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## Microstructurally controlled polymers of *rac*-lactide by lithium complexes

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### ABSTRACT

A series of polylactides was prepared by stereoselective ring-opening polymerization of *rac*-lactide.

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## 1. Introduction

Poly(lactides) (PLAs) have been extensively exploited for a wide range of applications, such as sutures, disposal containers, bone fracture fixation devices, controlled release drug carriers, scaffolds, textiles, and tissue engineering [1,2]. In addition, the availability of monomer feedstocks from renewable resources has given PLAs an increasing prominence in the market place. The methods for the synthesis of these polymers now rely on the controlled ring-opening polymerization (ROP) of lactide by well-defined

metal initiators, which produce high-molecular weight polymers with good mechanical properties. Also, the stereochemistry of PLAs is a major factor that affects the mechanical properties and biodegradability of these materials [3]. Accordingly, stereoselective ring-opening polymerization of lactides has attracted much interest, leading to a variety of microstructures from the enantiomerically pure monomer, *racemic* mixture, or *meso* lactide [4].

An alternative to fossil feedstocks involves using chemicals from renewable resources and also developing new catalytic processes [5,6]. There are strong demands for the development of catalysts and processes that are environmentally clean, safe, stable, and efficient to address today's urgent need to reduce global environmental pollution and to develop clean and renewable energy resources. In this regard, the past few years have witnessed a renaissance in lithium-based catalysis. Their abundance,

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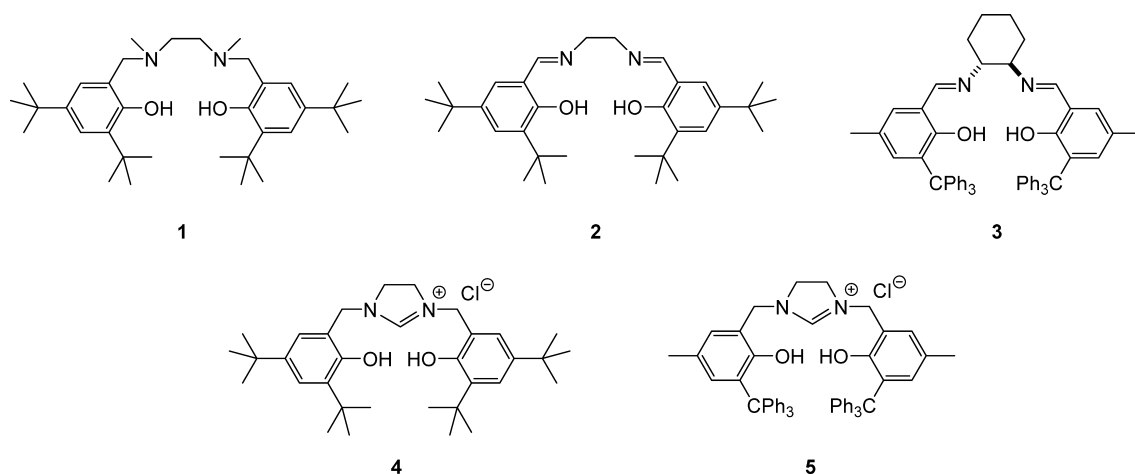


Fig. 1. Ligands screened in this study.

availability, and diversity make them useful for a variety of applications of industrial, economic, and environmental importance. For instance, the catalytic activity of lithium derivatives has been described for the ROP of different cyclic monomers, such as caprolactone, cyclic carbonates, and cyclic siloxanes. Lithium complexes are also able to produce PLA from lactide in a controlled manner [7]. For this purpose, several polydentate ligands were employed, such as phenolate scaffolds [8–14], or  $\beta$ -ketoiminate derivatives [15], usually in combination with an external alcohol. Despite numerous reports on ROP of *L*-lactide, very few studies are available in the literature that describe the stereoselective ROP of *rac*-lactide by metal alkali complexes [16]. Kasperczyk et al. first reported that in the presence of *t*BuOLi heterotactic-enriched PLA ( $P_r=0.75$ ) was obtained, albeit low conversion of *rac*-lactide was reported [17]. Since then, only iminophenolate lithium complexes could also produce PLA with similar heterotacticity [18].

Therefore, we were interested in investigating the ROP of *rac*-lactide with other lithium-based phenolate systems. As salen and salen ligands are interesting platforms which have not so far been evaluated for the ROP of lactide in the presence of lithium, our attention was drawn to the known salen [19] and salen ligands **1** and **2**, the new chiral salen derivative **3** and the new imidazolium salts **4** and **5** [tridentate *N*-heterocyclic carbenes (NHC) precursors] (Fig. 1). We report herein the synthesis of ligands **3–5** and the activity of the lithium complexes prepared *in situ* in the presence of ligands **1–5** for the heterotactic ROP of *rac*-LA.

## 2. Results and discussion

Ligand **3** was easily formed by condensation of 1,2-diaminocyclohexane and 2-hydroxy-5-methyl-3-trityl-benzaldehyde in excellent yield (94%). The synthesis of the new imidazolium salts **4** and **5** was also carried out by a conventional procedure. Symmetrical imidazolium salts are often prepared by cyclisation of a diamine with triethyl orthoformate in the presence of an appropriate salt [20]. Therefore, for the preparation of **4** and **5**, cyclisation of

the corresponding diamines **4a** and **5a** was performed at 80 °C for 20 hours in a chloroform/triethyl orthoformate (1:2) mixture with a catalytic amount of acetic acid. The presence of ammonium chloride was required to form the imidazolium chloride salts. Ligand **4** was obtained in a satisfying yield of 65%, while **5** was produced with a lower yield of 43%, probably due to the presence of a bulkier *ortho*-substituent (Scheme 1).

The complexes were prepared *in situ* by addition of 2 equiv of *n*BuLi in THF at low temperature. Single crystals suitable for X-ray structure determination of (**1**-Li)<sub>2</sub> were obtained from slow cooling of a warm THF/hexane solution. The molecular structure of (**1**-Li)<sub>2</sub> illustrates an aggregation mode in the solid state with four lithium atoms (Fig. 2). In the solid state, compound (**1**-Li)<sub>2</sub> possesses a ring-laddering conformation. This architectural structure of alkali metal chemistry has been discussed extensively in the literature [21,22]. We hypothesized that similar complexes with ligands **2** and **3** were obtained. We could also visualize the deprotonation of the phenols of the salen ligand **3** in the presence of 2 equiv of *n*BuLi by <sup>1</sup>H NMR (see Fig. S9). Regarding the NHC precursors **4** and **5**, no crystal structure was obtained but the <sup>1</sup>H NMR spectra of the *in situ* generated complexes showed that the imidazolium proton was deprotonated in the reaction conditions.

## 3. ROP of *rac*-LA with bimetallic complexes prepared *in situ*

As we recently reported the heterotactic ROP of *rac*-lactide using hetero-bimetallic Mg–Li and Zn–Li complexes in combination with bisphenol ligands, we decided to use the same reaction conditions in this study [23]. Therefore, the polymerization tests were performed in a THF/toluene (1:5) solvent mixture with 1 equiv of neopentyl alcohol (NpOH) and 50 equiv of *rac*-LA (Scheme 2). The bisphenol systems were first screened at room temperature. The resulting lithium-based complexes were active as they led to quantitative conversion of *rac*-LA in less than 15 minutes [the reaction times were not fully optimized therefore the turnover frequencies (TOF) up to 600 h<sup>-1</sup> are

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