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Ring-opening polymerization of ε-caprolactone and lactides promoted by *salan*- and *salen*-type yttrium amido complexes

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ABSTRACT

The ring-opening polymerization (ROP) of cyclic esters such as ε-caprolactone (ε-CL), L- and *rac*-lactide, promoted by yttrium silylamido complexes bearing binaphthyl-bridged *salen* (**1** and **2**) and diamine bisphenolate *salan* ligands (**3** and **4**) is described.

The yttrium silylamido complexes **1–4** are effective initiators for the ROP of ε-caprolactone, showing extremely high turnover frequencies (TOF up to 18000 h^{-1}) under mild reaction conditions. All complexes promote the ROP of *rac*-lactide in toluene solution at room temperature, providing atactic polymers with controlled molecular weights and relatively narrow polydispersities (M_w/M_n = 1.73–1.99). Interestingly, in THF solution the same catalysts produce heterotactic polylactides with P_r between 0.58 and 0.91 via a chain-end stereocontrol mechanism. The *salan* complexes **3** and **4** are more active than the binaphthyl *salen* complexes **1** and **2**, reasonably due to the presence of the more electron donating amino groups. On the other hand, the former resulted in a lower stereoselectivity than the latter. The rigidity of the "bridge" between the two nitrogen atoms seems to have a predominant role in governing the selectivity of the corresponding complexes, while the effect of the steric hindrance of the *ortho* substituents at the phenoxy rings appears less significant.

1. Introduction

Aliphatic polyesters, i.e. poly(lactide), poly(caprolactone), poly(hydroxybutyrate) and their copolymers are important biodegradable materials for biomedical, pharmaceutical and agricultural applications [1]. The ring-opening polymerization of cyclic esters initiated by metal initiators, via a coordination-insertion mechanism, is the most efficient approach to produce these polymers with high molecular weight in a controlled fashion. This mechanism, indeed, allows a fine control over the molecular weights and their distribution, an accurate tailoring of the end groups and of the stereochemical microstructure of the polymeric chains. In this regard, great research efforts have been devoted to the development of catalysts able to produce stereoregular polymers from racemic mixtures of either lactide or β-butyrolactone [2–6]. Since the breakthrough discovery of stereoselective polymerization of racemic lactides by a chiral binaphthyl Schiff base aluminum complex by Spassky et al. [7], aluminum complexes bearing tetradentate ligands have been the most studied initiators. Some of the most significant advances in stereocontrolled polymerization have been achieved using aluminum alkyls or alkoxides derivatives stabilized by *salen*- or *salan*-type ligands [8–15]. Besides isotactic poly(lactide) (PLA) prepared from enantiomerically pure L- or D-lactide, heterotactic [8], syndiotactic [9], stereoblock isotactic [10–12] and stereogradient isotactic [13,14] PLAs are now accessible from *rac*- or *meso*-lactide with mechanisms regulated by a *chain-end* or an *enantiomorphic site* control.

On the contrary, yttrium complexes stabilized by tetradentate *salen* or *salan*-type ligands have been far less explored [16–19]. Although largely more active than aluminum initiators, poor stereoselectivity was found for yttrium complexes, in comparison with the aluminum ones [2–6]. For instance, describing chiral aluminum and yttrium alkoxides complexes bearing *salen* ligands, Coates et al. found that the aluminum complex exhibited excellent stereocontrol in a range of lactide polymerizations, while the yttrium one bearing the same ligand did not effect stereocontrol in the polymerization of either *meso*- or *rac*-lactide [12]. As a result, highly active and stereoselective ROP yttrium initiators are sought after [20–22].

In the framework of our studies on the synthesis of aliphatic polyesters [23–29], we have recently described a series of yttrium amido complexes bearing tetradentate binaphthyl-bridged *salen*

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and diamine bisphenolate *salan* ligands as efficient initiators in the polymerization of *rac*-β-butyrolactone (*rac*-BBL) to syndiotactic enriched poly(hydroxybutyrate) [30]. Peculiar facets of the ligands design, i.e. the bridge between the phenoxy-imine moieties and the steric bulkiness of the substituents on the phenoxy groups have been changed in order to study their effects on the polymerization behavior. This study has been now extended to the ROP of other cyclic esters. The results of the polymerization of ε-CL and L-lactide and of the stereoselective polymerization of *rac*-lactide in the presence of these initiators are presented and discussed herein.

2. Experimental

2.1. General procedures

All manipulations of air- and/or water-sensitive compounds were carried out under nitrogen atmosphere using standard Schlenk or glovebox techniques. Solvents were purchased from Carlo Erba. Tetrahydrofuran (THF), toluene and hexane were distilled over sodium–benzophenone. Lactide was purified by crystallization from dry toluene. ε-CL was dried over CaH_2 for 24 h at room temperature and then distilled under reduced pressure.

The racemic binaphthyl-bridged *salen* [7] and diamine bisphenolate *salan* yttrium [30–32] initiators were synthesized according to previously reported procedures. All other chemicals were purchased from Sigma–Aldrich and used as received.

2.2. Instruments and measurements

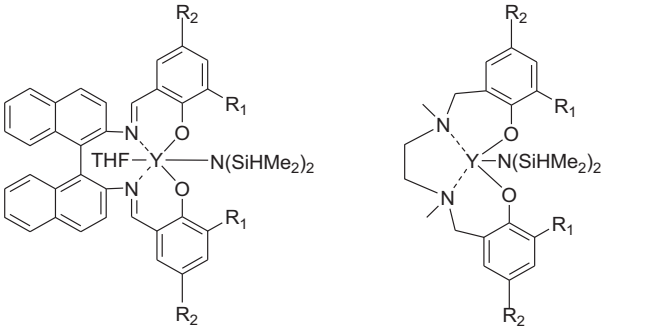
The NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H, 400.00 MHz; ^{13}C, 100.62 MHz) at 25 °C. Homonuclear decoupled ^{1}H NMR spectra of PLAs were recorded on 500 MHz Bruker Avance spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. degassed and dried over activated 3 Å molecular sieves prior to use. Chemical shifts (δ) are listed as parts per million and coupling constants (J) in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.26 ppm for $CDCl_3$. ^{13}C NMR spectra are referenced using the residual solvent peak at δ 77.23 ppm for $CDCl_3$.

The molecular weights (M_n) and the molecular mass distribution (M_w/M_n) of polymer samples were measured by Gel Permeation Chromatography (GPC) at 30 °C, using THF as solvent, flow rate of eluant 1.0 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1000–1,000,000 Å). Every value was the average of two independent measurements. The experimental values were corrected with the factor of 0.56 and 0.58 for PCL and PLA respectively [33].

Glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) using a DSC 2920TA Instruments in nitrogen flow with a heating and cooling rate of 10 °C min^{-1} in the range −100 to 200 °C. The data were reported for the second heating cycle.

2.3. Polymerization of ε-caprolactone and lactides

In a typical polymerization run, a magnetically stirred reactor vessel (20 and 50 cm^3) was charged sequentially with a solution of the initiator (in 4 mL of dry toluene) and monomer. The mixture was thermostated at the required temperature and, after the required polymerization time, poured into hexane. The precipitated polymer was recovered by filtration and dried at 40 °C in a vacuum oven. The polymer was characterized by NMR spectroscopy and GPC analysis.



1 R_1 = *t*-Bu, R_2 = H
2 R_1 = R_2 = CMe_2Ph

3 R_1 = 1-adamantyl, R_2 = Me
4 R_1 = R_2 = CMe_2Ph

Scheme 1. *rac*-Binaphthyl-bridged *salen* and diamine bisphenolate *salan* yttrium complexes used in this work.

PCL: ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.34 (m, 2 H, —CH_2—), 1.62 (m, 4H, —CH_2—), 2.29 (t, 2H, —$CH_2C(O)O$—), 4.04 (t, 2H, —$CH_2OC(O)$—), 3.62 (t, 2H, —CH_2OH), 3.65 (s, 3H, —C(O)—OCH_3).

^{13}C NMR ($CDCl_3$, 25 °C): δ = 24.7, 25.7, 28.5, 34.3, 64.3 (—$OCO(CH_2)_5$—), 51.7 (—$C(O)OCH_3$), 62.7 (—CH_2OH), 173.7 (—COO—).

PLA: ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.56 (m, 6H, —$CHCH_3$—), 3.79 (s, 3H, —$C(O)OCH_3$), 5.18 (m, 2H, —$CHCH_3$—). ^{13}C NMR ($CDCl_3$, 25 °C): δ = 16.8 (—$C(O)OCHCH_3$—), 69.2 (—C(O)—$OCHCH_3$—), 169.5, 169.8 (—COO—).

2.4. Kinetic experiments

In a Braun Labmaster glovebox, initiator solution from a stock solution in toluene was injected into a 20-mL vial loaded with monomer and suitable amount of dry solvent. After specified time intervals, a small amount of the polymerization mixture was transferred in a different vial containing wet $CDCl_3$. The determination of the monomer conversion of each fraction was performed by ^{1}H NMR analysis (in $CDCl_3$), by integration of the signals of the monomer vs the signals of the polymer.

3. Results and discussion

Racemic binaphthyl-bridged *salen* and diamine bisphenolate *salan* complexes of yttrium bearing different substituents on the phenoxy rings were synthesized according to previously reported procedure (Scheme 1) [30]. All complexes exhibited mononuclear structures. The complexes **1** and **2** showed hexacoordinate, octahedral geometries with an additional molecule of THF coordinated at yttrium, while pentacoordinate structures have been reported for complexes **3** and **4** [30].

Discrete group 3 metal complexes are well-established catalysts-initiators for the ROP of cyclic esters such as lactones and lactides. Activity, productivity, degree of control/living character and stereoselectivity, in the case of chiral monomers, depend crucially on the ancillary ligands that define the steric and electronic properties of the active metal center. We were therefore interested in evaluating the catalytic performance of synthesized compounds (**1–4**) in the ROP of ε-CL and L- and *rac*-lactide.

3.1. ROP of ε-caprolactone by complexes *1–4*

Complexes **1–4** were tested in the ring-opening polymerization of ε-CL (Scheme 2).

Polymerization screenings were performed under nitrogen atmosphere in a toluene solution of ε-CL and the proper yttrium