



Sidearm effect on the (Pyrrolylaldiminato)aluminum initiated ring opening polymerization of ϵ -caprolactone



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ABSTRACT

A series of pyrrolylaldiminato ligands and the corresponding five-member-chelate aluminum complexes were prepared and characterized. These metal complexes contain side arms bearing oxygen, sulfur and SO_2 moieties, which can influence their catalytic properties. In the presence of one equivalent of benzyl alcohol initiator, these complexes can initiate well-controlled ring opening polymerization of ϵ -caprolactone with high activities. Most interestingly, the well-controlled behavior was maintained in the absence of the benzyl alcohol initiator.

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1. Introduction

Poly(lactide) (PLA) and poly(ϵ -caprolactone) (ϵ -PCL) are two of the most extensively explored biodegradable polyesters due to their appealing properties such as biocompatibility and biodegradability as well as the corresponding biomedical and pharmaceutical applications [1]. In this field, ring opening polymerization (ROP) of cyclic esters (lactide, ϵ -caprolactone, etc) mediated by metal-based complexes has proven to be a viable method to access high molecular weight polyesters. Currently, the industrial scale preparation of poly(lactide) utilizes such a process using stannous octoate as initiator/catalyst. However, this system suffers from several drawbacks, including low activity, potential toxicity, and poor control over molecular weight and stereochemistry. As a result, the development of highly active catalysts for the production of structurally well-defined biodegradable polymers remains an ongoing challenge.

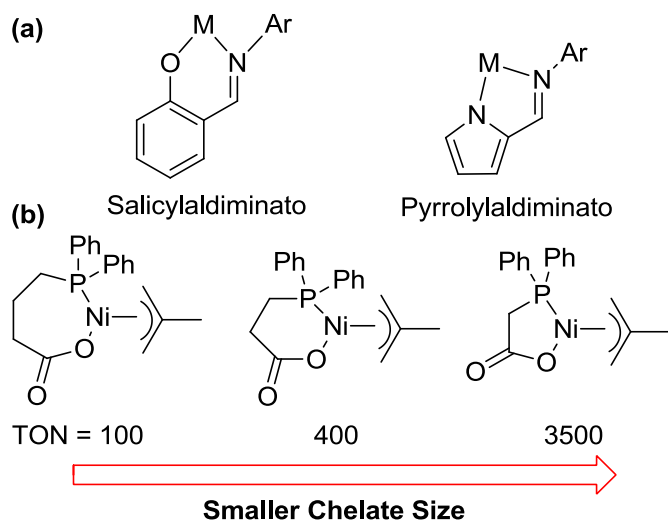
Olefin polymerization has enjoyed great successes since the Nobel Prize winning discovery of Ziegler and Natta catalysts. The major driving force in that field is the development of new ligands and new catalysts. For example, the study on α -diimine ligands enabled the development of Brookhart type catalysts, which could

generate a series of novel polyolefin materials that were not accessible previously [2]. The phosphine-sulfonate base palladium catalysts could copolymerize ethylene with a series of polar monomers [3]. Many of the ligands developed in olefin polymerization have been applied to prepare high performance catalysts for ROP of cyclic esters. For example, salicylaldiminato ligands were shown to be excellent ligands for zirconium and nickel complexes for olefin polymerization (Scheme 1a) [4]. Recently, there have been numerous reports on salicylaldiminato based zinc and aluminum complexes catalyzed ring opening polymerization (ROP) of cyclic esters [5]. In contrast, the structurally similar pyrrolylaldiminato ligands have not drawn as much attention. Both ligands are easily prepared and have similar steric effects. Moreover, their electronic and steric properties can be easily and finely tuned. The biggest difference is that the salicylaldiminato ligand forms six-membered ring system with metal ions, while pyrrolylaldiminato complexes tend to form five-membered rings. In the ring opening polymerization of cyclic esters, aluminum catalysts usually exhibit moderate efficiencies, which limited their potential industrial applications [6]. It was shown by Keim et al. that a reduction in chelate size led to dramatic increase in ethylene oligomerization activity in SHOP-type catalysts (Scheme 1b) [7]. Therefore, we were very interested in studying whether a smaller chelate sized pyrrolylaldiminato ligand would lead to highly active ring opening polymerization catalyst.

Roesky et al. reported the synthesis of pyrrolylaldiminato based

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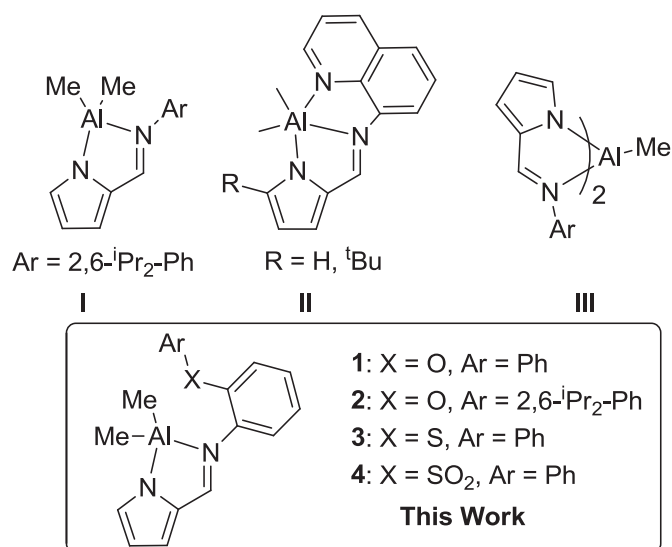


Scheme 1. (a) Salicylaldiminato and pyrrolylaldiminato based metal complexes; (b) Chelate size influence in the ethylene oligomerization with SHOP-type catalysts.

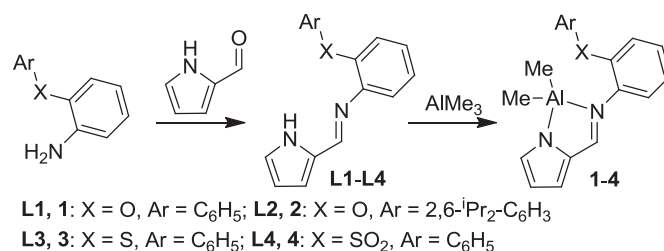
aluminum complexes in 2002 (Scheme 2, I) [8]. After that, several aluminum complexes bearing pyrrolylaldiminato ligand have been prepared and characterized [9]. However, the performance of these complexes in ring opening polymerization of cyclic esters has only recently been explored. For example, Wang et al. reported the polymerization of ϵ -caprolactone by an aluminum complexes bearing tridentate pyrrolylaldiminato-quinolin ligand (Scheme 2, II) [10]. In 2013, Phomphrai et al. reported the synthesis of a series of bis(pyrrolylaldiminato) aluminum complexes and studied their properties in polymerization of lactide (Scheme 2, III) [11]. Herein, we reported the synthesis and characterization of a series of pyrrolylaldiminato ligand bearing side-arms with different heteroatoms. Furthermore, the properties of their aluminum complexes (1–4) in the polymerization of ϵ -caprolactone were investigated.

2. Results and discussion

The pyrrolylaldiminato ligands (L1–L4) were prepared from the condensation reactions of commercially available 1H-pyrrole-2-



Scheme 2. Pyrrolylaldiminato-based aluminum complexes.



Scheme 3. Synthesis of the ligands and the aluminum complexes.

carboxaldehyde and the anilines at 89–95% yields (Scheme 3). Subsequently, the reactions with 1.1 equiv. of AlMe₃ led to the formation of the desired aluminum complexes (1–4) at 62–74% yields. These aluminum complexes were characterized by ¹H, ¹³C NMR and elemental analysis. Single crystals of complex 4 were grown from a concentrated toluene solution. The solid state structure of 4 was analyzed by X-ray diffraction (Fig. 1). The aluminum center adopts distorted tetrahedron geometry. The phenyl groups attached the side arm group (SO₂) is spatially close to the aluminum center. This indicates that the side arm substituents may be able to influence the properties of the metal complexes in polymerization.

These aluminum complexes are highly active in the ROP of ϵ -caprolactone when combined with 1 equiv. of benzyl alcohol. Almost quantitative conversion was observed at room temperature after 30 min (Table 1, entries 1–4). The kinetic studies were carried out and plotted as ln([M₀]/[M]) versus time shown in Fig. 2a. All polymerizations are pseudo first order in the concentration of ϵ -caprolactone. For complex 4, the molecular weight grows linearly versus monomer conversion, along with narrow PDI values (Fig. 2b). Most importantly, the polymer theoretical molecular weight values (*M_c*) agree very well with the molecular weight values (*M_n*) obtained from GPC analysis, suggesting the polymerizations are highly controlled. In addition, the PDI values are close to 1 for all the cases. When the polymerization was carried out at 80 °C, the process was not well controlled and the PDI values became relatively big (Table 1, entries 6–9). Interestingly, complex 3 bearing the sulfur containing side arm is the most active catalyst among the four aluminum complexes. The sulfur atom may be able

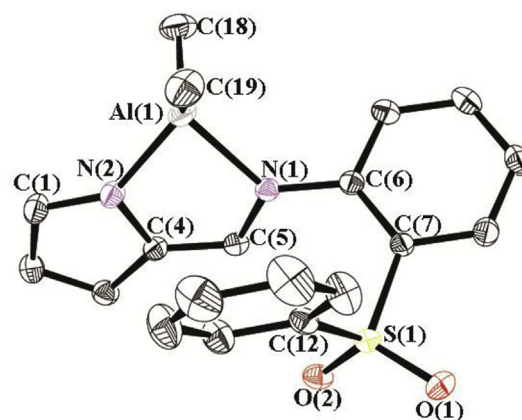


Fig. 1. The ORTEP diagram of 4. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)–N(1)1.9839(19), Al(1)–N(2)1.910(2), Al(1)–C(19)1.939(3), Al(1)–C(18)1.955(3), N(1)–C(5)1.309(3), N(1)–C(6)1.426(3), N(2)–C(4)1.391(3), N(2)–C(1)1.348(3), S(1)–O(2)1.4359(18), S(1)–O(1)1.4332(17), S(1)–C(7)1.781(2), S(1)–C(12)1.756(3), O(1)–S(1)–O(2)117.85(11), C(12)–S(1)–C(7)106.14(11), N(2)–Al(1)–N(1)84.19(8), C(19)–Al(1)–C(18)119.07(15), C(5)–N(1)–Al(1)109.84(15), C(4)–N(2)–Al(1)110.25(16), N(1)–C(5)–C(4)118.0(2).

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