

RESEARCH

Phenoxy-imine based Mononuclear Zn(II) Compounds: Applications as Polymerization Catalysts

Sourav Singha Roy¹ | Sriparna Sarkar¹ | Debashis Chakraborty^{1*} 

¹Department of Chemistry,
Indian Institute of Technology
Madras, Chennai 600036, India

*Corresponding author:
Prof. Debashis Chakraborty
E-mail: dchakraborty@iitm.ac.in
Tel.: +91 44 2257 4223

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ABSTRACT

The production of aliphatic polyesters (via ROP of cyclic esters) and aliphatic polycarbonates (via ROCOP of CO₂/epoxide) is an important synthetic pathway for the production of biodegradable and biocompatible polymers. The study focuses on the catalytic activity and selectivity of phenoxy-imine based zinc compounds for the ROP of cyclic esters (*rac*-LA and ϵ -CL) and ROCOP of carbon dioxide and CHO/PO. The monoligated and *bis*ligated zinc compounds have the same coordination number (four) but differed from each other in the binding mode of the ligand to the metal center (tridentate for monoligated and bidentate for *bis*ligated compounds) and thus the compounds adopt different symmetry. For the ROP of *rac*-LA, the monoligated zinc compounds gave isotactic-enriched PLA while the *bis*ligated zinc compounds gave heterotactic-enriched PLA. For the ROCOP of epoxide/CO₂, isotactic-enriched polycarbonates were obtained with a notable difference in catalytic activity with the variation of the number of ligands attached to the zinc center. In addition, a correlation is established between the percentage of carbonate linkage in the polycarbonate chain and the substituent attached to the phenolate core.

KEYWORDS

ROP, ROCOP, Phenoxy-imine, *rac*-LA, CO₂.

INTRODUCTION

The production of biodegradable polymers has gained significant attention from researchers as the synthetic polymers derived from petroleum feedstocks are non-renewable and the fossil fuel reserves used for their production are exhaustible. The ring-opening polymerization (ROP) of cyclic esters to produce aliphatic polyesters with improved properties in terms of molecular weight, molecular weight distribution and tacticity is an efficient method over conventional polycondensation pathway which usually requires high temperature and produces polymers with comparatively low-molecular weight [1]. The aliphatic polycarbonates derived from ring-opening copolymerization (ROCOP) of CO₂ with epoxide cannot compete with Bisphenol A (BPA)-based aromatic polycarbonates in terms of properties, but they have been put to different uses such as data storage devices, biomedical applications, and food packaging. The

increased dependence on aliphatic polycarbonates (APCs) has reduced the use of highly poisonous phosgene gas used in the production of BPA based polycarbonates [2].

The ROP of *racemic*-lactide (*rac*-LA) and ϵ -caprolactone (ϵ -CL) has been investigated by different research groups (**Fig. S3, Supporting Information**) [3] under melt conditions as well as in the presence of different solvent (toluene, THF, CH₂Cl₂). It was observed that the polymerization was more controlled in the solution conditions rather than the melt state as evident from narrow dispersity values [4]. The majority of phenoxy-imine based zinc complexes reported to date have shown excellent catalytic activity for the ROP of cyclic esters in the presence of exogenous alcohol [5]. The advantage of zinc-based catalyst systems is that the zinc metal is biocompatible and thus polymers generated have no harmful metal residues present in the polymer. The different possible tacticity arises in the polymeric chain when the monomer has stereogenic center [6]. For the ROP

of *rac*-LA, the reported literature showed an excellent correlation between the tacticity of the PLA chain and steric and electronic environment present around the metal center but little attention has been given regarding the correlation of tacticity to the symmetry associated with the metal compounds [7].

The ROCOP of epoxide/CO₂ was for the first time reported in 1969 by Inoue and coworkers [8]. They employed heterogeneous catalyst system based on ZnEt₂/H₂O for ROP of propylene oxide (PO) and CO₂. The catalytic activity was low but the polymer obtained showed 88% carbonate linkage in the polycarbonate chain. The homogeneous zinc-based catalyst for the ROCOP of epoxide/CO₂ was reported by Coates and coworkers in 2002 [9]. Over the years the studies reported by different research groups have shown that for ROCOP of CO₂/epoxide the most crucial parameters for the copolymerization include catalyst, optimum temperature, pressure, loading of cocatalyst and nature of cocatalyst. The mononuclear zinc-based catalyst has been seldom reported in the literature for the ROCOP of epoxide/CO₂ [10].

In the present work, the catalytic activity of the mononuclear Zn(II) compound is explored. A correlation is established between the tacticity of poly(lactic acid) (PLA) chain and the symmetry adopted by the metal compound. For the ROCOP of epoxide/CO₂, the connection between percentage of the carbonate linkage in the linear chain polycarbonate to the substituent attached to the phenolate core and the coordination mode of the ligand is explained.

EXPERIMENTAL

All the moisture and air sensitive reactions were performed in an argon-filled glove box. The monomer *rac*-LA was sublimed and stored inside glove box. The epoxide (CHO and PO) and ϵ -CL were dried over calcium hydride and freshly distilled before use. The NMR was recorded in Bruker Avance 400/500 NMR instrument and processed using Topspin software. Other details in Supporting Information.

RESULTS AND DISCUSSION

The *bis*ligated zinc compounds (**1-4**) and the monoligated zinc compounds (**5-8**) were prepared using diethylzinc (Et₂Zn) and Ethylzinc chloride (EtZnCl) as the metal precursor (**Scheme 1**). As evident from the stacked NMR spectra (**Figure S1** and **S2** Supporting Information) the disappearance of hydroxyl signal in the zinc compounds as compared to the free ligand indicated coordination of phenolate oxygen to the zinc atom. The coordination of imine nitrogen to the zinc atom resulted in the upfield shift of the imine hydrogen signal. For the *bis*ligated zinc compounds, the two iminophenolate moieties coordinate almost equivalently to the zinc center as evident from the single set of NMR signals for two iminophenoxide groups indicating the zinc compounds (**1-4**) adopt C_{2v} symmetry in solution. For (**1-4**), the four coordination around zinc atom

was satisfied from one nitrogen atom and one oxygen atom coming from each ligand. For the monoligated zinc compounds, (**5-8**) the two coordination of zinc atom is satisfied by nitrogen (N) and oxygen (O) of the iminophenoxide ligand, the third coordination site is occupied by chlorine atom coming from the metal precursor and the sulphur atom from imine side arm of the phenoxy-imine ligand fulfil the fourth coordination of the zinc center. The most interesting observation that arise due to coordination of sulphur to the zinc center is the splitting pattern of the methylene proton present in the side arm attached to the imine nitrogen atom. For **5-8**, the methylene protons give two separate signals as the protons become completely diastereotopic due to the coordination of sulphur to the zinc center that hinders any free rotation of the imine side arm (**Fig. 1B**). For compounds **1-4**, as the heteroatom sulphur is not coordinated to the zinc center the methylene protons for **3** and **4** show only one signal for the two methylene protons while for **1** and **2** the methylene proton signal is split into AB_q as the two protons become diastereotopic since the bulky *tert*-butyl group present at the *ortho* position of the phenolate core hinder the rotation of the imine side arm (**Fig. 1A**).

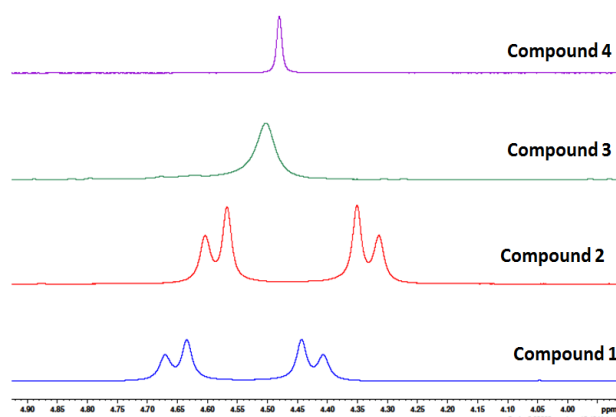


Fig. 1A. Stacked ¹H NMR of CH₂ portion compound **1-4**.

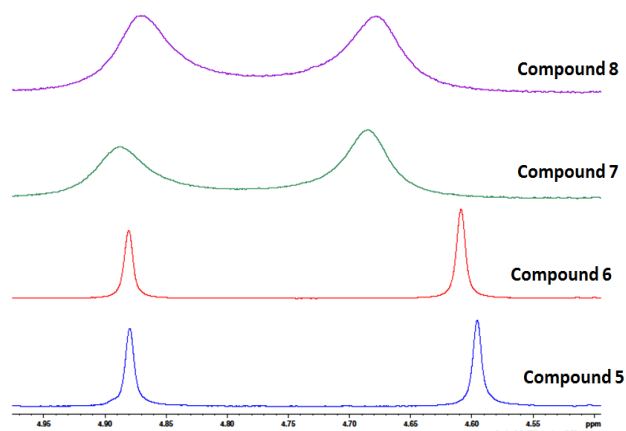
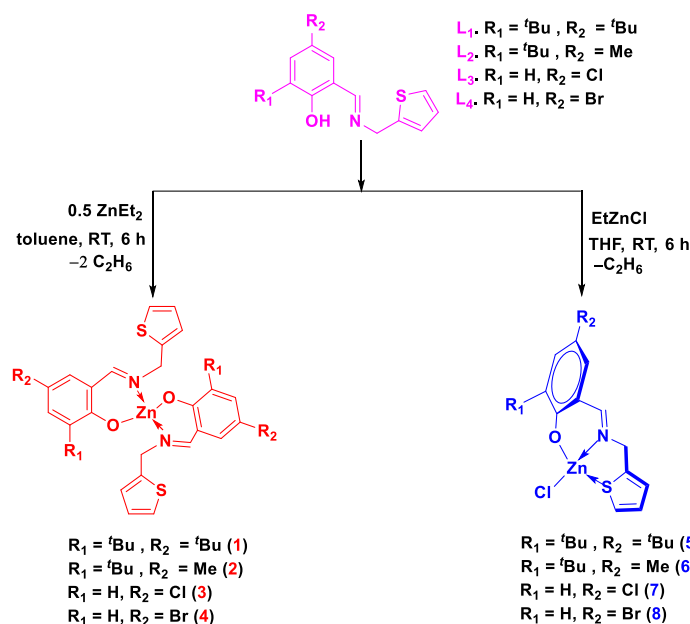


Fig. 1B. Stacked ¹H NMR of CH₂ portion compound **5-8**.



Scheme 1. Preparation of compounds 1-8.

The catalytic activity of the zinc compounds was investigated for the ROP of cyclic esters and ROCOP of epoxide/ CO_2 . For both ROP and ROCOP the driving force for the reaction is ring-strain of the cyclic monomers. The high-ring strain of the three membered epoxide helps to overcome the thermodynamic stability of carbon dioxide (CO_2) and ROCOP become feasible. The six-membered ring is more stable compared to seven-membered ring and thus ROP with zinc compounds was faster with ε -CL than *rac*-LA.

For the ROP of *rac*-LA and ε -CL it was observed that the *bis*ligated zinc compounds (1-4) showed higher catalytic activity compared to monoligated zinc compounds (5-8) as the TOF values were higher (Fig. 2) and (Table S1 and Table S2, Supporting Information) The difference in the catalytic activity can be accounted by considering two factors — (a) restricted rotation of imine side arm, (b) Lewis acidity of the zinc center. For compounds (5-8), the rotation of the side arm attached to the imine nitrogen atom is completely restricted due to which the approach of the monomer to the metal center is more hindered compared to compounds (1-4) where the imine side arm can rotate easily. In addition, the coordination of two ligands to the zinc center enhances the Lewis acidity of the soft Zn(II) center and thus zinc center becomes more electrophilic that allows easy coordination of monomers to the zinc center. It is also observed that the ROP of *rac*-LA and ε -CL with both *bis*ligated and monoligated compounds, the TOF value was highest when the phenolate core was substituted with the electron-withdrawing group as it enhances the Lewis acidity of the zinc center. Since the monomer lactide has stereogenic center it is expected that tacticity will arise in the PLA chains. It was observed that the *bis*ligated zinc compounds gave heterotactic-enriched PLA while the

monoligated zinc compounds gave isotactic-enriched PLA. The coordination environment around the zinc center for monoligated zinc compounds is completely unsymmetrical and thus the catalyst somehow mimics a chiral catalyst in spite of ligand being achiral and thus allows only a single enantiomer of lactide to approach the growing polymer chain end resulting in isotactic-enriched PLA. On the other hand, *bis*ligated metal compounds being more symmetrical resulted in heterotactic-enriched PLA. Compound 1-4, having a C_{2v} symmetry with a σ mirror plane containing the Zn atom and bisecting the O–N plane, prompting the approach of *R*, *R*- and *S*, *S*- fractions of *rac*-LA monomer to the metal center in an alternating manner produced heterotactic PLA. On the other hand, unsymmetrical 5-8 precisely select one enantiomer of LA producing isotactic PLA. The ^1H NMR and MALDI-TOF analysis of oligomers (Fig. S4 and S5, Supporting Information) suggested that the ROP of *rac*-LA results through the coordination–insertion mechanism.

The ROCOP of PO/CHO with CO_2 was carried in the presence of ionic cocatalyst TPPCl with [Epoxide]:[Catalyst]:[Cocatalyst] = 1000:1:1 under 80 °C and 40 bar CO_2 pressure for CHO and 40 °C, 60 bar CO_2 pressure for PO. The data obtained from the copolymerization studies revealed that the percentage of carbonate linkage in the polycarbonate chain was more for the monoligated zinc compounds than *bis*ligated zinc compounds. The higher Lewis acidity of *bis*ligated zinc compounds resulted in the successive approach of epoxide to the zinc center resulting in consecutive ring-opening of epoxide leading to polyether content in the polymer chain. The PO molecule being less bulky compared to CHO, the polymerization was easy as evident from high TOF values. In addition, the percentage of carbonate linkage was higher in the polycarbonate chain

when the phenolate core was substituted with an electron-donating group, for both monoligated and bisligated zinc compounds (Table S3 and Table S4, Supporting Information). The preliminary experiments done with monosubstituted and disubstituted aluminum compounds supported by same phenoxy-imine ligand gave similar results as obtained for zinc compounds.

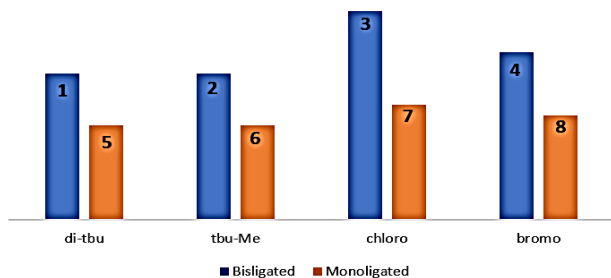


Fig. 2. TOF values for ROP of *rac*-LA with 1-8.

CONCLUSION

The two series of zinc compounds were prepared with one and two phenoxy-imine ligands attached to the zinc center. For the monosubstituted zinc compounds, the coordination around the zinc center is satisfied by four different groups and thus the catalyst becomes unsymmetrical that resulted in isotactic-enriched PLA, while disubstituted compounds being more symmetrical resulted in the formation of heterotactic-enriched PLA. For the ROP of cyclic esters, the TOF values were higher for the disubstituted zinc compounds than monosubstituted zinc compounds due to the higher Lewis acidity of the zinc center. On the other hand, for ROCOP studies the monosubstituted compounds resulted in high TOF values and higher carbonate linkage in the polycarbonate chain as the Lewis acidity of zinc center is such that approach of epoxide, as well as carbon dioxide, is favorable as higher Lewis acidity would disfavor the approach of CO₂. In future we are interested to check the potential effects of more Lewis acidic, group 13 and group 2 metals in ROP of *rac*-LA and ROCOP of epoxides/CO₂.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

SUPPORTING INFORMATION

Supporting informations are available online at journal website.

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AUTHORS BIOGRAPHY



Sourav Singha Roy completed his B.Sc. and M.Sc. degree in Chemistry. Currently he is pursuing doctoral research at Indian Institute of Technology, Madras under the supervision of Prof. Debashis Chakraborty. His major research focus is in the areas of Organometallics for polymer synthesis, homogeneous catalysis and CO₂ sequestration.



Sriparna Sarkar completed her B.Sc. and M.Sc. degree in Chemistry from Jadavpur University, Kolkata. She started her Ph.D. research at Indian Institute of Technology, Madras under the supervision of Prof. Debashis Chakraborty in 2018. Her PhD project focuses on development of catalytic systems for ring-opening polymerization reactions.



The Organometallic and Polymer Chemistry group at the Indian Institute of Technology Madras is headed by **Debashis Chakraborty** who is currently a faculty at the Department of Chemistry. The major research focus of this group lies in the areas of organometallics for polymer synthesis, homogeneous catalysis, CO₂ sequestration and water activation. He is a Fellow of IAAM since 2022. He is a Chartered Scientist (CSci) with professional registration with the Science Council, UK.



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GRAPHICAL ABSTRACT

