

Novel tripodal complexes of Zinc and Cobalt: Highly active and thermally robust catalysts for controlled ring opening polymerization of *rac*-Lactide under solvent free conditions

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Poly(lactide) (PLA) is an extensively acclaimed biopolyester in its utility and biodegradability. Lactide (LA) is a monomer that is being derived from annually renewable resources is broadly utilized for the synthesis of PLAs. Ring opening polymerization (ROP) of lactide (LA) is considered to be the most promising and generally used method to produce poly(lactides). As the physical and mechanical properties of PLAs mostly depend on their molecular mass, the stereochemistry and polydispersity indexes; a controlled and efficient route to polymer synthesis is highly desirable. In recent years ring opening polymerization of lactide using discrete metal catalysts has gained considerable attention due to their ability to produce a wide range of lactide architectures.¹ Based on previous knowledge and mechanistic studies;² we designed a series of new biomimetic tripodal metal complexes of zinc(II) and cobalt(II) bearing O, N and P donor atoms could act as model of metalloenzymes (Fig 1). These complexes were tested in the ring opening polymerization of *rac*-LA in presence of alcohol as a chain transfer agent.

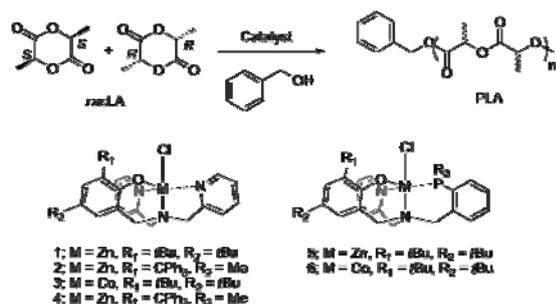


Fig 1. Tripod complexes of Zinc and Cobalt for the ring opening polymerization of *rac*-Lactide

Metalloenzymes are known to be highly atom efficient and selective catalysts for several chemical transformations.³ A tripodal ligand is particularly attractive as it resembles a constrained metalloenzyme active pocket and favors a facial approach of the monomer to the electrophilic metal centers. We envisioned that the nature of bulkier ligands than in a dipodal complex and the different

donor arms would bring unique characteristics to the reactivity patterns towards lactide polymerization.

Also the relatively bulky substituent around the metallic center prevents the complexes from nucleation and a reduction of catalyst activity. The crystal structure of the complexes proved that they are monomeric and adapt a trigonal bipyramidal geometry in solution state.

As solvent free polymerization is particularly significant in an industrial and green chemistry perspective,⁵ all the polymerizations were carried out in melt conditions at 130 °C. In the presence of benzyl alcohol as a reversible chain transfer agent, most of these complexes showed good to very high activity with controlled molecular mass and narrow polydispersity index. The most active complex (**2**) polymerized 2200 equivalents of lactide with a TOF of 8800 h⁻¹. This reactivity is superior over many other reported catalyst systems. The catalysts also showed very good thermal stability. These results suggest a number of new avenues in polymer catalysis and for biodegradable polymers.

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