	**2b**	**2c**(A) [a]	**2c**(B) [a]	**2c**(C) [a]
Al-C	1.947(3)	1.934(7)	1.930(7)	1.925(6)	1.939(6)
Al-O	1.739(2)	1.739(5)	1.713(4)	1.736(3)	1.720(4)
	1.740(2)	1.734(5)	1.736(3)	1.734(3)	1.724(3)
Al-N	2.022(2)	1.998(6)	1.985(4)	1.988(4)	1.991(3)
O-Al-O	112.07(10)	113.2(2)	114.23(19)	114.60(18)	114.63(19)
O-Al-N	98.71(10)	98.1(2)	99.79(18)	99.25(18)	99.00(18)
	98.27(9)	99.1(2)	99.58(16)	99.79(16)	100.15(16)
C-Al-N	123.69(11)	120.1(3)	116.0(2)	115.2(2)	115.5(2)
C-Al-O	113.88(13)	112.4(3)	115.3(2)	111.7(2)	115.4(2)
	109.06(13)	112.7(3)	110.6(2)	114.9(2)	110.7(2)

[a] Data for **2c** were selected from reference 42, representing three independent molecules found in the asymmetric unit cell.

Table 2. ROP of ε-CL by catalysts **2a**, **2b**, and **2c** in the presence of benzyl alcohol initiator [a]

Entry	cat.	[ε-CL]/[cat]/[I]	temp (°C)	time (min)	conv (%)[b]	*M*n (calc, kg mol^{-1}) [c]	*M*n (exp, kg mol^{-1}) [d]	corrected *M*n (exp, kg mol^{-1}) [e]	PDI[d]
1	**2c**	100/1/1	50	20	99	11.4	16.8	9.4	1.06
2	**2c**	400/1/1	50	35	99	45.3	58.0	32.5	1.32
3	**2b**	50/1/1	50	20	99	5.8	9.5	5.3	1.08
4	**2b**	100/1/1	50	20	99	11.4	13.9	7.8	1.07
5	**2b**	200/1/1	50	20	99	22.7	23.8	13.3	1.05
6	**2b**	300/1/1	50	30	99	34.0	37.8	21.2	1.06
7	**2b**	400/1/1	50	35	99	45.3	58.8	32.9	1.05
8	**2b**	1000/1/1	50	70	99	113.1	88.9	49.8	1.28
9[f]	**2b**	1000/1/1	50	120	78	89.1	82.3	46.1	1.04
10	**2b**	100(100)/1/1	50	20	99	11.4	13.7	7.7	1.06
				(20)	(99)	(22.7)	(27.3)	(15.3)	(1.05)
11	**2a**	100/1/1	50	840	33	3.9	N/A	N/A	N/A
12	**2a**	100/1/1	80	840	99	11.4	18.9	10.6	1.28
13	**2b**	100/1/0	50	20	44	5.0	61.0	34.2	1.10
14	**2b**	200/1/4	50	15	99	5.8	10.1	5.7	1.08
15	**2b**	400/1/8	50	15	99	5.8	11.2	6.3	1.08
16	$AlMe_3$	100/1/1	50	20	27	3.2	4.5	2.5	1.15
17	$AlMe_3$	100/1/0	50	20	<1	<0.1	N/A	N/A	N/A

[a] Unless otherwise noted, $[cat.]_0$ = 8.3 mM in 3 mL toluene. [b] Determined by ^1H NMR analysis. [c] Calculated from {fw of ε-CL × ($[ε\text{-}CL]_0/([cat.]_0 \cdot [I]_o)$) × conversion} + fw of BnOH, assuming one propagating chain per aluminum atom. [d] Measured by GPC in THF, calibrated with polystyrene standards. [e] Multiplied by a factor of 0.56. [73,74] [f] $[cat.]_0$ = 1.7 mM in 15 mL toluene.

early with increasing monomer consumed to catalyst ratios while keeping consistently low PDIs (Figure 4). Significantly, the propagating intermediates remain active even after complete consumption of monomers; upon addition of a second batch of monomers, the propagation resumes to produce PCLs with controlled *M*n and PDI values (entry 10).

The roles of benzyl alcohol were also investigated. Its participation in catalysis is evidently demonstrated (entries 4 and 13). Without benzyl alcohol, **2b** reacts with ε-CL at a much slower rate, producing PCLs with molecular weights much higher than the expected values, a result that is suggestive of the involvement of only a portion of **2b** in catalysis and the reactivity discrepancy between Al-Me and Al-O(propagating) functionalities. Once initiated, the ROP catalysis takes place at a much faster rate for Al-O(propagating) than for Al-Me. In the presence of benzyl alcohol, the catalysis was effectively initiated by the presumed forma-

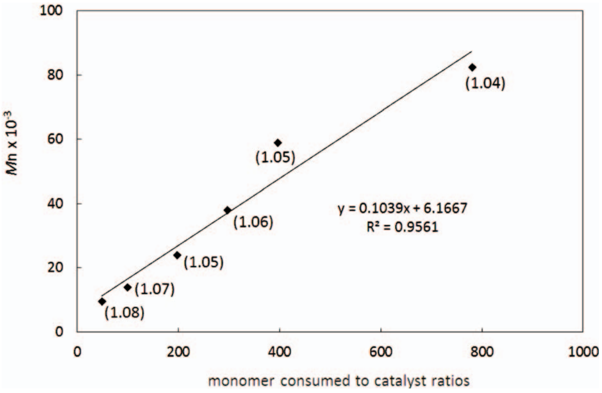


Fig. 4. Plot of *M*n of PCLs versus monomer consumed to catalyst ratios (entries 3-7 and 9 in Table 2). The corresponding PDI values are indicated in parentheses.

tion of reactive [**1b**]AlOBn, produced from alcoholysis of **2b** with HOBn. End group analysis on PCLs by ^{1}H NMR spectroscopy (Figure S4) clearly confirms the presence of the benzyl oxide functionality. Addition of more than one equiv of benzyl alcohol (entries 14 and 15) led to a decrease in molecular weights (in comparison with entries 5 and 7, respectively) that, however, are in good agreement with what is anticipated for propagating intermediates to undergo chain transfer reactions with benzyl alcohol at a statistical frequency corresponding to the equiv of added benzyl alcohol. Benzyl alcohol thus also functions as an efficient chain transfer reagent. The measured *M*n and PDI values in entries 14 and 15 are well comparable to those of entry 3; the low PDI of 1.08 in the former strongly suggests that both initiation and chain transfer steps proceed in a controlled fashion.

The amine biphenolate ligands also play an important role in this ROP catalysis. Entries 16 and 17 summarize the reactivity of trimethylaluminum with and without benzyl alcohol, respectively. With the coordination of the amine biphenolate ligand, **2b** (entry 4) polymerizes ε-CL apparently more efficiently than $AlMe_3$ (entry 16) under similar conditions. Both **2b** and **2c** catalyze ROP of ε-CL following pseudo-first order kinetics (Figure S5)[74] with the latter being about 2.86(2) times faster than the former. In view of the comparable electronic properties of isopropyl and *n*-propyl, we suggest that the discrepancy in catalysis rates is a consequence of the steric influence of these *N*-substituents. This result is also consistent with the much slower ROP rates found for **2a**.

It has been documented that the ^{27}Al chemical shifts of neutral aluminum complexes correlate well with their coordination number.[75] The ^{27}Al{^{1}H} NMR spectrum of **2b** in toluene-d_8 exhibits a broad singlet resonance at 150 ppm with the peak width at half height ($\Delta\nu_{1/2}$) of 11186 Hz. These values are within the expected region for a four-coordinate organoaluminum species. Similar chemical shifts were also found for Al_2Me_6 (156 ppm),[76] $AlEt_3$(thiophene) (154 ppm),[77] (*i*Pr_2-ATI)$AlMe_2$ (154 ppm, *i*Pr_2-ATI = *N*,*N*′-diisopropylaminotroponiminate),[78] (*i*Pr-NP)$AlMe_2$ (151 ppm, *i*Pr-NP = 2,6-*i*$Pr_2C_6H_3N(C_6H_4$-2-PPh_2)),[79] and (*i*Pr-NO)$AlEt_2$ (142 ppm, *i*Pr-NO = 2,6-*i*$Pr_2C_6H_3N(C_6H_4$-2-P(O)Ph_2)),[12] etc. In the presence of one equiv of ε-CL, the ^{27}Al chemical shift of **2b** moves upfield to 129 ppm ($\Delta\nu_{1/2}$ = 11157 Hz), consistent with an increase in coordination number for a neutral organo-aluminum complex.[75,80] The ^{1}H NMR spectrum of the same solution reveals the presence of an aluminum-bound methyl group instead of ketone methyl, indicating no ROP reaction occurs during these NMR acquisitions. The upfield change of the observed ^{27}Al chemical shift of **2b** upon addition of ε-CL is thus ascribable to the coordination of the heterocyclic monomer to aluminum, presumably via carbonyl oxygen atom. This hypothesis is consistent with the X-ray structure of an aluminum ε-CL complex supported by a biphenolate ligand as elucidated by Lewiński et al.[81] On the basis of the fact that the ROP rates of **2a-c** are governed by the *N*-substituents, we propose that the monomer coordination proceeds predominantly, though perhaps not exclusively, on the two X-N-O (X = C for **2a-c** or X = alkoxide for propagating intermediates) faces of the pseudo-tetrahedral catalysts. Attempts to corroborate this proposal are currently underway with unsymmetrically substituted $[ONO]^{2-}$ ligated complexes. We note that similar justifications have been proved for Schrock-type olefin metathesis catalysts.[82,83]

CONCLUSIONS

We have demonstrated that the identity of *N*-alkyl substituents in the aluminum complexes of amine biphenolate ligands has substantial impacts on both polymerization rates and polymer molecular weight distributions in the catalytic ROP of ε-CL. Though Mannich condensation does not afford effectively H_2[**1a**] or H_2[**1b**] carrying a tertiary or secondary *N*-substituted alkyl, respectively, nucleophilic substitution of the corresponding benzyl bromide with benzyl amines proves successful with the involvement of appropriate bases. Controlled experiments suggest that the participation of both potassium carbonate and triethylamine is critical under the conditions investigated. Similar to **2c** that contains an *n*-propyl substituent at the nitrogen donor, aluminum methyl complexes **2a** and **2b** are both four-coordinate, pseudo-tetrahedral in the solid state. Though coordination geometry, bond distances and angles about aluminum in these organoaluminum complexes are similar, their ROP rates with ε-CL differ apparently from one to another as a consequence of steric influence arising from the *N*-substituents. In spite of exhibiting similar controlled polymerization characteristics, complex **2b** appears a superior catalyst to **2c** in view of producing well-defined PCLs with narrower molecular weight distributions in a much wider range of molecular weights. Studies directed to delineate the reactivity of metal complexes of these amine biphenolate ligands involving other main group and transition metals are currently underway.

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SUPPLEMENTARY MATERIAL

X-ray crystallographic data for H_2[**1a**], H_2[**1b**], H_2[**1c**], **2a**, **2b**, **2c**, a representative ^{1}H NMR spectrum of PCLs, and semilogarithmic plots of ε-CL conversion with time (employing **2b** and **2c**).

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