



Ligand-free scandium alkyl and alkoxide complexes for immortal ring-opening polymerization of lactide

Hongyan Xie ^{a, b}, Chunji Wu ^b, Dongmei Cui ^{b, *}, Yang Wang ^c

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, China

^b China-Australia Institute for Advanced Materials and Manufacturing, Jiaying University, Jiaying, 314000, China

^c School of Fundamental Sciences, China Medical University, Shenyang, 110122, China

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ABSTRACT

Ligand-free Ln (CH₂SiMe₃)₃ (THF)₂ (**1**: Ln = Sc; **2**: Ln = Lu; **3**: Ln = Er; **4**: Ln = Y) and La(CH₂C₆H₄-o-NMe₂)₃ (**5**) are employed as the initiators for ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA). Complex **4** solely is active but uncontrolled, while complex **1** is inert. In presence of excess benzhydrol, complexes **1–5** can promote the ROP of LA smoothly, in which the molecular weight distribution values of the resultant polymer are related to the radii of the rare-earth metals. Complex **1** displays high activity for the controlled ROP of LA, in which the benzhydrol act a dual role as chain-transfer agent and activator. The polymerizations proceed smoothly and efficiently in a wide range of benzhydrol feeding (3–150 equiv). The molecular weights of the obtained PLAs can be precisely controlled by the monomer loading with respect to that of benzhydrol, while the molecular weight distribution (MWD) maintains a very narrow level (PDI = 1.05–1.18). Every scandium centre by means of chain-transfer reaction with benzhydrol to generate the active species Sc(OCHPh₂)₃·THF (**6**), grows apparently up to 150 PLA polymer chains, showing a typical feature of an immortal polymerization.

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1. Introduction

Nowadays, our society is facing numerous and great challenges, such as white pollution, shortages of source and energy et al. Thus, to develop environment-friendly, bio-derivation, and degradable materials is becoming more and more emergency and pivotal [1–3]. Polylactic acid (PLA) has been recognized as one of the most prospective alternatives for synthetic petrochemical-based plastics, which has been widely employed in the field of packaging materials, agriculture, and medicine, etc [4,5]. ROP of LA initiated by organometallic compounds is widely accepted as one of the most common and efficient strategies to obtain controlled and stereoregular PLA in the past decades [6–14]. In particular, rare-earth metal based organometallic catalysts have gained a lot of attention because of their facility to enhance catalytic activity and specific stereoselectivity in the past decades [15–25]. The amino-bis(phenolate) stabilized La, Nd, Y, and Lu complexes developed by Carpentier [15,26,27], Mountford [28], and our group [17,29,30]

can efficiently initiate the ROP of *rac*-LA, affording heterotactic-enriched PLA (*P_T* > 0.96). Phosphasalen yttrium complexes invented by Williams [20] and C₃-symmetric lanthanide complexes L₃Ln (L = (tBu)₂P(O)CH₂CH(tBu)O; Ln = Y, Eu, Er) reported by Arnold [18] are isoselective initiators for ROP of *rac*-LA. However, researches on Sc-based catalysts are much fewer than other lanthanide congeners. Scandium trifluoromethanesulfonate complex Sc(OTf)₃ is the first reported Sc-based initiator for ROP of LA [31]. 1,ω-Dithiaalkane-bridged bis(phenolate) scandium complexes pioneered by Okuda are highly heteroselective for ROP of *rac*-LA [16]. Recently, Williams and coworkers have demonstrated that phosphasalen scandium complex is slow and controlled initiator for ROP of ε-caprolactone (ε-CL) and inert for LA polymerization [22]. Highly active and controlled Sc-based initiators still remain unexplored.

Immortal polymerization (IMP), invented by Inoue in 1985, is one of the most popular manners for the ROP of cyclic esters [32]. In contrast to traditional living polymerization, the IMP process is full of rapid and reversible chain-transfer reactions, which provide plenty of advantages, such as atom economy, ease of polymer chain-end functionality, polymerization controllability, high catalytic efficiency, and lower catalyst loading [33–36]. Although the ancillary ligands can protect the organometallic catalysts from

* Corresponding author.

E-mail address: dmcui@ciac.ac.cn (D. Cui).

aggregation and inactivation, the ligand are always complicated and costly. To date, great effort has been made for ligand-free rare-earth metal based catalysts for ROP of LA, however, most of them do not have defined molecular structures [37–40], while the others have complex cluster structures, such as $Y_5(\mu-O)(O^iPr)_{13}$ [41]. There have been no researches focusing on their catalytic performance for IMP of LA, because of their low activity and “multisite” catalytic propensity, which is always related to broad MWD.

Herein, we report the ligand-free binary catalytic system of $Sc(CH_2SiMe_3)_3(THF)_2$ (**1**) and benzhydrol is highly active for the IMP of LA. By means of chain-transfer reaction with benzhydrol, the active species $Sc(OCHPh_2)_3 \cdot THF$ (**6**) is generated *in situ* to afford PLA with well-controlled molecular weights and narrow MWD, showing a typical feature of IMP.

2. Experimental section

2.1. General methods

All operations were performed under the argon atmosphere using standard Schlenk techniques or in a nitrogen gas filled MBraun glovebox. All the solvents, such as toluene, tetrahydrofuran, and *n*-hexane were distilled under nitrogen from sodium/benzophenone. Deuterated NMR solvents were purchased from Cambridge Isotopes, dried over Na (for C_6D_6 and $THF-d_8$) and molecular sieve (for $CDCl_3$), and stored in the glovebox. The benzhydrol was obtained from commercial sources and dried with $MgSO_4$ in THF solution prior to use. Rare-earth metal alkyl and benzyl complexes **1–5** were synthesized via a modified procedure according to literature [42,43]. $ScCl_3 \cdot 3THF$ was purchased from Sigma-Aldrich Company. *rac*- and *l*-Lactide were purchased from Sigma-aldrich and were recrystallized three times in dry ethyl acetate prior to use.

2.2. Instruments and measurements

Organometallic samples for NMR measurements were prepared in NMR tubes and sealed with paraffin film in the glovebox. 1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for 1H , 100 MHz for ^{13}C) spectrometer. Homonuclear decoupled 1H NMR spectra were recorded on a Bruker AV400 spectrometer. Elemental analyses were performed at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC). The number-average molar mass (M_n) and the MWD (M_w/M_n) of the polymer were measured by size exclusion chromatography (SEC) on a TOSOH HLC-8220 SEC instrument (column: Super HZM-H \times 3) at 40 °C using THF as eluent with a flowing rate of 0.35 mL/min; the values were relative to polystyrene standards.

2.3. Synthesis of $Sc(OCHPh_2)_3 \cdot THF$ (**6**)

To a THF (10 mL) solution of 0.451 g (10 mmol) $Sc(CH_2SiMe_3)_3(THF)_2$, 5 mL THF solution of Ph_2CHOH (0.618 g) was added dropwise. The mixture was stirred for 2 h at room temperature. Concentration and recrystallization in THF/hexane afforded white crystalline solids of complex **6** (0.520 g, 78%). 1H NMR (400 MHz, C_6D_6 , 25 °C): δ 7.40 (d, 12H, $^3J_{H-H} = 6.0$ Hz, *o*-Ph), 7.13 (dd, 12H, $^3J_{H-H} = 6.0$, 7.2 Hz *m*-Ph), 7.04 (t, 6H, $^3J_{H-H} = 7.2$ Hz, *p*-Ph), 6.01 (s, 3H, $CHPh_2$), 3.51 (m, 4H, THF), 1.09 (m, 4H, THF). ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): δ 148.22 (*ipso*-Ph), 128.62 (*o*-Ph), 127.10 (*m*-Ph), 126.81 (*p*-Ph), 82.33 ($CHPh_2$), 70.65 (THF), 25.19 (THF) ppm. Anal. Calcd for $C_{43}H_{41}O_4Sc$: C, 77.46; H, 6.20. Found: C, 77.28; H, 6.17.

2.4. General procedure for polymerization of *rac*-lactide

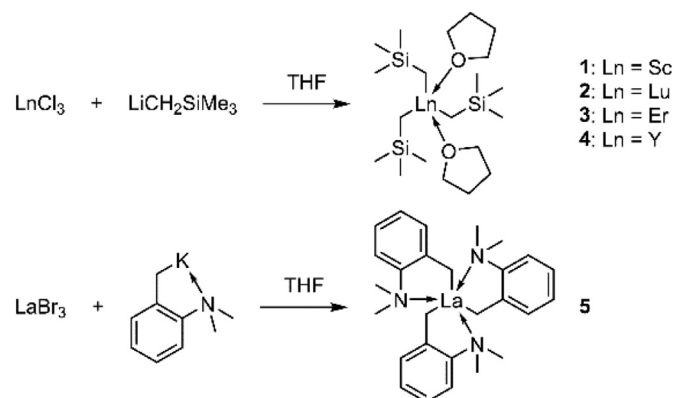
A typical procedure for polymerization of *rac*-LA was performed in a 25 mL round flask in a glovebox. To a stirred solution of *rac*-LA (1.296 g, 9 mmol) in 4 mL of THF was added a THF solution (1 mL) of the mixture of $Sc(CH_2SiMe_3)_3(THF)_2$ (9 mg, 20 μ mol) and Ph_2CHOH (55.2 mg, 0.3 mmol). The polymerization took place at room temperature. The system kept stirring for the respective time and then was terminated by 0.5 mL of acidified ethanol. The viscous solution was quenched by an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40 °C for 24 h *in vacuo* to give polymer product. The conversion was determined by 1H NMR spectroscopy. The molecular weight and the MWD of the resulting polymer was determined by GPC.

3. Results and discussion

3.1. ROP of *rac*-LA by complexes **1–5** and benzhydrol

A series of ligand-free $Ln(CH_2SiMe_3)_3(THF)_2$ (**1**: $Ln = Sc$; **2**: $Ln = Lu$; **3**: $Ln = Er$; **4**: $Ln = Y$) and $La(CH_2C_6H_4-o-NMe_2)_3$ (**5**) could be easily prepared as illustrating in Scheme 1. The complexes **1–5** in combination of benzhydrol were employed for the ROP of *rac*-LA, and the results were summarized in Table 1. Although complex **4** independently was highly active for ROP of *rac*-LA, the molecular weight of the obtained PLA was much larger than the theoretical value, indicating a non-living fashion (Table 1, entry 1). In contrast, complex **1** was completely inert for ROP of *rac*-LA (Table 1, entry 2), the mechanism of which has been confirmed by NMR spectra (*vide infra*).

The catalytic performance of complexes **1–5** in combination with benzhydrol was also investigated. After adding 5 equivalents of benzhydrol, all the alkyls of complex **1** were replaced by $-OCHPh_2$ (*vide infra*), and the polymerization could proceed smoothly (98% conversion was achieved within 3 h), showing excellent activity and controllability (Table 2, entry 3). In this case, the benzhydrol act a dual role: a) the activator to “switch on the power source” and initiate the chain-propagation; b) the chain-transfer agent to participate in the ROP process and endow the polymerization with an immortal mode. Other ligand-free rare-earth metal complexes **2–5** were more efficient than complex **1** (the monomer was completely consumed within 1 h). However, the MWD values of the resultant PLA showed an unexpected correlation to the ionic radii (Table 1, entries 4–7). With the ionic radii increasing (Sc : 0.73 Å; Lu : 0.848 Å; Er : 0.881 Å; Y : 0.892 Å; La : 1.061 Å) [44], the MWD values increased from 1.08 to 1.67. Such unexpected relationship may be arisen from the aggregated



Scheme 1. The preparation of complexes **1–5**.

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