

Synthesis, Characterization, and Catalytic Application of Aluminum Anilido-Oxazolate Complexes

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A family of aluminum complexes containing anilido-oxazolate ligands are described. Reactions of five anilido-oxazolate ligand precursors, HNPh^{TriMe}Oxa, HNPh^{DiPr}Oxa, HNPh^{OMe}Oxa, HNPh^{SMe}Oxa, or HNPhOxa, with 1 molar equiv. of AlMe₃ in toluene give the aluminum dimethyl complexes (NArOxa)AlMe₂ [Ar = 2,4,6-trimethylphenyl, (NPh^{TriMe}Oxa)AlMe₂ (**1**); Ar = 2,6-diisopropylphenyl, (NPh^{DiPr}Oxa)AlMe₂ (**2**); Ar = 2-methoxyphenyl, (NPh^{OMe}Oxa)AlMe₂ (**3**);

Ar = 2-methylthiophenyl, (NPh^{SMe}Oxa)AlMe₂ (**4**); Ar = phenyl, (NPhOxa)AlMe₂ (**5**), respectively]. The molecular structures are reported for compounds **1–4**. Their catalytic activities toward the ring-opening polymerization reactions of L-lactide or ϵ -caprolactone in the presence of BnOH are also under investigation.

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Introduction

Poly(ϵ -caprolactone) (PCL) and poly(lactide) (PLA), as well as their copolymers, are interesting candidates in both biocompatible and biodegradable polymers, which have a wide range of applications, such as tissue engineering, drug delivery, and environmentally friendly wrapping materials.^[1] One of the promising methodologies for the syntheses of these polymers is ring-opening polymerization that employs metal-based initiator/catalysts. Therefore metal complexes bearing auxiliary ligands as initiators/catalysts for ring-opening polymerization have attracted great interest, mainly because of their promising activities and great success in preparing the well-defined polyesters.^[1,2]

β -Diketiminato ligands, which normally act as hard monoanionic ancillary ligands,^[3] have received increasing attention for their successful application in ring-opening polymerization reactions.^[1,2,4] Therefore some metal complexes bearing structurally related ligands with similar chelating systems and isoelectronic features were synthesized and some of their catalytic activities in ring-opening polymerization have been examined.^[5] According to our previous catalytic studies on the zinc anilido-oxazolate complexes^[5k] and the catalytic activities demonstrated by some aluminum complexes bearing β -diketiminato or anilido-imino ligands in ring-opening polymerization,^[4,5k–5m] aluminum anilido-oxazolate complexes are expected to be efficient initiators/catalysts in ring-opening polymerization. In this paper, several ligand precursors and their aluminum

dimethyl complexes have been synthesized. Their catalytic activities in ring-opening polymerization are also investigated.

Results and Discussion

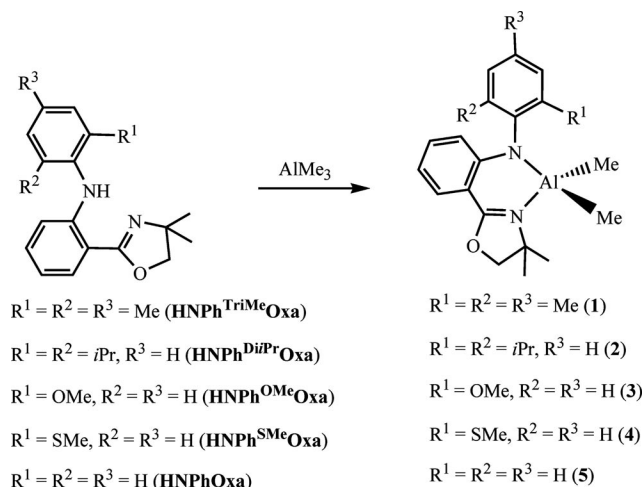
Synthesis and Characterization

Preparation of ligand precursors HNPh^{SMe}Oxa and HNPhOxa was straightforward, using palladium-catalyzed amination^[6] of 2-(2-bromophenyl)-4,4-dimethyl-2-oxazoline^[7a] (for HNPh^{SMe}Oxa) or 2-(4,4-dimethyl-4,5-dihydro-oxazo-2-yl)-phenylamine^[7b] (for HNPhOxa) with 2-methylthioaniline (for HNPh^{SMe}Oxa) or iodobenzene (for HNPhOxa) in the presence of Pd(OAc)₂, bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos), and sodium *tert*-butoxide in refluxing toluene to afford the target compounds in high yield.^[8] Compounds HNPh^{SMe}Oxa and HNPhOxa are characterized by NMR spectroscopy as well as elemental analyses.

Complexes **1–5** were synthesized by an alkane elimination reaction in moderate to high yields. Treatment of ligand precursors HNPh^{TriMe}Oxa,^[5k] HNPh^{DiPr}Oxa,^[5k] HNPh^{OMe}Oxa,^[5k] HNPh^{SMe}Oxa, or HNPhOxa with AlMe₃ in toluene yields the desired anilido-oxazolate aluminum dimethyl complexes **1–5**. Complexes **1–5** were all characterized by NMR spectroscopy and elemental analyses. The disappearance of the N–H signal of the ligand precursors and the appearance of the resonance for protons of methyl groups in the high-field region are consistent with the structures proposed in Scheme 1. Because of the symmetric environment around the metal center, one singlet corresponding to two methyl groups on the metal center

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and two singlets corresponding to two methyl groups and two protons of the methylene group on the oxazoline part were observed for **1**, **2**, and **5**. Splitting peaks were found around these regions because of the lower symmetry resulting from the substituents on the anilido groups of the ligands for **3** and **4**. However, only one singlet for the methyl group on the metal center was observed for **3**.



Scheme 1.

Suitable crystals for structural determination of **1–4** were obtained from concentrated hexane solution. Their molecular structures are depicted in Figures 1, 2, 3, and 4. The structures of **1–4** reveal that the Al centers adopt a distorted tetrahedral geometry with the metal center chelated by two nitrogen donor atoms of the anilido-oxazoline ligands and two methyl groups, even though the ligands bear potentially dative functionalities. Basically, compounds **1–4** are

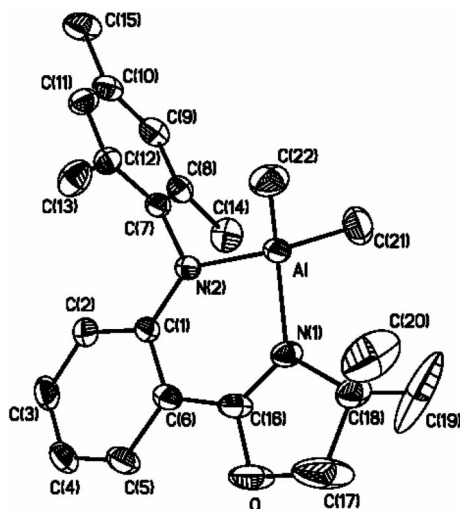


Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and bond angles [°]: Al–N(2), 1.8868(19); Al–N(1), 1.923(2); Al–C(21), 1.963(3); Al–C(22), 1.961(3); N(1)–C(16), 1.298(3); N(1)–C(18), 1.516(3); N(2)–C(1), 1.362(3); N(2)–C(7), 1.452(3); N(2)–Al–N(1), 93.66(8); N(2)–Al–C(22), 113.97(11); N(1)–Al–C(22), 109.13(13); N(2)–Al–C(21), 115.25(13); N(1)–Al–C(21), 110.06(13); C(22)–Al–C(21), 112.95(17). Hydrogen atoms on carbon atoms omitted for clarity.

quite similar with different substituents on the anilido groups. The Al–N_{amido} bond lengths [1.8868(19) Å for **1**; 1.8904(17) Å for **2**; 1.8864(18) Å for **3**; 1.8937(16) Å for **4**] are shorter than the Al–N_{oxazoline} bond lengths [1.923(2) Å for **1**; 1.9369(18) Å for **2**; 1.9370(16) Å for **3**; 1.9348(16) Å for **4**], which might result from the π -donation ability of the anionic amido nitrogen.^[9] The bond lengths of Al–N_{amido} and Al–N_{oxazoline} are comparable to those [1.870(4)–1.890(3) Å for Al–N_{amido}; 1.917(5)–1.963(1) Å for Al–

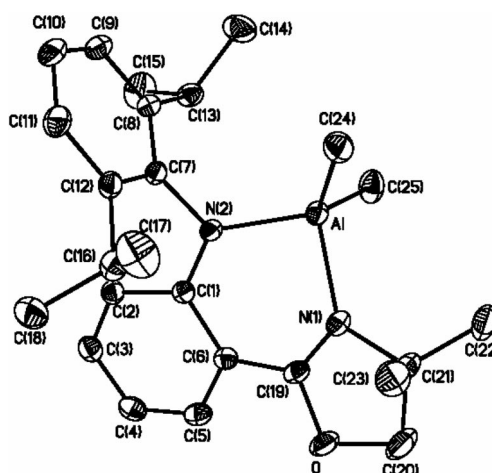


Figure 2. Molecular structure of **2**. Selected bond lengths [Å] and bond angles [°]: Al–N(2), 1.8904(17); Al–N(1), 1.9369(18); Al–C(24), 1.950(2); Al–C(25), 1.972(2); N(1)–C(19), 1.297(3); N(1)–C(21), 1.498(3); N(2)–C(1), 1.367(2); N(2)–C(7), 1.442(2); N(2)–Al–N(1), 92.65(8); N(2)–Al–C(24), 111.14(9); N(1)–Al–C(24), 113.67(10); N(2)–Al–C(25), 115.59(10); N(1)–Al–C(25), 104.54(10); C(24)–Al–C(25), 116.59(12). Hydrogen atoms on carbon atoms omitted for clarity.

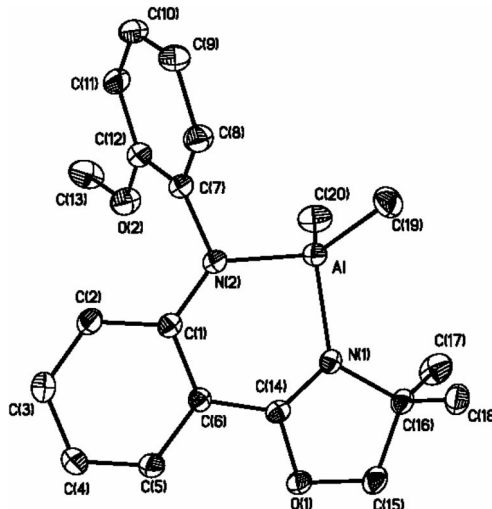


Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and bond angles [°]: Al–N(2), 1.8864(18); Al–N(1), 1.9370(16); Al–C(19), 1.974(2); Al–C(20), 1.958(3); N(1)–C(14), 1.307(2); N(1)–C(16), 1.502(3); N(2)–C(1), 1.365(2); N(2)–C(7), 1.449(2); N(2)–Al–N(1), 93.85(7); N(2)–Al–C(20), 111.70(12); N(1)–Al–C(20), 111.06(9); N(2)–Al–C(19), 112.46(10); N(1)–Al–C(19), 110.33(11); C(20)–Al–C(19), 115.43(13). Hydrogen atoms on carbon atoms omitted for clarity.

N_{imine}] found in aluminum anilido-imine complexes.^[5m,9] The N–Al–N angles [93.66(8)° for **1**; 92.65(8)° for **2**; 93.85(7)° for **3**; 93.88(7)° for **4**] in these complexes are close to those [93.79(5)–95.51(18)°] found in aluminum anilido-imine complexes.^[5m,9]

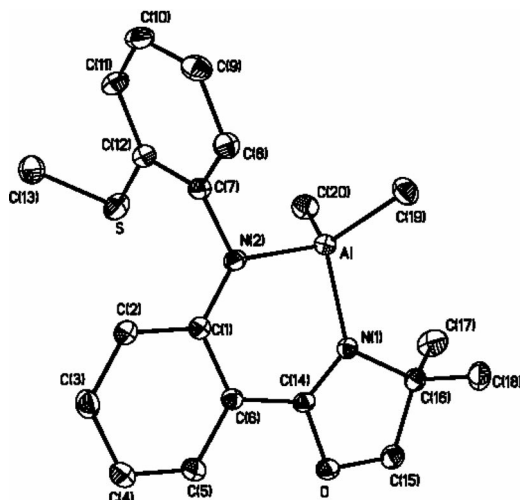


Figure 4. Molecular structure of **4**. Selected bond lengths [Å] and bond angles [°]: Al–N(2), 1.8937(16); Al–N(1), 1.9348(16); Al–C(19), 1.962(2); Al–C(20), 1.957(2); N(1)–C(14), 1.294(2); N(1)–C(16), 1.500(2); N(2)–C(1), 1.363(3); N(2)–C(7), 1.441(2); N(2)–Al–N(1), 93.88(7); N(2)–Al–C(20), 111.44(9); N(1)–Al–C(20), 110.82(9); N(2)–Al–C(19), 113.27(8); N(1)–Al–C(19), 109.95(9); C(20)–Al–C(19), 115.43(10). Hydrogen atoms on carbon atoms omitted for clarity.

Polymerization Studies

Several aluminum anilido-imino^[5l,5m] or aluminum β -diketiminate^[4] complexes are known as efficient initiators/catalysts in ring-opening polymerization (ROP); the structurally related aluminum complexes **1–5** were expected to work as catalysts toward the ROP of cyclic esters. The ring-open-

ing polymerization of L-lactide employing **1–5** as catalysts is examined under dry nitrogen. Representative results are collected in Table 1. The optimal conditions were found to be toluene (10 mL) at 80 °C in the presence of benzyl alcohol after several trials on running polymerization with CH_2Cl_2 , THF, and toluene using **3** as the catalyst (entries 1–5). The same conditions were applied to examine the catalytic activities of **1**, **2**, **4**, and **5** (entries 6–10). Experimental results show compounds **3–5** are efficient catalysts for the polymerization of L-lactide. However, only a trace amount of polymer can be isolated using **1** or **2** as a catalyst, implying the steric effect resulting from the anilido group prevents the metal center from the coordination of monomers. The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) exhibited by **3** (entries 8, 11–13) implies the “living” character of the polymerization process. Representative results initiated by **3** are demonstrated in Figure 5 (entries 8, 11–13). This controlled behavior is further confirmed by the resumption experiment (entry 14). The “immortal” character was examined using four equivalent ratios ($\text{on } [M]_0/[Al]_0$) of benzyl alcohol as the chain transfer agent (entry 15). The M_n of the polymer in each case became half of that found in the reaction with the addition of two equivalent ratios of benzyl alcohol. The end-group analysis is demonstrated by the ^1H NMR spectrum of the polymer produced from L-lactide and **3** ($[M]_0/[Al]_0 = 50$), as shown in Figure 6. Peaks are similar to those found on the ^1H NMR spectra of polymers produced by $[\text{Li}]/\text{BnOH}$ initiator^[10] and are assignable to the corresponding protons in the proposed structure. Compound **3** also demonstrates catalytic activity using isopropyl alcohol (IPA) as initiator under the same conditions (entry 16).

Complexes **1–5** were also investigated regarding their catalytic behavior in the ROP of ϵ -caprolactone. Representative results are collected in Table 2. The catalytic activities were proved to be affected by the steric effect of the substituents on the 2,6-position of the anilido group again by

Table 1. Polymerization of L-lactide using compounds **1–5** as catalysts in toluene at 80 °C if not otherwise stated.^[a]

Entry	Catalyst	$\{[M]_0/[Al]_0\}:[\text{BnOH}]$	Time [h]	M_n (obsd.) ^[b]	M_n (calcd.) ^[c]	% Conv. ^[d]	% Yield ^[e]	M_w/M_n ^[f]
1	3	100:0	24	–	–	trace	–	–
2 ^[f]	3	100:2	44	–	–	trace	–	–
3 ^[g]	3	100:2	24	–	–	trace	–	–
4 ^[g]	3	100:2	48	–	–	17	–	–
5 ^[h]	3	100:2	48	–	–	29	–	–
6	1	100:2	24	–	–	trace	–	–
7	2	100:2	24	–	–	trace	–	–
8	3	100:2	24	13000	6900	95	76	1.07
9	4	100:2	24	11900	6400	88	76	1.07
10	5	100:2	24	13000	6900	95	71	1.30
11	3	200:2	24	25300	14200	98	83	1.13
12	3	300:2	24	42300	20000	92	81	1.04
13	3	400:2	24	52800	27200	94	87	1.10
14	3	100 (100):2	24 (24)	14500	9600	95 (66)	53	1.08
15	3	200:4	24	9900	7100	97	62	1.04
16	3	100:2 (IPA)	24	13800	6900	95	80	1.15

[a] In 10 mL. [b] Obtained from GPC analysis. [c] Calculated from $[M(\text{lactide})] \times [M]_0/[Al]_0 \times \text{conversion yield}/([\text{BnOH}]_{\text{eq}}) + M(\text{BnOH})$. [d] Obtained from ^1H NMR analysis. [e] Isolated yield. [f] Dichloromethane, $T = 26$ °C. [g] THF, $T = 50$ °C. [h] $T = 50$ °C.

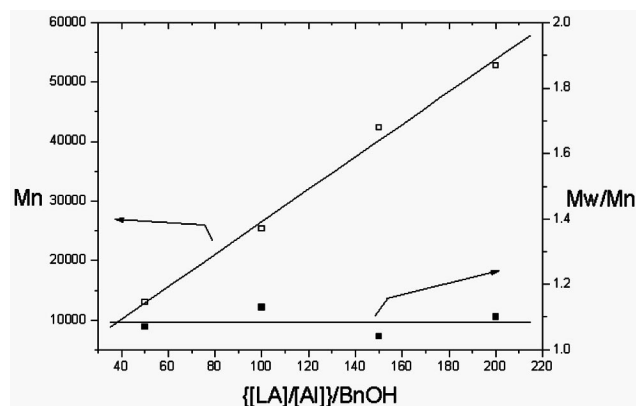


Figure 5. Polymerization of L-lactide initiated by **3** in toluene at 80 °C.

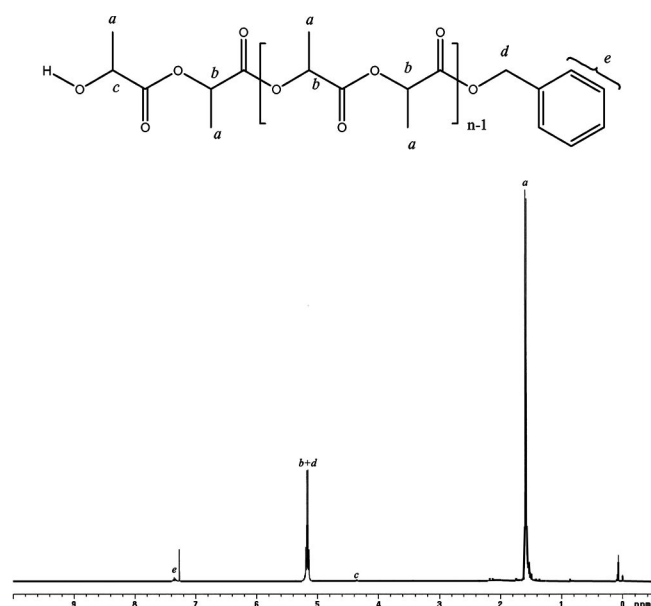


Figure 6. ^1H NMR spectrum of PLA-50 initiated by **3** in toluene.

using complexes **1–2** as catalysts (entries 1–2). Experimental results indicate that complexes **3–5** have higher activities in catalyzing ROP of ϵ -caprolactone than in catalyzing ROP of L-lactide (entries 3–6). This might result from the chelate effect caused by the opened monomer.^[11] Compound **3** also demonstrates better activities than the other two at 50 °C and 80 °C. The plot of Mn versus $([\text{M}]_0/[\text{I}]_0)$ demonstrated by those data initiated by **3** exhibits a linear relationship indicating the “living” character of the polymerization process, as shown in Figure 7 (entries 3, 7–9). A similar “living” character is seen in the polymerization reactions initiated by **3** (entries 4, 12–14) at 80 °C within 40 min, as shown in Figure 8. Compound **3** also demonstrates “immortal” character by using four equivalent ratios (on $[\text{M}]_0/[\text{Al}]_0$) of benzyl alcohol as the chain transfer agent at 50 °C and 80 °C (entries 10 and 15). The Mn of the polymer in each case became half of that found in the reaction with the addition of two equivalent ratios of benzyl alcohol. The ^1H NMR spectrum of PCL-50 prepared from ϵ -caprolactone and **3** ($[\text{M}]_0/[\text{Al}]_0 = 50$) for the chain-end studies is shown in Figure 9. Peaks are assignable to the corresponding protons in the proposed structure,^[51,12] indicating the metal benzyl oxide complex might form first, followed by the ring cleavage of the acyl-oxygen bond to form a metal alkoxide intermediate, which further reacts with excess lactones to yield polyesters.^[51,12] Poor activity was observed by using isopropyl alcohol (IPA) as initiator under the same conditions (entry 11).

In conclusion, a family of aluminum dimethyl complexes containing anilido-oxazolinato ligands have been prepared and fully characterized. Complexes **3–5** were employed as catalysts for the ring-opening polymerization of L-lactide and ϵ -caprolactone in the presence of benzyl alcohol. They all demonstrate efficient activities for the controlled polymerization of L-lactide and ϵ -caprolactone with both living and immortal characters. However, the poor performance of complexes **1–2** indicates bulky substituents on the 2,6-position of the anilido group might strongly affect the cata-

Table 2. Polymerization of ϵ -caprolactone using compounds **1–5** as catalysts at 50 °C.^[a]

Entry	Catalyst	$\{[\text{M}]_0/[\text{Al}]_0\}:\text{[BnOH]}$	Time [min]	Mn (obsd.) ^[b]	Mn (calcd.) ^[c]	% Conv. ^[d]	% Yield ^[e]	Mw/Mn ^[b]
1	1	100:2	120	—	—	trace	—	—
2	2	100:2	120	—	—	trace	—	—
3	3	100:2	120	9200	5500	96	88	1.06
4 ^[f]	3	100:2	9	13500	5500	98	97	1.08
5 ^[f]	4	100:2	75	11600	5500	99	98	1.09
6	5	100:2	120	13000	5500	95	94	1.06
7	3	200:2	240	16800	11000	96	96	1.07
8	3	300:2	330	26600	16700	97	87	1.12
9	3	400:2	420	31300	22200	97	87	1.13
10	3	200:4	120	8200	5400	95	77	1.05
11	3	100:2(IPA)	120	—	—	14	—	—
12 ^[f]	3	200:2	12	23300	10900	95	95	1.08
13 ^[f]	3	300:2	15	31200	16500	96	89	1.11
14 ^[f]	3	400:2	40	45900	22500	96	95	1.16
15 ^[f]	3	200:4	10	11200	5600	97	89	1.07

[a] In toluene (15 mL). [b] Obtained from GPC analysis. [c] Calculated from $[\text{M}(\text{caprolactone})] \times [\text{M}]_0/[\text{Al}]_0 \times \text{conversion yield}/([\text{BnOH}]_{\text{eq}}) + \text{M}(\text{BnOH})$. [d] Obtained from ^1H NMR analysis. [e] Isolated yield. [f] $T = 80$ °C.

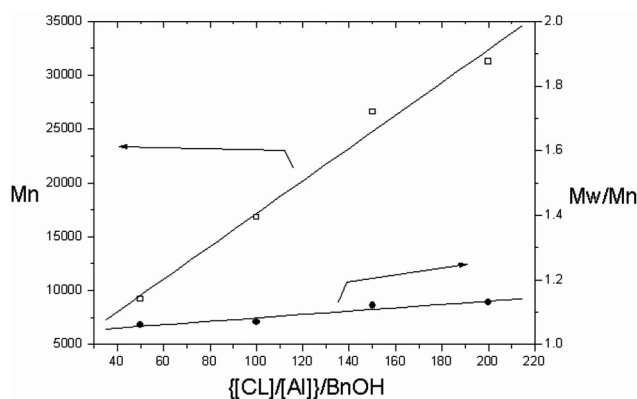


Figure 7. Polymerization of ϵ -caprolactone initiated by **3** in toluene at 50 °C.

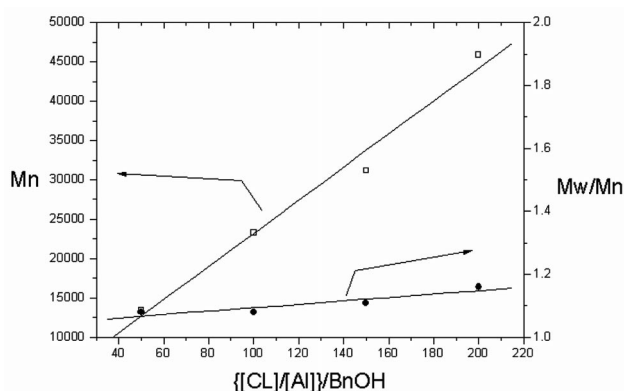


Figure 8. Polymerization of ϵ -caprolactone initiated by **3** in toluene at 80 °C.

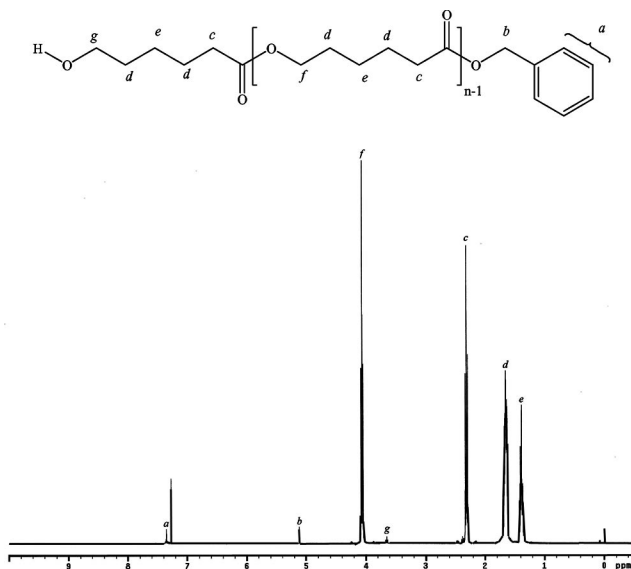


Figure 9. ^1H NMR spectrum of PCL-50 initiated by **3** in toluene.

lytic activities of ring-opening polymerization in this system. Preliminary studies on fine-tuning of ligand precursors and further application of metal complexes to the catalytic reactions are currently underway.

Experimental Section

General: All manipulations were carried out under dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried with molecular sieves.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with either Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in $[\text{D}]\text{chloroform}$ at ambient temperature unless stated otherwise, referenced internally to the residual solvent peak, and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by an Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard. Melting points were measured under dry dinitrogen using a MEL-TEMP II instrument and were not corrected.

$\text{Pd}(\text{OAc})_2$ (Acros), AlMe_3 (Aldrich, 2.0 M in toluene), NaOtBu (TCI), 2-methylthioaniline (Lancaster), L-proline (Lancaster), K_3PO_4 (Alfa), iodobenzene (Acros), and bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos, Strem) were used as supplied. 2-(2-Bromophenyl)-4,4-dimethyl-2-oxazoline,^[7a] 2-(4,4-dimethyl-4,5-dihydro-oxazol-2-yl)-phenylamine,^[7b] $\text{HNPh}^{\text{TriMe}}\text{Oxa}$,^[5k] $\text{HNPh}^{\text{DiPr}}\text{Oxa}$,^[5k] and $\text{HNPh}^{\text{OMe}}\text{Oxa}$ ^[5k] were prepared according to the literature. Benzyl alcohol was dried with magnesium sulfate and distilled before use. ϵ -Caprolactone was dried with magnesium sulfate and distilled under reduced pressure. L-Lactide was recrystallized from toluene prior to use.

Preparations

$\text{HNPh}^{\text{SMc}}\text{Oxa}$: Toluene (3 mL) was added to a flask containing 2-(2-bromophenyl)-4,4-dimethyl-2-oxazoline (0.61 g, 2.4 mmol), NaOtBu (0.27 g, 3.4 mmol), bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos, 0.065 g, 0.072 mmol), $\text{Pd}(\text{OAc})_2$ (0.018 g, 0.08 mmol), and 2-methylthioaniline (0.26 mL, 3.0 mmol) at room temperature. The reaction mixture was refluxed for five days. All the volatiles were pumped off and the residue was extracted with ethyl acetate (5 mL). Crude product was purified by column chromatography (hexane/ethyl acetate, 5:1) to afford a yellow solid; yield 0.52 g, 69%. ^1H NMR (600 MHz): δ = 1.40 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 2.43 (s, 3 H, SCH_3), 4.04 (s, 2 H, CH_2), 6.76 (m, 1 H, CH-Ph), 7.08 (m, 1 H, CH-Ph), 7.19 (m, CH-Ph , 2H overlap), 7.24 (m, 1 H, CH-Ph), 7.36 (m, 1 H, CH-Ph), 7.47 (m, 1 H, CH-Ph), 7.81 (m, 1 H, CH-Ph), 10.54 (br., 1 H, NH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz): δ = 16.1 (s, SCH_3), 28.5 [s, $\text{C}(\text{CH}_3)_2$], 67.9 [s, $\text{C}(\text{CH}_3)_2$], 77.4 (s, CH_2), 113.1, 117.0, 122.3, 123.7, 126.0, 128.6, 129.7, 131.6 (s, CH-Ph), 110.9, 132.1, 139.9, 145.5, 161.8 (C_{quat}) ppm. $\text{C}_{18}\text{H}_{20}\text{N}_2\text{OS}$ (312.43): calcd. C 69.20, H 6.45, N 8.97; found C 69.57, H 6.59, N 8.77.

HNPhOxa : Toluene (10 mL) was added to a flask containing 2-(4,4-dimethyl-4,5-dihydro-oxazo-2-yl)-phenylamine (0.95 g, 5.0 mmol), NaOtBu (0.67 g, 7.0 mmol), bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos, 0.081 g, 0.1 mmol), $\text{Pd}(\text{OAc})_2$ (0.022 g, 0.1 mmol), and 0.61 mL iodobenzene (5.5 mmol) at room temperature. The reaction mixture was refluxed for six days. All the volatiles were pumped off and the residue was extracted with CH_2Cl_2 (25 mL). Crude product was purified by column chromatography (hexane/ethyl acetate, 40:1) to afford a white solid; yield 1.20 g, 90%. ^1H NMR (400 MHz): δ = 1.38 (s, 6 H, CH_3), 4.02 (s, 2 H, CH_2), 6.74 (m, 1 H, Ph), 7.07 (m, 1 H, Ph), 7.22–7.36 (m, 6 H, Ph), 7.78 (m, 1 H, Ph), 10.44 (s, 1 H, NH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR

(100 MHz): δ = 28.7 (s, CH₃), 67.9 (s, C_{quat}), 77.4 (s, CH₂), 110.5 (s, C_{quat}), 113.0, 116.8, 122.0, 122.8, 129.2, 129.8, 131.8 (s, C₆H₅), 141.5, 145.7, 162.1 (s, C_{quat}) ppm. C₁₇H₁₈N₂O (266.34): calcd. C 76.66, H 6.81, N 10.52; found C 77.02, H 6.88, N 10.58.

(NPh^{TriMe}Oxa)AlMe₂ (1): AlMe₃ (0.35 mL, 2.0 M in toluene, 0.7 mmol) was added to a flask containing HNPh^{TriMe}Oxa (0.15 g, 0.5 mmol) and toluene (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 13 h of stirring, all the volatiles were removed under reduced pressure to afford a yellowish-green solid; yield 0.09 g, 49%; m.p. 149.5–151.1 °C. ¹H NMR (600 MHz): δ = –0.89 (s, 6 H, Al-CH₃), 1.53 [s, 6 H, C(CH₃)₂], 2.05 (s, 6 H, 2,6-CH₃), 2.30 (s, 3 H, 4-CH₃), 4.28 (s, 2 H, CH₂), 6.07 (d, J = 8.4 Hz, 1 H, CH-Ph), 6.43 (m, 1 H, CH-Ph), 6.93 (s, 2 H, 3,5-C₆H₂), 7.06 (m, 1 H, CH-Ph), 7.71 (m, 1 H, CH-Ph) ppm. ¹³C{¹H} NMR (150 MHz): δ = –7.5 (s, Al-CH₃), 18.3 (s, 2,6-CH₃), 20.9 (s, 4-CH₃), 27.5 [s, C(CH₃)₂], 66.2 [s, C(CH₃)₂], 79.2 (s, CH₂), 113.2, 116.0, 129.3, 130.6, 135.4 (s, CH-Ph), 104.6, 134.3, 136.2, 140.3, 156.1, 168.8 (C_{quat}) ppm. C₂₂H₂₉AlN₂O (364.46): calcd. C 72.50, H 8.02, N 7.69; found C 72.84, H 8.44, N 7.56.

(NPh^{DiPr}Oxa)AlMe₂ (2): AlMe₃ (1.4 mL, 2.0 M in toluene, 2.8 mmol) was added to a flask containing HNPh^{DiPr}Oxa (0.71 g, 2 mmol) and toluene (15 mL) at 0 °C. The reaction mixture was warmed to room temperature and reacted for 2.5 h. All the volatiles were removed under reduced pressure to afford a yellowish-green solid; yield 0.66 g, 81%. Suitable crystals of **2** for structural determination were recrystallized from concentrated hexane solution; m.p. 189.0–191.0 °C. ¹H NMR (600 MHz): δ = –0.92 (s, 6 H, Al-CH₃), 0.95 [d, J = 7.2 Hz, 6 H, CH(CH₃)₂], 1.16 [d, J = 6.6 Hz, 6 H, CH(CH₃)₂], 1.54 [s, 6 H, C(CH₃)₂], 3.12 [septet, J = 7.2 Hz, 2 H, CH(CH₃)₂], 4.32 (s, 2 H, CH₂), 6.17 (d, J = 8.4 Hz, 1 H, CH-Ph), 6.47 (m, 1 H, CH-Ph), 7.07 (m, 1 H, CH-Ph), 7.19 (m, 1 H, CH-Ph), 7.22–7.26 (m, 2 H, CH-Ph), 7.70 (m, 1 H, CH-Ph) ppm. ¹³C{¹H} NMR (150 MHz): δ = –8.7 (s, Al-CH₃), 24.4 [s, CH(CH₃)₂], 25.1 [s, CH(CH₃)₂], 27.5 [s, C(CH₃)₂], 27.7 [s, CH(CH₃)₂], 66.0 [s, C(CH₃)₂], 79.4 (s, CH₂), 113.8, 119.0, 124.0, 125.7, 130.4, 134.5 (s, CH-Ph), 105.6, 141.5, 146.6, 157.5, 168.6 (C_{quat}) ppm. C₂₅H₃₅AlN₂O (406.54): calcd. C 73.86, H 8.68, N 6.89; found C 73.62, H 8.90, N 7.00.

(NPh^{OMe}Oxa)AlMe₂ (3): AlMe₃ (2.1 mL, 2.0 M in toluene, 4.2 mmol) was added to a flask containing HNPh^{OMe}Oxa (0.89 g, 3 mmol) and toluene (30 mL) at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 13 h of stirring, all the volatiles were removed under reduced pressure to afford a yellow solid; yield 0.92 g, 87%. Suitable crystals of **3** for structural determination were recrystallized from a concentrated hexane solution; m.p. 138.5–140.5 °C. ¹H NMR (600 MHz): δ = –0.92 (s, 6 H, Al-CH₃), 1.45 [s, 3 H, C(CH₃)₂], 1.57 [s, 3 H, C(CH₃)₂], 3.78 (s, 3 H, OCH₃), 4.19 (d, J = 8.4 Hz, 1 H, CH₂), 4.28 (d, J = 8.4 Hz, 1 H, CH₂), 6.53 (m, 1 H, CH-Ph), 6.85 (d, J = 8.4 Hz, 1 H, CH-Ph), 6.91 (m, CH-Ph, 2H overlap), 7.03 (m, 1 H, CH-Ph), 7.14 (m, CH-Ph, 2H overlap), 7.70 (m, 1 H, CH-Ph) ppm. ¹³C{¹H} NMR (150 MHz): δ = –9.4 (s, Al-CH₃), –8.2 (s, Al-CH₃), 26.8 [s, C(CH₃)₂], 28.1 [s, C(CH₃)₂], 54.7 (s, OCH₃), 66.4 [s, C(CH₃)₂], 79.4 (s, CH₂), 111.0, 114.6, 118.3, 121.2, 123.3, 125.7, 130.2, 134.3 (s, CH-Ph), 107.4, 137.2, 153.6, 155.9, 167.8 (C_{quat}) ppm. C₂₀H₂₅AlN₂O₂ (352.41): calcd. C 68.16, H 7.15, N 7.95; found C 67.75, H 7.43, N 8.05.

(NPh^{SMc}Oxa)AlMe₂ (4): AlMe₃ (0.45 mL, 2.0 M in toluene, 1.2 mmol) was added to a flask containing HNPh^{SMc}Oxa (0.18 g, 0.56 mmol) and toluene (15 mL) at 0 °C. After 13 h of stirring, all the volatiles were removed under reduced pressure to afford a yellowish-green solid; yield 0.15 g, 73%. Suitable crystals of **4** for structural determination were recrystallized from a concentrated hexane solution; m.p. 184.0–186.0 °C. ¹H NMR (600 MHz): δ = –0.91 (s, 3 H, Al-CH₃), –0.81 (s, 3 H, Al-CH₃), 1.53 [s, 3 H, C(CH₃)₂], 1.54 [s, 3 H, C(CH₃)₂], 2.30 (s, 3 H, SCH₃), 4.26 (d, J = 8.4 Hz, 1 H, CH₂), 4.30 (s, J = 8.4 Hz, 1 H, CH₂), 6.17 (d, J = 8.4 Hz, 1 H, CH-Ph), 6.49 (t, J = 7.2 Hz, 1 H, CH-Ph), 7.05 (d, J = 7.8 Hz, 1 H, CH-Ph), 7.11 (m, 1 H, CH-Ph), 7.17 (m, 1 H, CH-Ph), 7.22 (m, CH-Ph, 2H overlap), 7.72 (m, 1 H, CH-Ph) ppm. ¹³C{¹H} NMR (150 MHz): δ = –9.2 (s, Al-CH₃), –6.9 (s, Al-CH₃), 14.9 (s, SCH₃), 27.3 [s, C(CH₃)₂], 27.7 [s, C(CH₃)₂], 66.4 [s, C(CH₃)₂], 79.2 (s, CH₂), 114.0, 116.6, 125.5 (two C intensities), 125.7, 128.9, 130.5, 135.1 (s, CH-Ph), 105.2, 138.2, 143.3, 156.0, 168.8 (C_{quat}) ppm. C₂₀H₂₅AlN₂OS (368.47): calcd. C 65.19, H 6.84, N 7.60; found C 64.71, H 7.08, N 7.76.

(NPhOxa)AlMe₂ (5): AlMe₃ (0.70 mL, 2.0 M in toluene, 1.4 mmol) was added to a flask containing HNPhOxa (0.27 g, 1.0 mmol) and toluene (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 14 h of stirring, all the volatiles were removed under reduced pressure. The crude product was washed with hexane (5 mL) to afford a yellowish-green solid; yield 0.25 g, 76%; m.p. 130.5–132.5 °C. ¹H NMR (600 MHz): δ = –0.87 (s, 6 H, Al-CH₃), 1.53 [s, 6 H, C(CH₃)₂], 4.27 (s, 2 H, CH₂), 6.40 (d, J = 8.4 Hz, 1 H, CH-Ph), 6.44 (m, 1 H, CH-Ph), 7.07–7.11 (m, 3 H, CH-Ph), 7.18 (t, J = 7.8 Hz, 1 H, CH-Ph), 7.38 (m, 2 H, CH-Ph), 7.69 (m, 1 H, CH-Ph) ppm. ¹³C{¹H} NMR (150 MHz): δ = –7.6 (s, Al-CH₃), 27.5 [s, C(CH₃)₂], 66.3 [s, C(CH₃)₂], 79.2 (s, CH₂), 113.5, 116.9, 124.6, 128.2, 129.6, 130.5, 135.1 (s, CH-Ph), 104.9, 146.8, 156.9, 168.8 (C_{quat}) ppm. C₁₉H₂₃AlN₂O (322.38): calcd. C 70.79, H 7.19, N 8.69; found C 70.05, H 6.55, N 8.11.

Polymerization Procedure of L-Lactide or ϵ -Caprolactone: Typically, toluene (10 mL containing 0.1 mmol benzyl alcohol for L-lactide or 15 mL containing 0.25 mmol benzyl alcohol for ϵ -caprolactone) was added to a flask containing a prescribed amount of monomers (L-lactide or ϵ -caprolactone) and catalyst (0.05 mmol for L-lactide, 0.125 mmol for ϵ -caprolactone). The reaction mixture was stirred at the prescribed temperature for the prescribed time. After the reaction was quenched by the addition of acetic acid solution (10 mL, 0.35 N), the resulting mixture was poured into *n*-heptane (50 mL) to precipitate polymers. Crude products were recrystallized from THF/hexane and dried in vacuo up to a constant weight.

Crystal Structure Data: Crystals were grown from concentrated hexane solution (for **1–4**) and isolated by filtration. Suitable crystals of **1–4** were sealed in thin-walled glass capillaries under nitrogen and mounted on a Bruker CCD Smart-1000 diffractometer. The absorption correction was based on the symmetry equivalent reflections using the SADABS program.^[13] The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.^[14] All non-hydrogen atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms and fixed isotropic parameters were used for hydrogen atoms. Some details of the data collection and refinement are given in Table 3.

CCDC-701925 (for **1**), -701926 (for **2**), -701927 (for **3**), and -701928 (for **4**) 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.

Table 3. Summary of crystal data for compounds 1–4.

	1	2	3	4
Empirical formula	C ₂₂ H ₂₉ AlN ₂ O	C ₂₅ H ₃₅ AlN ₂ O	C ₂₀ H ₂₅ AlN ₂ O ₂	C ₂₀ H ₂₅ AlN ₂ OS
Formula mass	364.45	406.53	352.40	368.46
<i>T</i> [K]	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁
<i>a</i> [Å]	10.4262(12)	10.0961(8)	16.9986(14)	16.8403(9)
<i>b</i> [Å]	8.1808(10)	12.0705(10)	8.3598(7)	8.1689(4)
<i>c</i> [Å]	25.597(3)	20.2512(16)	13.6445(12)	14.0728(8)
α [°]	90	90	90	90
β [°]	95.933(2)	101.105(2)	90	90
γ [°]	90	90	90	90
<i>V</i> [Å ³]	2171.6(4)	2421.7(3)	1939.0(3)	1935.95(18)
<i>Z</i>	4	4	4	4
ρ_{calcd} [Mg/m ³]	1.115	1.115	1.207	1.264
$\mu(\text{Mo-}K_{\alpha})$ [mm ^{−1}]	0.105	0.101	0.119	0.223
Reflections collected	11879	13554	10455	10362
Number of parameters	265	262	226	226
<i>R</i> ₁ ^[a]	0.057	0.0428	0.0305	0.0296
<i>wR</i> ₂ ^[a]	0.1635	0.1170	0.0854	0.0752
Gof ^[b]	1.086	0.807	1.034	1.022

[a] $R_1 = [\Sigma|F_o| - |F_c|]/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 0.10$. [b] Gof = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{refl}} - N_{\text{params}})]^{1/2}$.

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