



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

## Aluminum amine-bis(phenolate) complexes for ring-opening polymerization of rac-lactide and -caprolactone

### Citation for published version:

Cross, E, Tennekone, G, Decken, A & Shaver, M 2013, 'Aluminum amine-bis(phenolate) complexes for ring-opening polymerization of rac-lactide and -caprolactone' Green Materials, vol. 1, no. 2, pp. 79-86. DOI: 10.1680/gmat.12.00006

### Digital Object Identifier (DOI):

[10.1680/gmat.12.00006](https://doi.org/10.1680/gmat.12.00006)

### Link:

[Link to publication record in Edinburgh Research Explorer](#)

### Document Version:

Publisher's PDF, also known as Version of record

### Published In:

Green Materials

### Publisher Rights Statement:

Copyright © 2012 ICE Publishing; all rights reserved. Permission is granted by ICE Publishing to print one copy for personal use. Any other use of these PDF files is subject to reprint fees.

### General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



# Aluminum amine-(bis)phenolate complexes for ring-opening polymerization of *rac*-lactide and $\epsilon$ -caprolactone

**1 Edward D. Cross** BSc

Department of Chemistry, 450 University Avenue, Charlottetown, PE, Canada

**2 Gayan K. Tennekone** BSc

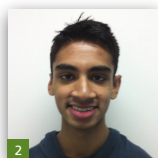
Department of Chemistry, 450 University Avenue, Charlottetown, PE, Canada

**3 Andreas Decken** PhD

Department of Chemistry, University of New Brunswick, Fredericton, NB, Canada

**4 Michael P. Shaver** PhD\*

Department of Chemistry, 450 University Avenue, Charlottetown, PE, Canada



Five aluminum-based amine-*bis*(phenolate) complexes, three of them novel, with variation of the pendant donor arm were synthesized in excellent yields, and characterized by NMR spectroscopy and X-ray crystallography. The quantitative conversion of the aluminum alkyl species to the corresponding benzyl alkoxide was achieved by the addition of 1 mol eq. of benzyl alcohol, and was confirmed by  $^1\text{H}$  NMR spectroscopy. The aluminum alkoxides were excellent mediators for the ring-opening polymerization (ROP) of *rac*-lactide, yielding atactic poly(lactic acid), having excellent correlation between theoretical and calculated molecular weights accompanied by narrow molecular weight distributions. ROP of  $\epsilon$ -caprolactone by the aluminum alkoxides showed modest control at 50°C in toluene, but much greater control was achieved when polymerizations were conducted at 25°C, with narrower molecular weight distributions observed in some cases. A relationship between the complex pendant donor arm and the resulting activity in the ROP of both *rac*-lactide and  $\epsilon$ -caprolactone is discussed. Supplementary information is available at [http://www.icevirtuallibrary.com/upload/10.1680gmat.12.00006\\_SupplementaryInformation.pdf](http://www.icevirtuallibrary.com/upload/10.1680gmat.12.00006_SupplementaryInformation.pdf)

## 1. Introduction

Catalyst development for ring-opening polymerization (ROP) of lactones has been of particular interest with the goal of accessing biodegradable aliphatic polyesters.<sup>1</sup> These biodegradable polyesters, such as poly(glycolic acid), poly( $\epsilon$ -caprolactone) (PCL), poly(lactic acid) (PLA) and their copolymers, serve as potential alternatives to traditional polymers which are not biodegradable, and are derived from non-renewable petrochemical feedstocks. A significant motivating factor for continuing research of biodegradable aliphatic polyesters is a result of the lactones used in ROP, as glycolide,  $\epsilon$ -caprolactone and lactide can be derived from renewable chemical feedstocks.<sup>2,3</sup> Of these aliphatic polyesters, PLA remains the most popular, as polymer properties can be readily modified through control of the PLA microstructure, as a result of the two stereocentres present in the lactide monomer. Through careful selection of a lactide stereoisomer

(*DD*-, *LL*-, *DL*-) and the complex mediating the ROP, the resulting PLA microstructure may be manipulated. This control of PLA properties and its biodegradable nature have sparked much interest in the biomedical industry with PLA-based materials employed as stents, tissue scaffolds and drug delivery vectors.<sup>4-6</sup> The principle catalyst used to synthesize these materials on an industrial scale has been tin(2-ethylhexanoate) ( $\text{Sn}(\text{Oct})_2$ ).<sup>7</sup>

As the use of PLA-based biomedical materials in the human body continues to increase, there is a growing desire for organocatalysts<sup>8,9</sup> and biocompatible metal-based catalysts such as Al, Ca, Mg, and Zn to mediate the ROP.<sup>10-14</sup> The ideal catalyst would possess similar or higher activity than  $\text{Sn}(\text{Oct})_2$ , be easily modifiable to fine tune polymer chain microstructure and unavoidable trace metals in the material would be easily metabolized by the body. While all of these

\*Corresponding author e-mail address: [mshaver@upei.ca](mailto:mshaver@upei.ca)

biocompatible metals have shown quite high activity and phenomenal control in ROP of lactide, complexes based on aluminum provide the greatest control of molecular weight and molecular weight distribution, while frequently inducing extremely high stereoregularity of PLA chains synthesized. Many aluminum-based complexes have been synthesized using a diverse array of ligand frameworks containing both nitrogen and oxygen donors. Despite significant success with a number of metals including lithium,<sup>15</sup> magnesium,<sup>16</sup> lanthanides<sup>17–27</sup> and group 4,<sup>28,29</sup> amine-*bis*(phenolate) ligands based on aluminum display significant activity and control in the ROP of *rac*-lactide<sup>30</sup> and  $\epsilon$ -caprolactone.<sup>31,32</sup> This activity and control of the ROP was achieved with both of these monomers mainly by alteration of the steric and electron-withdrawing character of aryl substituents present on the phenolate rings.

In an attempt to further expand the versatility of these catalysts, we wished to modify the pendant donor arm to observe its effect on activity and stereoregularity of PLA synthesized by these amine-*bis*(phenolate) supported Al centres. The amine pendant donor arm plays an important role in altering the coordination sphere of the Al centre, and thus we set out to further explore this relationship. With this in mind, the steric and electronic properties of the donor arm were manipulated, along with introduction of additional donor sites (Scheme 1), with particular attention paid to changes in control and stereoregularity of the ROP of *rac*-lactide and  $\epsilon$ -caprolactone.

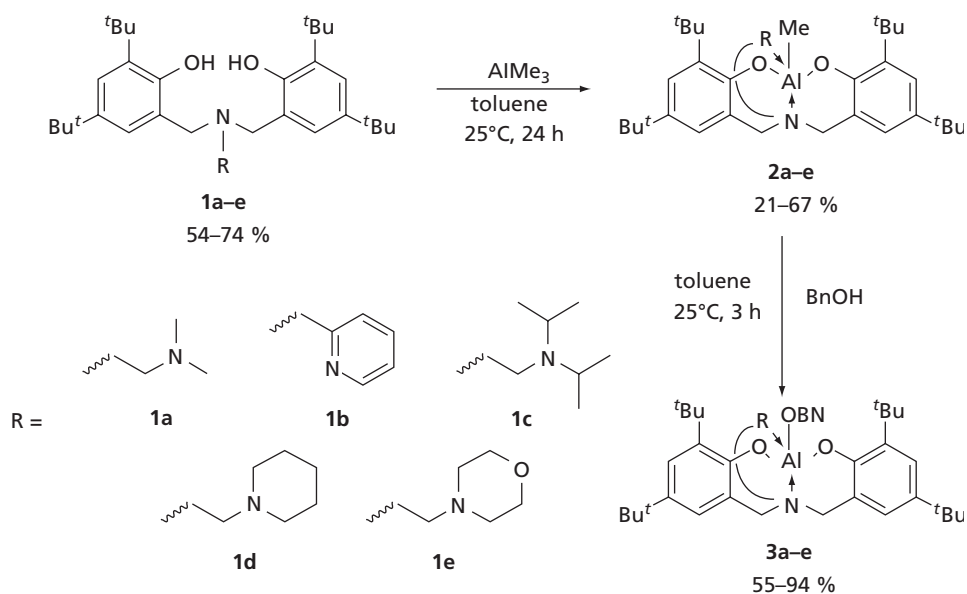
## 2. Results and discussion

Amine-*bis*(phenolate) ligands were prepared by a Mannich condensation adapted from a literature procedure between 2,4-di-*tert*-butylphenol, formaldehyde and the desired primary

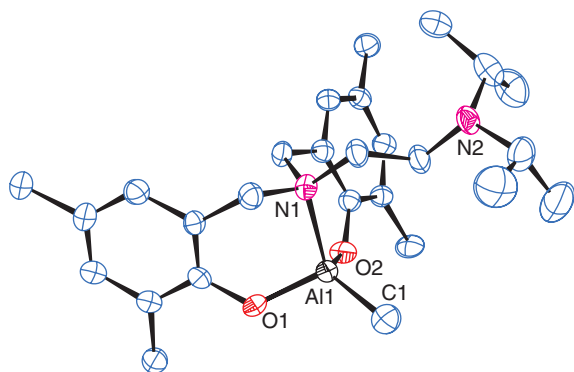
amine (Scheme 1).<sup>30</sup> Ligands **1a–e** were synthesized in yields ranging from 54%–74%. The appearance of a signal at ~3.5 ppm in <sup>1</sup>H NMR spectra corresponding to the Ar-CH<sub>2</sub>-N bridging protons confirmed the formation of the desired product. Treatment of **1a–e** with 1 equivalent of trimethylaluminum in 10 mL of toluene at ambient temperature for 24 h allowed access to Al-Me complexes **2a–e** in yields from 24%–67%. Disappearance of the phenolic proton signals at ~10 ppm accompanied by the appearance of a signal at ~-0.55 ppm for Al-CH<sub>3</sub> in <sup>1</sup>H NMR spectra were diagnostic for successful synthesis **3a–e** (Scheme 1).

Single crystals of **2c** suitable for X-ray crystallographic analysis were obtained by slow evaporation of an ether/hexamethyl-*bis*-siloxane solution (Figure 1). The molecular structure of **2c** determined by X-ray crystallographic analysis reveals a distorted tetrahedral aluminum center with O(1)-Al(1)-O(2), O(1)-Al(1)-N(1), O(2)-Al(1)-N(1), O(1)-Al(1)-C(1), O(2)-Al(1)-C(1), and C(1)-Al(1)-N(1) of 113.20(14)°, 99.05(12)°, 98.14(12)°, 108.43(16)°, 120.54(17)°, and 115.21(16), respectively. Bond distances from the aluminum center to C(1), N(1), O(1), and O(2) are 1.946(4), 1.998(3), 1.736(3), and 1.738(3) Å, respectively. These values resemble those for similar four-coordinate amine-*bis*(phenolate) aluminum complexes where the pendant amine functionality does not coordinate to the aluminum center.<sup>32</sup> While the data are of only moderate quality due to disorder of the di-isopropylamino groups, repeated attempts to grow better crystals of these catalysts were unsuccessful.

The corresponding benzyl alkoxy species **3a–e** were synthesized directly to avoid inefficient in situ formation of the alkoxy species during polymerization. Al-Me complexes **2a–e** were treated with



**Scheme 1.** Synthesis of aluminum-alkoxide complexes supported by amine-*bis*(phenolate) frameworks.



**Figure 1.** Molecular structure of **2c** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and tert-butyl methyl groups have been omitted for clarity.

1 mol equivalent of benzyl alcohol and allowed to stir at ambient temperature for 3 h to afford the benzyl alkoxy species in isolated yields ranging from 27 to 97% after washing with pentane. The  $^1\text{H}$  NMR spectra of the isolated benzyl alkoxy species showed the disappearance of the singlet at  $-0.55$  ppm, with a new signal observed at  $5.2$  ppm, corresponding to  $\text{Al-OCH}_2\text{Ph}$  protons. The  $\text{Al-OBn}$  complexes **3a–e** were then used in the ROP of *rac*-lactide and  $\epsilon$ -caprolactone.

### 2.1 Ring-opening polymerization of *rac*-lactide

ROP of *rac*-lactide using aluminum complexes **3a–e** was originally screened in toluene at  $70^\circ\text{C}$  with a  $[\text{M}]/[\text{Al}]$  of 50, as catalysts **3a** and **3b** were active under these conditions.<sup>30</sup> However, when this procedure was employed, low activity was observed with only low-molecular weight PLA obtained after workup. Thus, the polymerization conditions were modified by conducting the ROP in molten *rac*-lactide at  $120^\circ\text{C}$  in the absence of solvent. This adjustment proved successful, as at a loading of  $[\text{M}]/[\text{Al}] = 100$  the ROP of *rac*-lactide reached higher conversion after 6 h, and was accompanied by narrow molecular weight distributions of  $<1.20$  (Table 1). No loss of control was observed when employing **3a** and **3b** in the ROP, when compared to polymerizations in solvent. A much greater degree of polymerization was observed for **3c** compared to the other complexes, especially **3a**. The increased activity is attributed to the lack of a coordinating amine pendant donor in **3c**, thus resulting in a more available coordination sphere for an incoming lactide monomer. However, **3b** provides the best combination of control and activity compared to the other complexes. This is likely to be due to coordination of the pyridyl pendant donor to the aluminum centre, decreasing its electrophilic character. **3d** shows the greatest control of all the complexes examined, and it is speculated that the morpholine pendant donor may play a significant role by controlling the coordination number of the metal centre.  $^1\text{H}$  NMR studies show significant broadening in the pendant donor resonances, suggesting its fluxional coordination in solution, although thermodynamic parameters of this process were not determined.

### 2.2 Ring-opening polymerization of $\epsilon$ -caprolactone

A significant difference in activity for ROP of  $\epsilon$ -caprolactone was observed when modifications were made to the pendant donor arm of the aluminum complex. **3a** and **3b**, in which the pendant arm is coordinated to the aluminum center, showed excellent correlation between experimental and theoretical molecular weights accompanied by narrow molecular weight distributions for the resulting PCL. In contrast, **3c–e**, produced PCL with broadened molecular weight distributions of  $1.36$ – $1.56$  at  $50^\circ\text{C}$ . Decreasing the polymerization temperature to  $25^\circ\text{C}$ , along with a reduction of polymerization time to 30 min, decreased molecular weight distributions drastically for **3d** and **3e**, with no loss in activity or control (Table 2). However, a significant discrepancy between theoretical and experimental molecular weight was observed for **3d**. **3a** had significantly lower activity at  $25^\circ\text{C}$  compared to polymerizations conducted at  $50^\circ\text{C}$ , and **3b** produced only trace amounts of PCL at  $25^\circ\text{C}$  which is likely caused by inefficient initiation at the lower temperature.

Kinetic studies of **3a** and **3b** at  $50^\circ\text{C}$  in  $\text{C}_6\text{D}_6$  displayed pseudo-first order kinetics and a linear correlation between molecular weight and percent conversion (Figure 2). Attempts were made to collect kinetic data for **3c** and **3e**, however, the rate of ROP resulted in nearly quantitative conversion before the first measurement could be taken, even after significant reduction of complex concentration. Kinetic data were collected for **3d** at higher percent conversion, but provided no significant insight with regard to any living character present. From these observations, it is clear that the pendant donor arm has a drastic effect on the activity and control in ROP of  $\epsilon$ -caprolactone. It is likely that at lower temperatures, the pendant arm of **3d** and **3e** becomes coordinated to the Al centre, thus mimicking the control observed with **3a** and **3b**. Coordination of the pendant donor arm to the Al centre appears crucial in obtaining control in the ROP of  $\epsilon$ -caprolactone, and thus future modifications to this ligand framework as well as careful modification of polymerization conditions should be explored. Therefore, it can be concluded that the pendant donor arm plays a more important role in tuning the control these complexes impart in ROP of  $\epsilon$ -caprolactone when compared to the ROP of *rac*-lactide.

## 3. Experimental

### 3.1 Materials

All chemicals and solvents were obtained from Sigma Aldrich unless otherwise stated. 99% 2,4-di-tert-butylphenol, formaldehyde, and all primary amines, including *N,N*-dimethylethylenediamine, 2-(diisopropylamino)ethylamine, 1-(2-aminoethyl)-piperidine, 4-(2-aminoethyl)-morpholine, and 2-(aminomethyl)pyridine were used as received. Trimethylaluminum (2.0-M solution in heptane) was used as obtained. PURASORB *dl*-lactide was obtained from PURAC Biochem by Gorinchem and sublimed 3 times under vacuum prior to use.  $\epsilon$ -Caprolactone was dried over calcium hydride, distilled under inert atmosphere and degassed prior to use. **1a**, **1b**, **2a**, and **2b** were synthesized according to literature procedures.<sup>30,31</sup>

Entry	Complex <sup>a</sup>	M <sub>n,th</sub> <sup>b</sup>	M <sub>n</sub> <sup>c</sup>	PDI <sup>c</sup>	% conversion <sup>d</sup>
1	3a	640	7600	1.19	44
2	3b	10700	9500	1.10	74
3	3c	11800	10600	1.18	81
4	3d	5700	6500	1.08	39
5	3e	9000	8500	1.16	62

<sup>a</sup>Polymerizations conducted at 120°C for 6 h under solvent free conditions with [M]/[Al] = 100.

<sup>b</sup>Calculated by ([M]/[Al]) × MW(*rac*-lactide-) × (% conversion) + MW(endgroup).

<sup>c</sup>Calculated by gel permeation chromatography (size exclusion chromatography) at 50°C in tetrahydrofuran using polystyrene standards (conversion factor = 0.58).

<sup>d</sup>Determined gravimetrically.  
PDI, polydispersity index.

**Table 1.** Polymerization of *rac*-lactide mediated by amine-(bis)phenolate aluminum complexes **3a–e**.

Toluene, pentane, and ether were obtained from an Innovative Technologies glovebox equipped with an inline Solvent Purification System, consisting of columns of alumina and copper catalyst. The solvents were degassed by three freeze-pump-thaw cycles prior to use. All air-sensitive manipulations were performed in an MBraun LABmaster sp glovebox equipped with a –35°C freezer, (O<sub>2</sub>) and (H<sub>2</sub>O) analyzers and a built-in Siemens Simantic Touch Panel or on a dual manifold Schlenk line using standard Schlenk techniques.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a 300 MHz Bruker Avance Spectrometer. Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories PL-GPC 50 Plus integrated GPC system with two 300 × 7.8 mm Jordi Gel DVB mixed bed columns using HPLC grade THF at a flow rate of 1 mL per minute at 50°C, using poly(styrene) standards for molecular weight determinations. Elemental analyses were conducted by Guelph Analytical Laboratories.

## 3.2 Synthesis and characterization of ligands

### 3.2.1 Synthesis of [H<sub>2</sub>O<sub>2</sub>NN]<sup>PPr</sup> (1c)

Adapted from literature procedures,<sup>30</sup> 2,4-di-tert-butylphenol (7.01 g, 34.0 mmol), formaldehyde (3.50 mL, 34.0 mmol) and *N,N*-diisopropylethylenediamine (2.00 mL, 17.0 mmol) was dissolved in 12 mL of methanol. The solution was allowed to reflux at 65°C for 24 h. After 24 h, a yellow precipitate formed. The solution was cooled at –15°C overnight after which the yellow solid was collected via filtration and washed with cold methanol

Entry	Complex <sup>a</sup>	M <sub>n,th</sub> <sup>c</sup>	M <sub>n</sub> <sup>d</sup>	PDI <sup>d</sup>	% conv. <sup>e</sup>
1	3a <sup>a</sup>	10100	8000	1.04	89
2	3b <sup>a</sup>	9200	10000	1.20	81
3	3c <sup>a</sup>	8600	8900	1.34	76
4	3d <sup>a</sup>	9400	14500	1.56	82
5	3e <sup>a</sup>	8100	6000	1.32	71
6	3a <sup>b</sup>	4300	3400	1.21	38
7	3b <sup>b</sup>	—	—	—	Trace
8	3c <sup>b</sup>	10900	16400	1.43	93
9	3d <sup>b</sup>	11700	6400	1.20	96
10	3e <sup>b</sup>	10100	10600	1.09	89

<sup>a</sup>Polymerizations conducted at 50°C for 3 h in 5 mL toluene with [M]/[Al] = 100.

<sup>b</sup>Polymerization conducted at 25°C for 30 min in 5 mL toluene with [M]/[Al] = 100.

<sup>c</sup>Calculated by ([M]/[Al]) × MW ( $\epsilon$ -caprolactone) × (% conv.) + MW (endgroup).

<sup>d</sup>Calculated by gel permeation chromatography (size exclusion chromatography) at 50°C in tetrahydrofuran using polystyrene standards (conversion factor = 0.57).

<sup>e</sup>Determined gravimetrically.  
PDI, polydispersity index.

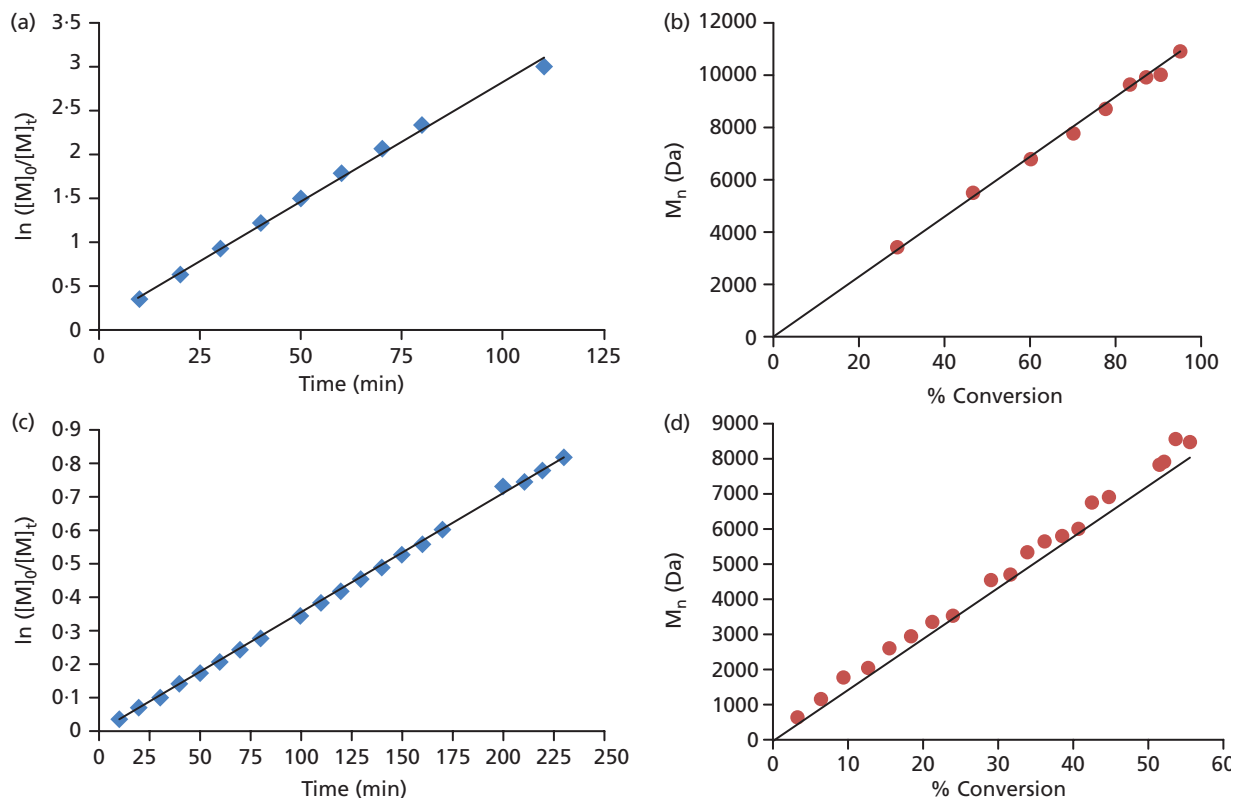
**Table 2.** Polymerization of  $\epsilon$ -caprolactone mediated by amine-(bis)phenolate aluminum complexes **3a–e**.

to yield 6.01 g (68%) of [H<sub>2</sub>O<sub>2</sub>NN]<sup>PPr</sup> as a white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.81 (s, OH, 2H), 7.18 (d, CH-phenoxide, 2H, *J* = 2 Hz), 6.89 (d, CH-phenoxide, 2H, *J* = 2 Hz), 3.60 (s, CH<sub>2</sub>, 4H), 3.26 (sep, CH(CH<sub>3</sub>)<sub>2</sub>, 2H, *J* = 6.6 Hz), 2.79 (t, -N(CH<sub>2</sub>)<sub>2</sub>N-, 2H, *J* = 6.2 Hz), 2.59 (t, -N(CH<sub>2</sub>)<sub>2</sub>N-, 2H, *J* = 6.2 Hz), 1.38 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.27 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.07 (d, C(CH<sub>3</sub>)<sub>2</sub>, 12H, *J* = 6.6 Hz) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 140.8, 136.2, 125.1, 123.7, 121.7, 57.1, 56.8, 49.7, 46.7, 35.3, 34.5, 32.1, 30.0, 20.2 ppm. EA found: C 78.66, H 11.03, N 4.87; calculated: C 78.57, H 11.10, N 4.82%.

### 3.2.2 Synthesis of [H<sub>2</sub>O<sub>2</sub>NN]<sup>Pip</sup> (1d)

Following the procedure outlined for 1c, 2,4-di-tert-butylphenol (7.04 g, 34.0 mmol), formaldehyde (3.50 mL, 34.0 mmol) and 1-(2-aminoethyl)-piperidine (2.50 mL, 17.0 mmol) yielded 5.23 g (54%) of [H<sub>2</sub>O<sub>2</sub>NN]<sup>Pip</sup> as a white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.62 (s, OH, 2H), 7.20 (d, CH-phenoxide, 2H, *J* = 2 Hz), 6.89 (d, CH-phenoxide, 2H, *J* = 2 Hz), 3.57 (s, CH<sub>2</sub>, 4H), 2.60 (m,





**Figure 2.** Plots of  $\ln([M]_0/[M]_t)$  versus time ( $\blacklozenge$ ) and  $M_n$  versus percent conversion ( $\bullet$ ) for ring-opening polymerization of  $\epsilon$ -caprolactone by 3a (2a and 2b) and 3b (2c and 2d) at 50°C in benzene- $d_6$  with  $[M]/[A] = 100$ .  $[A]$  for 3a = 6.2  $\mu$ M,  $[A]$  for 3b = 4.2  $\mu$ M. For plots of  $M_n$  versus percent conversion, the solid line represents the theoretical molecular weight of poly( $\epsilon$ -caprolactone) calculated.

$CH_2$ , 8H), 1.77 (br,  $CH_2$ , 4H), 1.56 (br,  $CH_2$ , 2H), 1.41 (s,  $C(CH_3)_3$ , 18H), 1.28 (s,  $C(CH_3)_3$ , 18H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  153.3, 140.4, 136.1, 124.9, 123.5, 121.5, 56.6, 55.8, 55.1, 48.6, 35.1, 34.2, 31.9, 29.8, 24.9, 24.6 ppm. EA found: C 76.10, H 10.20, N 5.15; calculated: C 76.28, H 10.31, N 4.94%.

### 3.2.3 Synthesis of $[H_2O_2NN]^{Mor}$ (1e)

Following the procedure outlined for 1c, 2,4-di-tert-butylphenol (7.03 g, 34.0 mmol), formaldehyde (3.50 mL, 34.0 mmol) and 4-(2-aminoethyl)-morpholine (3.00 mL, 17.0 mmol) yielded 6.72 g (70%) of  $[H_2O_2NN]^{Mor}$  as a white powder.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  9.26 (s, OH, 2H), 7.21 (d, CH-phenoxide, 2H,  $J = 2$  Hz), 6.89 (d, CH-phenoxide, 2H,  $J = 2$  Hz), 3.91 (m,  $CH_2$ , 4H,  $J = 2$  Hz), 3.60 (br,  $CH_2$ , 4H), 2.66 (s,  $CH_2$ , 4H), 2.54 (s,  $CH_2$ , 4H), 1.39 (s,  $C(CH_3)_3$ , 18H), 1.27 (s,  $C(CH_3)_3$ , 18H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  152.9, 140.8, 136.2, 125.1, 123.7, 121.4, 66.0, 56.4, 55.2, 53.8, 48.2, 35.1, 34.2, 31.9, 29.8 ppm. EA found: C 78.60, H 10.60, N 5.02; calculated: C 78.67, H 10.71, N 4.96%.

## 3.3 Synthesis and characterization of Al-alkyl complexes

### 3.3.1 Synthesis of $AlMe[O_2NN]^{iPr}$ (2c)

Adapted from a literature procedure,<sup>30</sup>  $[H_2O_2NN]^{iPr}$  (4.40 g, 7.50 mmol) and trimethylaluminum (3.00 g, 7.50 mmol) dissolved in 10 mL of toluene was stirred under an inert nitrogen atmosphere for 24 h at ambient temperature. The toluene was removed under reduced pressure and the remaining white residue was washed with 5 mL of pentane, followed by the removal of any remaining volatiles under reduced pressure to yield 2.09 g (45%) of  $AlMe[O_2NN]^{iPr}$  as a white powder.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.29 (d, CH-phenoxide, 2H,  $J = 2$  Hz), 6.89 (d, CH-phenoxide, 2H,  $J = 2$  Hz), 3.90 (d,  $CH_2$ , 2H,  $J = 13$  Hz), 3.81 (d,  $CH_2$ , 2H,  $J = 13$  Hz), 2.95 (sep, CH, 2H), 2.78 (m,  $CH_2$ , 4H), 1.42 (s,  $C(CH_3)_3$ , 18H), 1.28 (s,  $C(CH_3)_3$ , 18H), 0.94 (d,  $C(CH_3)_2$ , 12H,  $J = 7$  Hz), -0.56 (s, Al- $CH_3$ , 3H) ppm.  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  155.2, 139.9, 138.6, 125.0, 124.2, 121.0, 57.6, 57.1, 56.0, 49.4, 46.7, 38.1, 35.3, 34.3, 31.9, 29.7, 21.1, 22.5 ppm. EA found: C 75.17, H 10.68, N 4.29; calculated: C 75.44, H 10.55, N 4.51%.

### 3.3.2 Synthesis of AlMe[O<sub>2</sub>NN]<sup>Pip</sup> (2d)

Following the procedure outlined for 2c, [H<sub>2</sub>O<sub>2</sub>NN]<sup>Pip</sup> (3.50 g, 6.18 mmol) and trimethylaluminum (2.41 g, 6.18 mmol) yielded 0.98 g (26%) of AlMe[O<sub>2</sub>NN]<sup>Pip</sup> as a white powder. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.26 (d, CH-phenoxide, 2H, J = 2 Hz), 6.89 (d, CH-phenoxide, 2H, J = 2 Hz), 3.97 (d, CH<sub>2</sub>, 2H, J = 13 Hz), 3.95 (d, CH<sub>2</sub>, 2H, J = 13 Hz), 3.82 (d, CH<sub>2</sub>, 2H, J = 13 Hz), 2.98 (br, CH<sub>2</sub>, 2H), 2.70 (br, CH<sub>2</sub>, 2H), 2.41 (br, CH<sub>2</sub>, 4H), 1.59 (d, CH<sub>2</sub>, 4H, J = 6 Hz), 1.42 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.28 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), -0.57 (s, Al-CH<sub>3</sub>, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 155.3, 140.0, 138.6, 125.5, 124.6, 121.0, 56.8, 55.8, 51.9, 50.3, 35.3, 34.4, 32.0, 29.8, 26.2, 24.5, 22.6 ppm. EA found: C 72.90, H 9.57, N 4.44; calculated: C 73.23, H 9.80, N 4.62%.

### 3.3.3 Synthesis of AlMe[O<sub>2</sub>NN]<sup>Mor</sup> (2e)

Following the procedure outlined for 2c, [H<sub>2</sub>O<sub>2</sub>NN]<sup>Mor</sup> (4.02 g, 7.10 mmol) and trimethylaluminum (2.71 g, 7.10 mmol) yielded 2.90 g (67%) of AlMe[O<sub>2</sub>NN]<sup>Mor</sup> as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.27 (d, CH-phenoxide, 2H, J = 3 Hz), 6.82 (d, CH-phenoxide, 2H, J = 2 Hz), 3.94 (d, CH<sub>2</sub>, 2H, J = 13 Hz), 3.81 (d, CH<sub>2</sub>, 2H, J = 13 Hz), 3.69 (m, CH<sub>2</sub>, 4H), 2.98 (t, CH<sub>2</sub>, 2H, J = Hz), 2.71 (t, CH<sub>2</sub>, 2H, J = 6 Hz), 2.43 (t, CH<sub>2</sub>, 4H, J = 6 Hz), 1.39 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.26 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), -0.60 (s, Al-CH<sub>3</sub>, 3H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 155.2, 140.1, 138.6, 125.5, 124.5, 120.7, 66.6, 56.4, 53.9, 51.0, 49.5, 33.8, 33.7, 31.4, 29.2, 26.2, 21.1 ppm. EA found: C 75.22, H 10.10, N 4.45; calculated: C 75.45, H 10.16, N 4.63%.

## 3.4 Synthesis of characterization of Al-alkoxide complexes

### 3.4.1 Synthesis of AlOBn[O<sub>2</sub>NN]<sup>Me</sup> (3a)

To a solution of AlMe[O<sub>2</sub>NN]<sup>Me</sup> (0.500 g, 0.886 mol) dissolved in 5 mL of toluene was added benzyl alcohol (0.116 g, 1.07 mmol). The mixture was allowed to stir for 3 h at ambient temperature. The toluene was then removed under reduced pressure and the remaining white residue was washed with 5 mL of pentane. The white solid was dried under reduced pressure yielding 0.140 g (27%) of AlOBn[O<sub>2</sub>NN]<sup>Me</sup>. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.82 (d, CH-phenoxide, 2H, J = 2 Hz), 7.60 (d, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H, J = 2.5 Hz), 7.43 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H, J = 7.4 Hz), 7.23 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 1H, J = 7.4 Hz) 6.79 (d, CH-phenoxide, 2H, J = 2 Hz), 5.73 (s, PhCH<sub>2</sub>O, 2H), 3.10-3.30 (br, ArCH<sub>2</sub>, 4H), 2.11 (s, N(CH<sub>3</sub>)<sub>2</sub>, 6H), 1.73 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.43 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 155.6, 138.3, 138.1, 126.3, 127.6, 127.3, 123.6, 123.2, 121.1, 64.0, 58.5, 54.3, 48.0, 34.9, 33.7, 31.5, 29.4 ppm. EA found: C 75.09, H 9.23, N 4.38; calculated: C 74.96, H 9.36, N 4.26%.

### 3.4.2 Synthesis of AlOBn[O<sub>2</sub>NN]<sup>Pyr</sup> (3b)

Following the procedure for 3a, AlMe[O<sub>2</sub>NN]<sup>Pyr</sup> (1.50 g, 2.49 mmol) and benzyl alcohol (0.240 g, 2.22 mmol) yielded 1.11 g (81%) of AlOBn[O<sub>2</sub>NN]<sup>Pyr</sup> as a white solid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 9.86 (d, CH-Pyr, 1H, J = 7.2 Hz), 7.97 (m, CH-Py, 1H),

7.58 (d, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H, J = 2.7 Hz), 7.46 (m, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H), 7.26 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 1H, J = 7.2 Hz), 6.80 (d, CH-phenoxide, 2H, J = 1.5 Hz), 6.59 (t, CH-Pyr, 1H, J = 6.9 Hz), 6.25 (t, CH-Pyr, 1H, J = 6.3 Hz), 5.99 (bs, CH-phenoxide, 2H), 5.90 (d, CH-Pyr, 1H, J = 7.8 Hz), 5.38 (s, PhCH<sub>2</sub>O, 2H), 3.60–3.90 (br, ArCH<sub>2</sub>, 6H), 1.43 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.29 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 157.1, 156.3, 153.1, 141.1, 139.2, 139.0, 129.6, 128.9, 128.5, 128.2, 127.5, 125.9, 124.5, 124.1, 123.8, 122.7, 121.6, 65.0, 57.0, 35.3, 34.3, 32.0, 29.7 ppm. EA found: C 76.11, H 8.44, N 4.02; calculated: C 76.30, H 8.49, N 4.14%.

### 3.4.3 Synthesis of AlOBn[O<sub>2</sub>NN]<sup>Pip</sup> (3c)

Following the procedure for 3a, AlMe[O<sub>2</sub>NN]<sup>Pip</sup> (0.500 g, 0.805 mmol) and benzyl alcohol (0.110 g, 1.10 mmol) yielded 0.32 g (56%) of AlOBn[O<sub>2</sub>NN]<sup>Pip</sup> as a white solid. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.69 (d, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H, J = 6 Hz), 7.66 (d, CH-phenoxide, 2H, J = 2.5 Hz), 7.36 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 2H, J = 7.4 Hz), 7.22 (t, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 1H, J = 7.4 Hz), 6.82 (d, CH-phenoxide, 2H, J = 2.4 Hz), 5.31 (s, PhCH<sub>2</sub>O, 2H), 3.67 (d, CH<sub>2</sub>, 2H, J = 14 Hz), 3.34 (d, CH<sub>2</sub>, 2H, J = 14 Hz), 2.79 (m, CH, 2H), 2.55 (m, CH<sub>2</sub>, 4H), 1.77 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.49 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 0.87 (d, C(CH<sub>3</sub>)<sub>2</sub>, 12H, J = 7 Hz) ppm. <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ 156.1, 140.6, 139.4, 128.9, 128.6, 128.2, 127.5, 125.3, 124.6, 121.9, 59.3, 58.2, 49.6, 39.1, 35.8, 34.7, 32.4, 30.3, 21.4 ppm. EA found: C 75.44, H 9.75, N 3.96; calculated: C 75.50, H 9.75, N 3.93%.

### 3.4.4 Synthesis of AlOBn[O<sub>2</sub>NN]<sup>Pip</sup> (3d)

Following the procedure outlined for 3a, AlMe[O<sub>2</sub>NN]<sup>Pip</sup> (0.500 g, 0.826 mmol) and benzyl alcohol (0.110 g, 1.01 mol) yielded 0.320 g (55%) of AlOBn[O<sub>2</sub>NN]<sup>Pip</sup> as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.35–7.14 (bm, CH-phenoxide and C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 7H), 6.82 (d, CH-phenoxide, 2H, J = 2 Hz), 5.30 (s, PhCH<sub>2</sub>O, 2H), 3.50-3.00 (br, CH<sub>2</sub>, 8H), 3.14 (t, CH<sub>2</sub>, 2H, J = 2 Hz), 2.67 (br, CH<sub>2</sub>, 2H), 2.36 (s, CH<sub>2</sub>, 2H), 1.58 (br, CH<sub>2</sub>, 4H), 1.41 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.27 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 155.7, 148.2, 138.7, 128.4, 127.7, 126.4, 125.5, 124.0, 123.5, 121.0, 66.0, 58.8, 49.6, 46.9, 35.2, 34.2, 32.0, 29.7, 23.2, 21.6, 20.1 ppm. EA found: C 74.11, H 8.84, N 3.72; calculated: C 73.99, H 9.09, N 4.01%.

### 3.4.5 Synthesis of AlOBn[O<sub>2</sub>NN]<sup>Mor</sup> (3e)

Following the procedure for 3a, AlOBn[O<sub>2</sub>NN]<sup>Mor</sup> (1.00 g, 1.65 mmol) and benzyl alcohol (0.215 g, 1.97 mmol) yielded 1.11 g (97%) of AlOBn[O<sub>2</sub>NN]<sup>Mor</sup> as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.37 (d, CH<sub>2</sub>-phenoxide, 2H, J = 3 Hz), 7.35-7.00 (br, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O, 5H) 6.82 (d, CH-phenoxide, 2H, J = 2 Hz), 5.10 (s, PhCH<sub>2</sub>O, 2H), 3.91–3.59 (m, CH<sub>2</sub>, 8H), 2.87 (s, CH<sub>2</sub>, 2H), 2.75 (br, CH<sub>2</sub>, 2H), 2.36 (br, CH<sub>2</sub>, 4H), 1.38 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H), 1.26 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 155.4, 140.0, 138.5, 128.8, 125.0, 124.1, 124.0, 120.5, 124.8, 124.1, 65.0, 66.6, 53.6, 51.0, 49.5, 33.8, 35.3, 34.3, 29.4, 22.5 ppm. EA found: C 76.01, H 9.22, N 3.88; calculated: C 75.82, H 9.40, N 4.02%.

### 3.5 General polymerization procedure for *rac*-lactide

A total of 0.020 g of Al-alkoxide catalyst (**3a–e**) and 100 molar equivalents of *rac*-lactide were added to an oven-dried ampoule charged with a magnetic stirrer bar. The ampoule was sealed and heated to 120°C with stirring for 6 h, after which the resulting viscous mixture was dissolved in a 10:1 dichloromethane:methanol solution. Once fully dissolved, the solution was left to stir at ambient temperature for 30 min, followed by precipitation into 100 mL of cold methanol. The resulting white precipitate was filtered and dried under vacuum to constant weight.

### 3.6 General polymerization procedure for $\epsilon$ -caprolactone

A total of 0.020 g of Al-alkoxide catalyst (**3a–e**) was dissolved in 5 mL of toluene and added to an oven-dried ampoule charged with a magnetic stirrer bar. To this solution, 100 molar equivalents of  $\epsilon$ -caprolactone was added. The ampoule was sealed and heated to 50°C with stirring for 3 h, or at 25°C for 30 min. Once the desired polymerization time was reached, the polymerization was quenched with 1 mL of glacial acetic acid. The solution was left to stir at ambient temperature for 30 min which was followed by precipitation into 40 mL of cold pentane. The resulting white precipitate was filtered and dried under vacuum to constant weight.

## 4. Conclusion

Al-alkyl amine-(bis(phenolate)) complexes **2a–e** were prepared in reasonable isolated yields by treatment of ligands **1a–e** with trimethylaluminum. Single crystals of **2c** showed a distorted tetrahedral aluminum complex where the pendant amine donor was uncoordinated in the solid state. The active aluminum-alkoxide initiating species was synthesized through addition of benzyl alcohol to **2a–e**, allowing access to **3a–e** in acceptable yields. The ability of novel complexes **3c–e** to mediate ROP of *rac*-lactide was excellent, as there was excellent correlation between experimental and theoretical molecular weights accompanied by narrow molecular weight distributions. Living polymerization character was observed in kinetic studies of these polymerizations. **3c–e** successfully controlled the ROP of  $\epsilon$ -caprolactone when polymerization temperatures were lowered to 25°C. A drastic increase in control was observed for **3d** and **3e**, but this increase was not observed for **3c**. **3a** was only moderately active at this temperature, and **3b** produced only trace amounts of PCL. A substantial loss of control was observed when the polymerization temperature was increased 50°C for **3c–e**. Kinetic studies could not be completed for **3c–e** due to high activity at room temperature, however **3a** and **3b** showed living character at 50°C. It has been concluded that while not crucial for ROP of *rac*-lactide, coordination of the pendant donor arm plays a significant role in controlling ROP of  $\epsilon$ -caprolactone. It appears as though coordination of the pendant arm limits access of  $\epsilon$ -caprolactone to the aluminum center, thus improving molecular weight distributions.

## 5. Supplementary information

X-ray crystallography data tables for complex **2c** can be found in the supplementary information. In order to access this data file please refer to the supplementary data URL as mentioned at the end of the abstract.

## Acknowledgments

The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC), Innovation PEI, Canadian Foundation for Innovation (CFI), Atlantic Canada Opportunities Agency and University of Prince Edward Island for funding.

## REFERENCES

1. Thomas, C. M. Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. *Chemical Society Reviews* **2010**, *39*, 165.
2. Stanford, M. J.; Dove, A. P. Stereocontrolled ring-opening polymerisation of polylactide. *Chemical Society Reviews* **2010**, *39*, 486.
3. Arbaoui, A.; Redshaw, C. Metal catalysts for  $\epsilon$ -caprolactone polymerization. *Polymer Chemistry* **2010**, *1*, 801.
4. Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. Poly(lactic acid) modifications. *Progress in Polymer Science* **2010**, *35*, 338.
5. Gunatillake, P.; Mayadunne, R.; Adhikari, R. Recent developments in biodegradable synthetic polymers. *Biotechnology Annual Review* **2006**, *12*, 301.
6. Alexis, F. Factors affecting the degradation and drug-release mechanism of poly(lactic acid) and poly[(lactic acid)-co-(glycolic acid)]. *Polymer International* **2005**, *54*, 36.
7. Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. Controlled ring-opening polymerization of lactide and glycolide. *Chemical Reviews* **2004**, *104*, 6147.
8. Platel, R. H.; Hodgson, L. M.; Williams, C. K. Biocompatible initiators for lactide polymerization. *Polymer Reviews* **2008**, *48*, 11.
9. Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. Organocatalytic ring-opening polymerization. *Chemical Reviews* **2007**, *107*, 5813.
10. Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. Study of ligand substituent effects on the rate and stereoselectivity of lactide polymerization using aluminum salen-type initiators. *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 15343.
11. Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P.; Williams, D. J. J. Remarkable stereocontrol in the polymerization of racemic lactide using aluminum initiators supported by tetradentate aminophenoxide ligands. *Journal of the American Chemical Society* **2004**, *126*, 2688.
12. Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. Well-Defined Calcium Initiators for Lactide Polymerization. *Inorganic Chemistry* **2004**, *43*, 6717.



13. Wang, L.; Ma, H. Highly active magnesium initiators for ring-opening polymerization of rac-Lactide. *Macromolecules* **2010**, *43*, 6535.
14. Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. Polymerization of lactide with zinc and magnesium  $\beta$ -diiminate complexes: stereocontrol and mechanism. *Journal of the American Chemical Society* **2001**, *123*, 3229.
15. Huang, C.-A.; Chen, C.-T. Lithium complexes supported by amine bis-phenolate ligands as efficient catalysts for ring-opening polymerization of l-lactide. *Dalton Transactions* **2007**, 5561.
16. Ejfler, J.; Krauzy-Dziedzic, K.; Szafert, S.; Jerzykiewicz, L. B.; Sobota, P. Synthesis, characterization, and catalytic studies of (aryloxido)magnesium complexes. *European Journal of Inorganic Chemistry* **2010**, *2010*, 3602.
17. Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. Ring-opening polymerization of lactide with group 3 metal complexes supported by dianionic alkoxy-amino-bisphenolate ligands: combining high activity, productivity, and selectivity. *Chemistry - A European Journal* **2006**, *12*, 169.
18. Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. Exploring electronic versus steric effects in stereoselective ring-opening polymerization of lactide and  $\beta$ -butyrolactone with amino-alkoxy-bis(phenolate)-yttrium complexes. *Chemistry - A European Journal* **2011**, *17*, 1872.
19. Chai, Z.-Y.; Zhang, C.; Wang, Z.-X. Synthesis, characterization, and catalysis in  $\epsilon$ -caprolactone polymerization of aluminum and zinc complexes supported by N,N,N-chelate ligands. *Organometallics* **2008**, *27*, 1626.
20. Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. Dicationic and zwitterionic catalysts for the amine-initiated, immortal ring-opening polymerisation of rac-lactide: facile synthesis of amine-terminated, highly heterotactic PLA. *Chemical Communications* **2010**, *46*, 273.
21. Delbridge, E. E.; Dugah, D. T.; Nelson, C. R.; Skelton, B. W.; White, A. H. Synthesis, structure and oxidation of new ytterbium(ii) bis(phenolate) compounds and their catalytic activity towards [ $\epsilon$ ]-caprolactone. *Dalton Transactions* **2007**, 143.
22. Dyer, H. E.; Huijser, S.; Schwarz, A. D.; Wang, C.; Duchateau, R.; Mountford, P. Zwitterionic bis(phenolate)amine lanthanide complexes for the ring-opening polymerisation of cyclic esters. *Dalton Transactions* **2008**, 32.
23. Dyer, H. E.; Huijser, S.; Susperregui, N.; Bonnet, F.; Schwarz, A. D.; Duchateau, R.; Maron, L.; Mountford, P. Ring-opening polymerization of rac-lactide by bis(phenolate) amine-supported samarium borohydride complexes: an experimental and DFT study. *Organometallics* **2010**, *29*, 3602.
24. Kerton, F. M.; Whitwood, A. C.; Willans, C. E. A high-throughput approach to lanthanide complexes and their rapid screening in the ring opening polymerisation of caprolactone. *Dalton Transactions* **2004**, 2237.
25. Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. Achiral lanthanide alkyl complexes bearing N,O multidentate ligands. synthesis and catalysis of highly heteroselective ring-opening polymerization of rac-lactide. *Organometallics* **2007**, *26*, 2747.
26. Yao, Y.; Ma, M.; Xu, X.; Zhang, Y.; Shen, Q.; Wong, W.-T. Synthesis, reactivity, and characterization of amine bis(phenolate) lanthanide complexes and their application in the polymerization of  $\epsilon$ -caprolactone. *Organometallics* **2005**, *24*, 4014.
27. Zhou, H.; Guo, H.; Yao, Y.; Zhou, L.; Sun, H.; Sheng, H.; Zhang, Y.; Shen, Q. Ytterbium(II) complex bearing a diamino-bis(phenolate) ligand: synthesis, structure, and one-electron-transfer and  $\epsilon$ -caprolactone polymerization reactions. *Inorganic Chemistry* **2007**, *46*, 958.
28. Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F.; Johnson, A. F.; Khunkamchoo, P.; Roberts, S. L.; Wong, S. S. F. Group 4 complexes with aminebisphenolate ligands and their application for the ring opening polymerization of cyclic esters. *Macromolecules* **2006**, *39*, 7250.
29. Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. Titanium, zinc and alkaline-earth metal complexes supported by bulky O,N,N,O-multidentate ligands: syntheses, characterisation and activity in cyclic ester polymerisation. *Dalton Transactions* **2006**, 340.
30. Tang, Z.; Gibson, V. C. rac-Lactide polymerization using aluminum complexes bearing tetradentate phenoxy-amine ligands. *European Polymer Journal* **2007**, *43*, 150.
31. Chen, C.-T.; Huang, C.-A.; Huang, B.-H. Aluminium metal complexes supported by amine bis-phenolate ligands as catalysts for ring-opening polymerization of  $\epsilon$ -caprolactone. *Dalton Transactions* **2003**, 3799.
32. Chen, C.-T.; Huang, C.-A.; Huang, B.-H. Aluminum complexes supported by tridentate aminophenoxide ligand as efficient catalysts for ring-opening polymerization of  $\epsilon$ -caprolactone. *Macromolecules* **2004**, *37*, 7968.

#### WHAT DO YOU THINK?

To discuss this paper, please email up to 500 words to the managing editor at [gmat@icepublishing.com](mailto:gmat@icepublishing.com)

Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editors-in-chief, will be published as a discussion in a future issue of the journal.

ICE Science journals rely entirely on contributions sent in by professionals, academics and students coming from the field of materials science and engineering. Articles should be within 5000-7000 words long (short communications and opinion articles should be within 2000 words long), with adequate illustrations and references. To access our author guidelines and how to submit your paper, please refer to the journal website at [www.icevirtuallibrary.com/gmat](http://www.icevirtuallibrary.com/gmat)