

Short communication

# Titanium complexes bearing benzotriazole iminophenolate ligands as efficient catalysts for ring-opening polymerization of cyclic esters

Dei-Cheng Liu<sup>a</sup>, Chen-Yu Li<sup>a,b</sup>, Pei-Hua Lin<sup>a</sup>, Jhy-Der Chen<sup>a</sup>, Chen-Yen Tsai<sup>a,\*</sup>,  
Chia-Her Lin<sup>a,\*</sup>, Bao-Tsan Ko<sup>a,c,\*\*</sup>

<sup>a</sup> Department of Chemistry, Chung Yuan Christian University, Chung-Li 32023, Taiwan

<sup>b</sup> Technology Research Development, Plastic Industrial Development Center, Taichung 407, Taiwan

<sup>c</sup> Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan

## ARTICLE INFO

## Article history:

Received 26 December 2017

Received in revised form 17 January 2018

Accepted 19 January 2018

Available online xxxx

## Keywords:

Titanium complex

Catalyst

Benzotriazole iminophenolate ligand

Ring-opening polymerization

$\epsilon$ -caprolactone

Lactide

## ABSTRACT

Titanium catalysts incorporated by imino-benzotriazole phenolate (**IBTP**) ligands (<sup>C1NN</sup>**IBTP**, <sup>C1Fu</sup>**IBTP** and <sup>C1NO</sup>**IBTP**) were synthesized and structurally characterized. The reaction of Ti(O<sup>i</sup>Pr)<sub>4</sub> with <sup>C1NN</sup>**IBTP**-H (1.0 molar equiv.) in toluene produced hexa-coordinated mono-adduct titanium complex [(<sup>C1NN</sup>**IBTP**)Ti(O<sup>i</sup>Pr)<sub>3</sub>] (**1**). However, six-coordinated bis-adduct Ti complex [(<sup>C1Fu</sup>**IBTP**)<sub>2</sub>Ti(O<sup>i</sup>Pr)<sub>2</sub>] (**2**) or [(<sup>C1NO</sup>**IBTP**)<sub>2</sub>Ti(O<sup>i</sup>Pr)<sub>2</sub>] (**3**) resulted from treatment of Ti(O<sup>i</sup>Pr)<sub>4</sub> with <sup>C1Fu</sup>**IBTP**-H or <sup>C1NO</sup>**IBTP**-H in CH<sub>2</sub>Cl<sub>2</sub> using a Ti to ligand precursor ratio of 1:2. Catalytic studies for ring-opening polymerization of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) or L-lactide utilizing complex **1** were detailedly investigated. Titanium complex **1** was shown to effectively catalyze the  $\epsilon$ -CL polymerization not only in a “controlled” fashion but also an “immortal” manner, giving narrowly dispersed polymers having the expected molecular weights.

© 2018 Elsevier B.V. All rights reserved.

Metal-promoted ring-opening polymerization (ROP) of lactones remains a promising topic in the field of polymerization synthesis because of its capability for preparations of stereocontrolled and high-molecular weight environmentally friendly polyesters, such as poly( $\epsilon$ -caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers. Accordingly, numerous effective homogeneous catalysts/initiators which were designed and developed as discrete metal complexes coordinated by appropriate ancillary ligands have been reviewed over the past few decades [1–16]. Of these investigations, metal catalysts/initiators based on nitrogen heterocycle-containing phenolate derivatives have received growing attention since this kind of ligand scaffolds can offer at least one *N,O*-bidentate bonding to modify the electronic and steric effect of metal center(s) of such complexes [16]. For instance, a series of benzotriazole phenolate (**BTP**)-supporting titanium alkoxides were synthesized and structurally characterized [17], and such well-defined titanium complexes demonstrated well catalytic performance towards the ROP of  $\epsilon$ -caprolactone ( $\epsilon$ -CL) and lactide (L-LA) with the ‘controlled’ and ‘immortal’ manners.

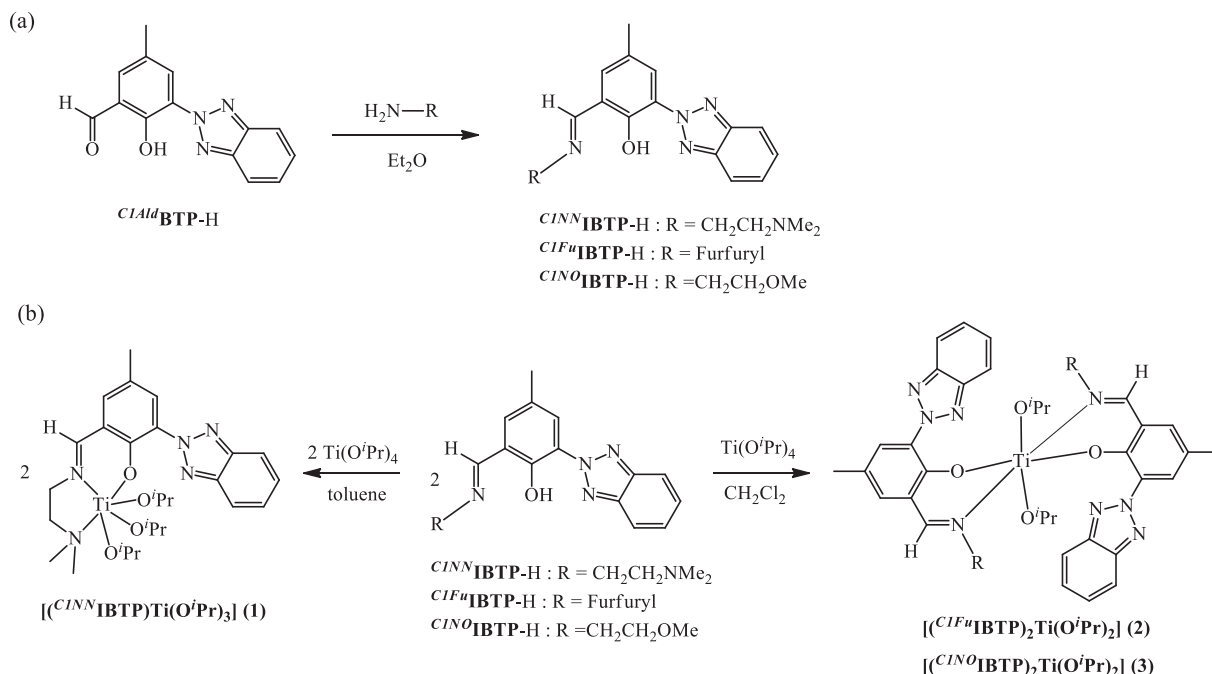
Inspired by the satisfactory catalytic systems originated from **BTP** derivatives, we were motivated to further develop the functionalized **BTP** ligands that could provide more effective denticity to stabilize metal atom(s). As a result, a family of imino-**BTP** (**IBTP**) derivatives via the two-step synthetic procedure without a chromatographic technique were prepared [18,19], and di zinc complexes incorporating such ligands were proved to be very active catalysts for the  $\epsilon$ -CL polymerization with high catalytic activity (55 °C, 15 min, monomer conversion >99%) and good controlled character (PDI < 1.30) [19]. However, no **IBTP**-related alkoxide complex of group 4 was reported for ROP catalysis to date, and minor changes of the metal fragment in the **IBTP**-based complexes might affect their bonding mode and catalytic efficiency of lactones polymerization. In this study, we present the synthesis and characterization of **IBTP**-ligated titanium complexes as well as their use in the ROP catalysis of  $\epsilon$ -CL and L-LA polymerization.

The synthetic routes of imino-benzotriazole phenol ligand precursors (<sup>C1NN</sup>**IBTP**-H, <sup>C1Fu</sup>**IBTP**-H and <sup>C1NO</sup>**IBTP**-H) and their corresponding titanium alkoxides **1–3** are shown in Scheme 1. Such <sup>R</sup>**IBTP**-H derivatives (*R* = **C1NN**, **C1Fu** and **C1NO**) were readily synthesized in high yield (>80%) on condensation of <sup>C1Al</sup>**BTP**-H and a series of amines (1.1 equiv.) with different pendant-functionalized groups in Et<sub>2</sub>O [18,20–21]. Alcohol elimination of titanium *tetra*-alkoxide precursor with **IBTP** pro-ligands was accomplished to generate alkoxy titanium complexes bearing imino-benzotriazole phenolate derivatives. The reaction of 2-(2H-benzotriazol-2-yl)-6-(((2-(dimethylamino)ethyl)

\* Corresponding authors.

\*\* Correspondence to: B.-T. Ko, Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan.

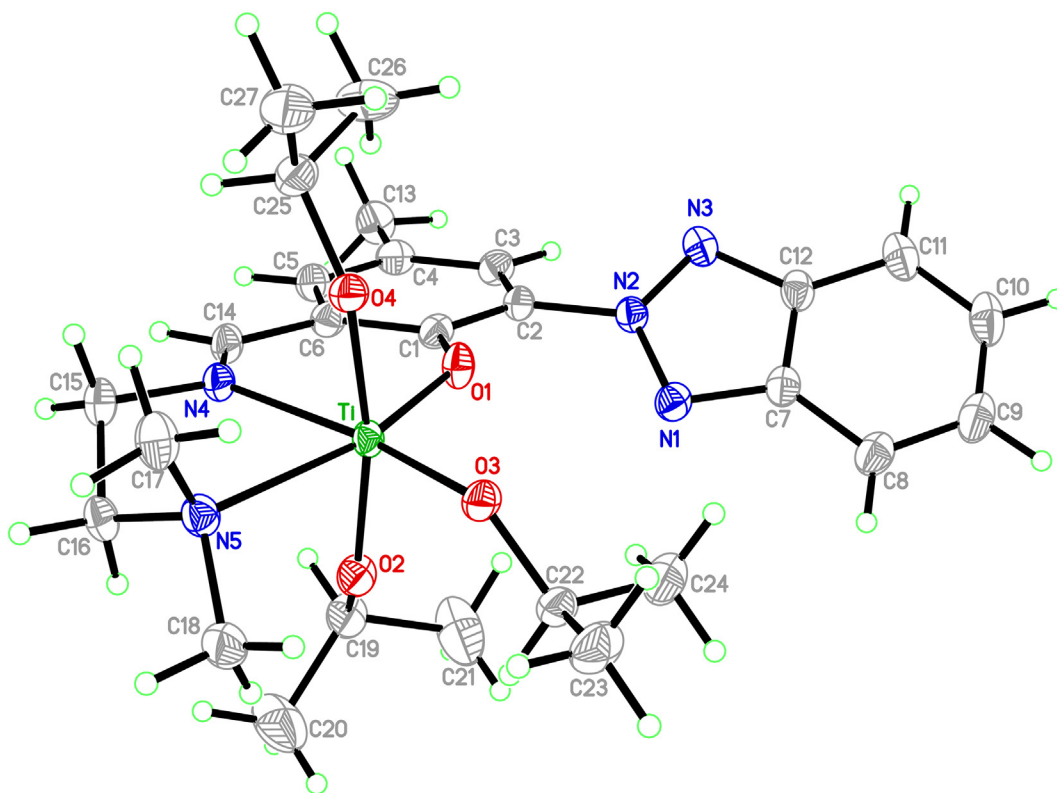
E-mail addresses: [chenyentsai@cycu.edu.tw](mailto:chenyentsai@cycu.edu.tw) (C.-Y. Tsai), [chiaher@cycu.edu.tw](mailto:chiaher@cycu.edu.tw) (C.-H. Lin), [btko@dragon.nchu.edu.tw](mailto:btko@dragon.nchu.edu.tw) (B.-T. Ko).



**Scheme 1.** Synthetic routes of (a) ligand precursors,  $\text{C1NNIBTP-H}$ ,  $\text{C1FuIBTP-H}$  and  $\text{C1NOIBTP-H}$  as well as (b) titanium complexes 1–3.

imino)methyl)-4-methylphenol ( $\text{C1NNIBTP-H}$ ) with 1.0 molar equiv. of  $\text{Ti(O}^i\text{Pr)}_4$  in toluene gave mononuclear titanium complex  $[(\text{C1NNIBTP})\text{Ti(O}^i\text{Pr)}_3]$  (**1**) [22]. However, the six-coordinated bis-adduct titanium species,  $[(\text{C1FuIBTP})_2\text{Ti(O}^i\text{Pr)}_2]$  (**2**) [23] or  $[(\text{C1NOIBTP})_2\text{Ti(O}^i\text{Pr)}_2]$  (**3**) [24], was obtained from 2-(2H-benzotriazol-2-yl)-6-(((furan-2-

ylmethyl)imino)-methyl)-4-methylphenol ( $\text{C1FuIBTP-H}$ ) or 2-(2H-benzotriazol-2-yl)-6-(((2-methoxyethyl)imino)-methyl)-4-methylphenol ( $\text{C1NOIBTP-H}$ ) as the pro-ligand with  $\text{Ti(O}^i\text{Pr)}_4$  under the similar condition. Alternatively, Ti complex **2** or **3** could be prepared in good yield from the reaction of  $\text{C1FuIBTP-H}$  or  $\text{C1NOIBTP-H}$  with



**Fig. 1.** Molecular structure of complex 1. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg.): Ti–O(1) 1.9502(11), Ti–O(2) 1.8574(11), Ti–O(3) 1.8367(11), Ti–O(4) 1.8604(11), Ti–N(4) 2.2074(13), Ti–N(5) 2.2902(13), O(3)–Ti–O(2) 94.42(5), O(3)–Ti–O(4) 93.49(5), O(2)–Ti–O(4) 169.32(5), O(3)–Ti–O(1) 105.21(5), O(2)–Ti–O(1) 92.10(5), O(4)–Ti–O(1) 92.74(5), O(3)–Ti–N(4) 170.43(5), O(2)–Ti–N(4) 84.95(5), O(4)–Ti–N(4) 86.06(5), O(1)–Ti–N(4) 84.35(5), O(3)–Ti–N(5) 94.44(5), O(2)–Ti–N(5) 84.00(5), O(4)–Ti–N(5) 88.25(5), O(1)–Ti–N(5) 160.22(5), N(4)–Ti–N(5) 76.00(5).

Download English Version:

<https://daneshyari.com/en/article/7748566>

Download Persian Version:

<https://daneshyari.com/article/7748566>

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