

Research paper

Structurally diverse dysprosium and yttrium complexes containing an amine-bis(benzotriazole phenolate) ligand: Synthesis, characterization and catalysis for lactide polymerization



Kuan-Chin Lee, Hui-Ju Chuang, Bor-Hunn Huang, Bao-Tsan Ko, Po-Heng Lin*

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan

ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 22 June 2016

Accepted 23 June 2016

Available online 24 June 2016

Keywords:

Dysprosium

Yttrium

Air-stable catalyst

ROP

ABSTRACT

The syntheses, structures and catalytic properties for lactones polymerization of six new dysprosium and yttrium complexes containing an amine-bis(benzotriazole phenolate) ($C^{INN}BiBTP$) ligand with different protonated/deprotonated forms of ligands are reported. Complexes $[M(C^{INN}BiBTP-H_3)(NO_3)_4]$ (M: Dy(**1**) and Y(**2**)) were obtained from the reaction of the $C^{INN}BiBTP-H_2$ proligand with $M(NO_3)_3 \cdot 6H_2O$ without an additional base in a dichloromethane (DCM)/acetonitrile (MeCN) mixer. Applying trimethylamine (Et_3N) to deprotonate the proligand, bis-nitrate complexes $[M(C^{INN}BiBTP-H)(NO_3)_2(H_2O)] \cdot THF$ (M: Dy (**3-THF**) and Y(**4-THF**)) were obtained from a mixture solution of with tetrahydrofuran (THF) and DCM. Further tuning base-to-proligand ratio followed by MeOH solution yielded mono-nitrate complexes $[M(C^{INN}BiBTP)(NO_3)(MeOH)_2]$ (M: Dy(**5**) and Y(**6**)). Air-stable $BiBTP$ -ligated complexes **1–6** were demonstrated to be active catalysts for lactide (LA) polymerization, and the catalytic performance for these complexes was compared. Particularly, yttrium complex **6** with two coordinating methanol molecules was found to effectively catalyze bulk polymerization of LA in a controlled character due to the presence of alcohol initiators.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Considerable efforts have been devoted to the development of metal-catalyzed ring-opening polymerization (ROP) due to the productions of environmentally benign polymers, such as poly(ϵ -caprolactone) (PCL), poly(β -butyrolactone) (PHB) and poly(lactide) (PLA) as well as the related copolymers [1,2]. Such biodegradable polyesters also have been regarded as a promising replacement of traditional petrochemical based polymers. Consequently, ROP using various catalytic systems with the single-site metal catalysts modified by diverse ancillary ligands has been extensively investigated, and several of them are able to achieve great catalytic activities in a controlled manner as well as high stereoselectivity for the utilization of racemic monomers [3–10]. In particular, well-defined metal complexes incorporated by amine bridged-phenolate ligands attract increasing attention because of the successful catalytic systems of amine-bis(phenolate) rare-earth metal complexes in the stereoselective ROP of *rac*- β -butyrolactone (*rac*- β -BL) and *rac*-lactide (*rac*-LA) [11]. For instance, a series of aminoalkoxybis(phenolate) yttrium complexes were developed

by Carpentier and co-workers; such a yttrium amide with the bulkier *ortho* substituents installed on the amine-phenolate ligands was shown to be a high active initiator with great stereocontrol for producing highly heterotactic PLAs [12,13]. Recently, Yao and Shen et al. reported group 3 metal catalysts featuring diamine-bis(phenolate) ligands, and these lanthanide alkoxides (metal = Yb or Er) were found to display not only outstanding performances but also the highest stereoselectivity ($P_r = 0.99$) for heteroselective polymerization of *rac*-LA [14–16]. These group 3/rare-earth catalytic systems with bis(phenolate) ligands gave advantages of good activity, excellent controllability and high heterotactic selectivity of lactide polymerization. Although there are many other ROP catalysts claimed to be quite stable towards moisture [17–19], no air-stable rare-earth complex bearing such ligands that catalyze ROP effectively has been reported to date. It becomes of our great interest and importance to develop air- and moisture-stable group 3 and/or lanthanide catalyst to polymerize lactones. Inspired by excellent catalysis results from the aforementioned metal catalysts based on amine bridged-phenolate ligands, we are interested in developing a new type of multidentate amine-bis(phenolate) derivatives containing the nitrogen-heterocyclic donors, benzotriazole groups. As a result, novel amine-bis(benzotriazole phenoxide) ligands including the pendant arm of dimethylamine or piperidinyl

* Corresponding author.

E-mail address: poheng@nchu.edu.tw (P.-H. Lin).

group have been synthesized recently; tri-nuclear magnesium alkoxides [20] and oxo-bridged bimetallic group 4 metal complexes [21] bearing such ligands were demonstrated to be active and versatile catalysts toward ROP of cyclic esters as well as coupling of CO₂ with cyclohexene oxide. These results prompted us to further investigate the potential utilization for ROP catalysis of trivalent lanthanide (Ln^{III}) complexes derived from amine-bis(benzotriazole phenolate) (**BiBTP**) ligands and ancillary nitrate groups. On the other hand, the synthesis of series lanthanide complexes with the same ligand but modifying the core structure continues to be a challenge due to the variable and high coordination numbers as well as poor directionality [22–23]. Applying the **BiBTP** ligand with *N, O, N, O, N, N*-based multichelating sites may offer a good control of the coordination environment [24–26]. Herein, we report the synthesis and structural determinations of dysprosium mononuclear complexes containing a **BiBTP** ligand with different coordination modes. Although the selectivity and activity of the complexes are not pronounced, all the products are insensitive to air and moisture and easily prepared under atmosphere. This is the first example using well-defined Dy complex to be a catalyst for ROP of lactide in our knowledge. The numbers of coordinated nitrate molecules varied from **1** to **4** in order to further understand the correlation between structure and catalytic properties. The yttrium analogs were also synthesized for comparing their catalytic properties of lactide polymerization.

2. Results and discussion

2.1. Synthesis and characterization

The amine-bis(benzotriazole phenol) pro-ligands (^{C1NN}**BiBTP**-H₂ & ^{C1PP}**BiBTP**-H₂) have been applied for the complexes synthesis of alkaline earth metal and transition metal, such as Mg, Ti, Zr and Hf, and all mononuclear, di-nuclear and tri-nuclear complexes were coordinated with the fully deprotonated ligand, **BiBTP** [20,21]. It is noteworthy that this kind of ligand precursor, such as ^{C1NN}**BiBTP**-H₂ can easily undergo diverse protonated-deprotonated forms with various charges in neutral or basic reaction condition (Scheme 1). This provides rich and versatile coordination chemistry with rare-earth metal centers. Accordingly, reaction of the ^{C1NN}**BiBTP**-H₂ with dysprosium(III) and yttrium(III) nitrate precursors, [M(NO₃)₃·6H₂O] (M: Dy and Y) under varying reaction conditions yielded six novel mononuclear complexes as shown in Scheme 2.

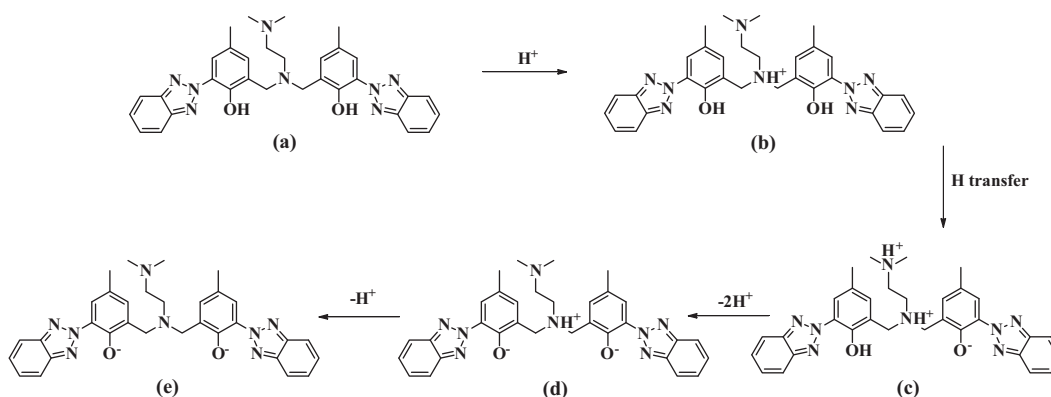
Mononuclear complex, [M(^{C1NN}**BiBTP**-H₃)(NO₃)₄] (M: Dy (**1**) and Y (**2**)), was obtained in a MeCN/DCM mixer. Mixed solvents are necessary for this reaction because of the considerations for solubility of M(NO₃)₃·6H₂O and the proligand. The ligand in complexes

1 and **2** was formally protonated due to the lack of base in the synthetic condition. The proton may come from the hydrate since the pK_a values of solvents are both higher than H₂O. The differences in the ligand coordination can arise from the addition of a base in the reaction mixture due to the deprotonated ligand. The chosen organic base, Et₃N, deprotonates the ^{C1NN}**BiBTP**-H₂ ligand, promoting the metal ion coordination in the N, O, O, N pocket of the negatively charged ^{C1NN}**BiBTP** ligand. To further investigate structural diversity of complexes with deprotonated ligand, the synthetic condition with the additional base was processed. Indeed, under the synthetic conditions of [Dy^{III}]/[^{C1NN}**BiBTP**-H₂]/[Et₃N] = 1/1/1 in a THF/DCM mixing solution, a structurally diverse mononuclear complex, [M(^{C1NN}**BiBTP**-H)(NO₃)₂(H₂O)]·THF (M: Dy (**3**·THF) and Y (**4**·THF)), could be synthesized. The same products were also isolated in different base-to-proligand ratio but the suitable crystals for single-crystal XRD only afforded in the 1:1 base-to-proligand ratio.

The presence of alcohol such as MeOH, BnOH or ^tPrOH can be initiators and further improve the activity and molecular weight controllability of ROP [27]. However, the role of coordinated MeOH in metal-catalyzed ROP was not fully understood. We used MeOH as a solvent in the syntheses in order to obtain the mononuclear complex with coordinate MeOH molecules. Comparing the catalytic properties of series mononuclear metal complexes with and without coordinating MeOH can further understand how MeOH effects the activity and selectivity of ROP catalysis. Reaction of ^{C1NN}**BiBTP**-H₂ with two equivalents of M(NO₃)₃·6H₂O (M = Dy and Y) in the presence of two equivalent Et₃N in a MeOH solution gave the mononuclear complex, [M(^{C1NN}**BiBTP**)(NO₃)(MeOH)₂] (M: Dy (**5**) and Y (**6**)). Pale yellow crystals of **5** were grown from the mother liquor over half hour at ambient temperature. A slower growth of suitable crystals for single-crystal XRD was obtained by the dilute solution. MeOH is crucial for the formation of complexes **5** and **6** since two terminal MeOH molecule coordinated on metal center. Moreover, acid–base equilibria (ligand–base equilibria) will be different in aprotic and protic solvents [28]. Using MeOH instead of THF/DCM may also offer an opportunity to obtain the complex contained a ligand of form (e). The reaction mixture contained an excess of Dy^{III} ions because the 2:1 metal-to-proligand ratio gave a higher yield and the better quality crystals than those of a 1:1 metal-to-proligand ratio. All complexes were obtained as air-stable crystalline solids and were fully characterized on the basis of IR spectra and elemental analysis as well as single-crystal X-ray crystallography.

2.2. Crystal structures of complexes 1–6

Single crystal structure analysis reveals that complexes **1** and **2**, **3** and **4**, **5** and **6** are isostructural, respectively. The X-ray structures



Scheme 1. Different deprotonated forms of the ligand.

Download English Version:

<https://daneshyari.com/en/article/1305416>

Download Persian Version:

<https://daneshyari.com/article/1305416>

[Daneshyari.com](https://daneshyari.com)