



Group 1 salts of the imino(phenoxide) scaffold: Synthesis, structural characterization and studies as catalysts towards the bulk ring opening polymerization of lactides



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ARTICLE INFO

Article history:

Received 30 July 2014

Received in revised form 23 September 2014

Accepted 16 October 2014

Available online 23 October 2014

Keywords:

Group 1

Imino(phenoxide)

Lactide

ROP

ABSTRACT

A series of lithium, sodium and potassium salts containing various iminophenoxide ligand scaffolds have been successfully synthesized in high yields and purity. These complexes were completely characterized with different spectroscopic techniques and single crystal X-ray diffraction studies on a few of them. These compounds were found to be active towards the solvent free ring opening polymerization (ROP) of *l*-lactide (*L*-LA) and *rac*-lactide (*rac*-LA), yielding polymers with high number average molecular weight (M_n) and controlled molecular weight distribution (MWDs). Poly(lactic acid) (PLA) derived from the ROP of lactides using the Na complexes showed a close proximity between the observed M_n and theoretical molecular weight (M_n^{theo}). In addition, the MWDs were found to be narrow. These complexes were also found to be active for the ROP of lactides in the presence of benzyl alcohol as a co-initiator. The kinetics and mechanistic studies associated with these polymerizations have been performed and reported.

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1. Introduction

The rapid reduction of petrochemical resources has resulted in a decelerating impact towards basic research related to the synthesis of materials that rely upon petrochemical feedstock [1]. An increasing environmental and pollution concern regarding the ultimate fate of conventional polyolefins has provided active impetus towards research in the area of biodegradable polymer synthesis, especially towards the synthesis of PLA [1–4]. PLA has long been considered as an alternative environmentally friendly polymer due to its unique properties, such as bio-renewability, biodegradability and biocompatibility

[5–7]. It is synthesized from completely renewable natural resources such as corn and sugar-beet [5–7] and has been proved useful in a variety of biomedical applications such as sutures, dental devices, orthopedic fixation devices, controlled drug delivery systems, and tissue engineering [8,9]. The conventional method of producing PLA is through the catalytic ROP of the cyclic dimer of lactic acid namely lactide. Although the popular methodologies in the ROP reaction contain metal catalysts, recent activities in this area prove the role of organo catalytic reagents as other alternatives [10–19]. For *in vivo* biomedical applications of PLA, it is essential that the catalyst residues found in the synthesized PLA are potentially nontoxic. A conveniently adopted approach is to research new catalysts that contain metals identical to those found in the mammalian anatomy. As a result, the alkali metals like lithium, sodium and potassium have become lucrative for

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research involving catalyst synthesis for the ROP of lactides [20–24]. Catalysts containing other biocompatible metals such as zinc [25–28], magnesium [27–31], calcium [32–37] and iron [38,39] have been reported recently. Although simple alkoxides of lithium, sodium and potassium have shown activity for the ROP of lactides [40–51], those were accompanied by significant intervention as a result of undesirable transesterification reactions [52–54]. Lithium and sodium salts of 2,2'-ethylidenebis(4,6-di-*t*-butylphenol) (EDBPH₂) were proven to be very good catalysts in the ROP of lactides [55–57]. Polyamine stabilized sodium aryloxides [58] also have shown good activity towards the ROP of *rac*-LA. However, the derived PLA was predominantly atactic.

Our continued interest in the study of catalytic ROP reactions [59–66] prompted us to investigate the catalytic behavior of group 1 salts derived from the imino(phenoxide) ligands as viable catalysts towards the ROP of lactides.

2. Results and discussion

2.1. Synthesis and structural characterization

The imino phenol ligands were synthesized according to the procedures reported in the literature [67,68]. Reactions of one equivalent ⁿBuLi, NaH and KH with one equivalent of the various imino(phenoxide) ligands in toluene under ambient temperature resulted in the formation of homoleptic dimeric complexes **1–24** respectively (Scheme 1) accompanied by the elimination of butane or hydrogen gas. These reactions were monitored by recording the ¹H NMR of aliquots removed from the reaction mixture through the disappearance of the phenolic –OH signal from the neutral ligand which generally appears in the region of 13–14 ppm. These compounds were crystallized from suitable solvent mixtures like 1:1 pentane and toluene mixture or 1:1 pentane and THF mixture, and isolated in very high yields (more than 90%) and purity as yellow to yellowish-orange solids.

These compounds were characterized using spectroscopic techniques such as ¹H and ¹³C NMR and mass spectral analyses. Each compound contains two metals and two ligands. The NMR data suggest that all the complexes are symmetrical in nature. ¹H NMR of the compounds **1–24** reveals all the signals corresponding to the different moiety present in the ligands. The signals in **1–24** are slightly shifted to upfield as compared to the corresponding signals from the neutral ligands. The aromatic protons in these complexes **1–24** are shifted upfield around 0.1–0.3 ppm, whereas the aliphatic protons are shifted 0.1–0.4 ppm upfield. The imine protons from the CH=N fragment in **1–24** are shifted upfield around 0.1–0.5 ppm. A similar trend was observed from the analysis of ¹³C NMR spectrum of **1–24**. From the ⁷Li NMR spectrum of compounds **1–8**, (Supplementary Data) it was observed that for the compounds **1–4**, where the *ortho* and *meta* positions of the phenolic ring is substituted by bromine appeared at a higher δ value (δ = 2.64–2.00 ppm.) than tertiary butyl (^tBu) group substituted compounds **5–8** (δ = 1.84–1.40 ppm.). This is because the more electronegative

bromine atom deshielded the Li centre largely as compared to the ^tBu group. The analyses of these results suggest that in bromine substituted compounds (**1–4**), the lithium centre is more Lewis acidic as compared to the ^tBu substituted complexes (**5–8**). The results of electrospray ionization mass spectrometry (ESI–MS) suggest clearly the existences of such compounds are dinuclear in nature. The purity of **1–24** was completely assured by the close proximity of the elemental analyses values to the theoretical figures.

2.2. Single crystal X-ray diffraction studies

Single crystals of **6**, **8**, **12** and **20** were grown in a glove box at 23 °C over a period of two weeks through slow evaporation of different solvent mixtures (1:1 mixture of toluene and pentane for **6**, **8** and **20**, 1:1 mixture of THF and pentane for **12**). The single crystal X-ray analysis for the structures of **6**, **8**, **12** and **20** proved that these complexes are dimer in nature. The molecular structure of **6** is depicted in Fig. 1 and the crystal data for **6**, **8**, **12** and **20** is shown in Table 1. (For the molecular structure of **8**, **12** and **20**, see Supplementary Data).

Compound **6** and **8** crystallized in the monoclinic space group *P*2₁/*c* and *C*2/*c* respectively and were found to contain 4 molecules in the unit cell. Each lithium centre is tri-coordinated, bonded with two bridging oxygen atoms from the phenol groups and a nitrogen atom from the imine moiety. The bond lengths and bond angles suggest that the Li centre adopted a distorted planar geometry.

Compound **12** crystallized in the triclinic space group *P* – 1 and was found to contain coordinated THF molecules in the unit cell. Each sodium centre is tetra-coordinated, bonded to two bridging oxygen atoms from the phenol groups and oxygen atom from coordinated THF and a nitrogen atom from the imine moiety present in the ligand. The analysis of bond length and bond angles suggested that the sodium centre adopted a distorted tetrahedral geometry.

The potassium complex **20** crystallized in the triclinic space group *P* – 1 and contained one molecule in the unit cell. Each potassium centre is tri-coordinated and adopts a distorted planar geometry. Analysis of all the crystal data reveals that all the bond lengths and bond angles match well with the literature precedents [69–71].

2.3. Ring opening polymerization studies

Compounds **1–24** were tested for catalytic activity towards the bulk ROP of *rac*-lactide (*rac*-LA) and *l*-lactide (*L*-LA) respectively. These polymerizations were performed under solvent free condition at 140 °C in a sealed tube. The polymerization data is depicted in Tables 2 and 3 respectively.

These compounds were found to show potent catalytic activity towards the ROP of lactides. Complete conversion was achieved in a short span of time. The polymerization trend (Tables 2 and 3) reveals that the sodium (**9–16**) containing complexes showed more catalytic activity towards ROP. The potassium (**17–24**) containing complexes are less reactive than sodium complexes, whereas the lithium (**1–8**) complexes showed less reactivity. The ring opening polymerizations are anticipated to proceed

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