

Aluminum complexes with benzoxazolphenolate ligands: Synthesis, characterization and catalytic properties for ring-opening polymerization of cyclic esters



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ABSTRACT

A family of bidentate ligands, **1–3**, were synthesized by the reactions of 5-diethylamino-2-nitrosophenol with bromomethylphenol derivatives. Treatment of the ligands **1–3** with one equivalent of AlMe_3 gave the corresponding aluminum complexes **4–6**, respectively. All the complexes were characterized by ^1H and ^{13}C NMR spectroscopy, along with elemental analysis. Single crystal X-ray diffraction analysis of complex **5** revealed that the Al complex has a distorted tetrahedral geometry around the metal center. All the aluminum complexes are efficient initiators for the ring-opening polymerization of ϵ -caprolactone and lactide in the presence of benzyl alcohol in a living fashion. The aluminum complexes produced PLA with a slight heterotactic bias.

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1. Introduction

Poly(ϵ -caprolactone) (PCL) and polylactide (PLA), as well as their copolymers, are interesting alternative candidates to traditional petrochemical-base polymers, due to their biodegradability and biocompatibility [1,2]. The most promising methodology for the synthesis of these polymers is the ring-opening polymerization (ROP) of cyclic esters initiated by metal-based catalysts, such as Sn [3–8], Al [9–39], Zn [40–49], Mg [50–59], Fe [60–66], Ti [67–76], In [77–81] and rare-earth metals [82–87] with ancillary ligands. Among the reported catalysts, aluminum catalysts have been studied the most for the ROP of cyclic esters because of their great controllability over the molecular weight and distribution of the polymers by modification of the ancillary ligands [88–92]. Recent research indicates that aluminum complexes with phenoxy-imine/amine ligands acting as bulky monoanionic ligands have attracted great attention for their successful application in the ROP reaction [9–12]. Nomura's group reported a facile and efficient system for the ROP of ϵ -caprolactone (ϵ -CL) at room temperature using a salicylaldehyde–Al complex [9]. In addition, Pappalardo's group reported the synthesis of dimethyl(salicylaldehyde)aluminum complexes and their reactivity toward the ROP of ϵ -CL

and lactide (LA) [10]. Therefore, some aluminum complexes bearing a similar structure with phenoxy-imine/amine ligands were synthesized and their catalytic properties for the ROP reaction have been investigated. Ko's group showed that aluminum complexes bearing sterically bulky benzotriazole-phenoxide ligands were efficient catalysts for the ROP of *l*-LA [13]. Wang's group also showed that aluminum complexes supported by functionalized phenolate ligands were active in the polymerization of *rac*-LA [14]. According to the catalytic properties for aluminum complexes bearing bulky monoanionic ligands in the ROP reaction, Al complexes with benzoxazolphenolate ligands were expected to be efficient catalysts in the ROP reaction. In this paper, a family of benzoxazolphenolate ligands and their aluminum complexes have been synthesized. Additionally, their catalytic properties for the ROP of ϵ -CL and LA have also been examined.

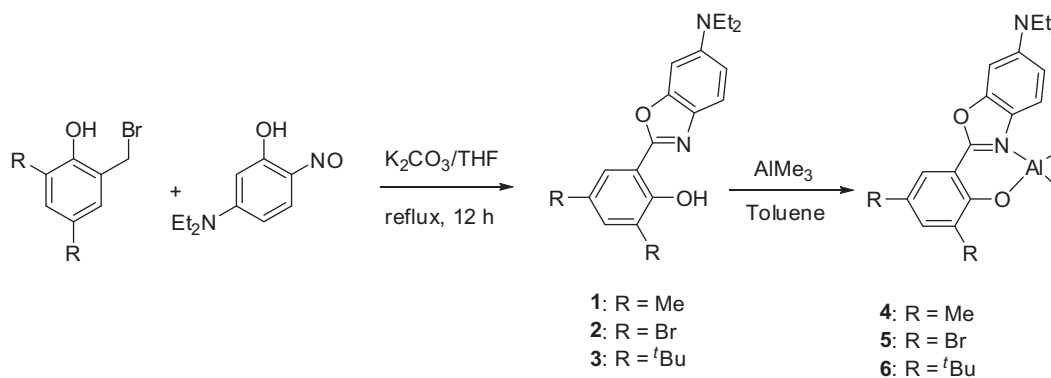
2. Results and discussion

2.1. Synthesis and characterization

The synthesis of the ligands **1–3** and their aluminum complexes **4–6** are presented in Scheme 1. The ligands **1–3** were synthesized according to a literature procedure by the reaction of 5-diethylamino-2-nitrosophenol with the corresponding 2-bromomethylphenol in THF [93]. The ligands **1–3** were characterized by ^1H and ^{13}C NMR spectra. The NMR spectral signals were consistent with the respective structures. The proton signals of the OH groups

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Scheme 1. Synthesis of complexes **1–6**.

of **1–3** appeared in the low field region (δ 11.48–12.29 ppm), showing the existence of intramolecular hydrogen bonds. Treatment of **1–3** with one equivalent of AlMe_3 in toluene afforded the aluminum complexes **4–6** through an alkane elimination reaction. The aluminum complexes **4–6** were also characterized by ^1H and ^{13}C NMR spectra and elemental analyses. The absence of the O–H signal of the ligands and the appearance of new protons signals for AlMe_2 (δ –0.63 to –0.79 ppm) demonstrated the formation of the desired aluminum complexes.

Crystals of complex **5** suitable for X-ray crystal structure determination were crystallized from *n*-hexane at room temperature. Its molecular structure is shown in Fig. 1 with selected bond lengths and angles. X-ray analysis reveals that the Al center adopts a slightly distorted tetrahedral geometry, as evidenced by the bond angles for O1–Al1–N1 92.33(1)°, N1–Al1–C19 105.95(2)°, C18–Al1–N1 111.18(2)°, C18–Al1–O1 114.23(2)°, O1–Al1–C19 114.93(2)°

and C18–Al1–C19 115.40(2)°. The six-membered chelating ring is nearly planar, with the aluminum atom lying out of the plane by 0.0894 Å. The torsion angles between the six-membered chelating ring and C19–Al1–C18 is 93.1(2)°. The Al–O bond length [1.782(2) Å] is slight longer than those in salicylaldiminato aluminum complexes [1.7688(2)–1.7792(1) Å]. In contrast, the Al–N bond length of complex **5** [1.960(3) Å] is slight shorter as compared with the salicylaldiminato aluminum complexes [1.9664(1)–1.9896(1) Å] [9–12]. There is, however, no significant differences observed in the Al–C bond distances.

2.2. ROP of ϵ -CL using complexes **4–6**

The catalytic performances of complexes **4–6** toward the polymerization of ϵ -CL were investigated and the results are shown in Table 1. All the aluminum complexes **4–6** showed high activities for the ring-opening polymerization of ϵ -CL in the presence of benzyl alcohol (BnOH) (Table 1, entries 1–6). The highest catalytic activity was obtained with a BnOH/Al molar ratio of 2:1 (Table 1, entries 2, 5, 7 and 8). Under the same conditions, the activities of the complexes were compared with each other. The catalytic activity decreased when the bromine groups at the 3 and 5 position on the phenol ring were replaced by methyl groups (Table 1, entries 4 and 5). Additionally, entry 6 shown that catalytic activity was reduced upon the addition of tertiary butyl groups to the phenol backbone. This could be due to the steric and electronic effects of the substituents. In comparison with related known catalytic systems, the activities of complexes **4–6** (turnover frequency (TOF): 441.4, 735.0 and 582.0 h^{-1}) were lower than those of the phenolate Al catalyst systems (TOF: 7698.6 h^{-1}) [9].

To investigate the catalytic properties for the ROP of ϵ -CL, the catalytic precursor **5** was studied under different reaction conditions. A linear relationship between the number average molecular weight (M_n) and $([\epsilon\text{-CL}]_0/[\text{BnOH}]_0)$ indicated the “living” character of the polymerization process, as shown in Fig. 2 (Table 1, entries 5, 9–12). The effect of the BnOH/Al molar ratio on the ROP of ϵ -CL was also examined (Table 1, entries 5, 7 and 8). The results imply that the Al complexes initiate the polymerization reaction in a controlled fashion. Remarkably, complex **5** was tolerant to the protic BnOH. The addition of 10 equivalents of BnOH did not degrade the complex (Fig. 3). The ^1H NMR spectrum of PCL-50 prepared from ϵ -CL and **5** ($[\epsilon\text{-CL}]_0/[\text{BnOH}]_0 = 50$) for chain-end studies is shown in Fig. 4. The polymer chain should be capped with one benzyl ester and one hydroxy chain end.

2.3. ROP of *rac*-LA using complexes **4–6**

Complexes **4–6** were also examined with regard to their catalytic behavior in the ROP of LA. The ROP was carried out in toluene

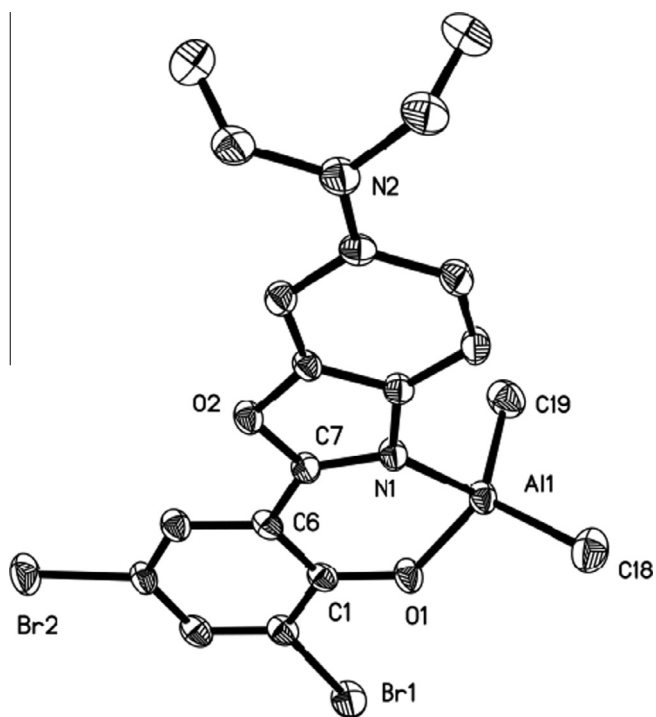


Fig. 1. The molecular structure of complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms and solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1–N1 1.960(3), Al1–O1 1.782(2), Al1–C18 1.950(4), Al1–C19 1.958(4), N1–C7 1.310(4), O1–C1 1.319(4), O1–Al1–N1 92.33(1), N1–Al1–C19 105.95(2), C18–Al1–N1 111.18(2), C18–Al1–O1 114.23(2), O1–Al1–C19 114.93(2), C18–Al1–C19 115.40(2).

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