

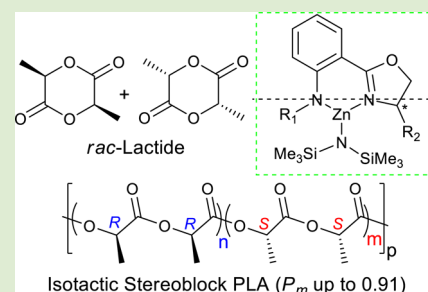
Zinc-Catalyzed Highly Isolelective Ring Opening Polymerization of *rac*-Lactide

Srinivas Abbina and Guodong Du*

Department of Chemistry, University of North Dakota, 151 Cornell Street Stop 9024, Grand Forks, North Dakota 58202, United States

Supporting Information

ABSTRACT: A family of chiral zinc amido-oxazolinates are shown to be highly active and isolelective initiators for the ring-opening polymerization (ROP) of *rac*-lactide, yielding isotactic stereoblock polylactides (PLA) with P_m up to 0.91. This represents the highest isolelectivity observed with zinc-based catalysts for ROP of *rac*-lactide.

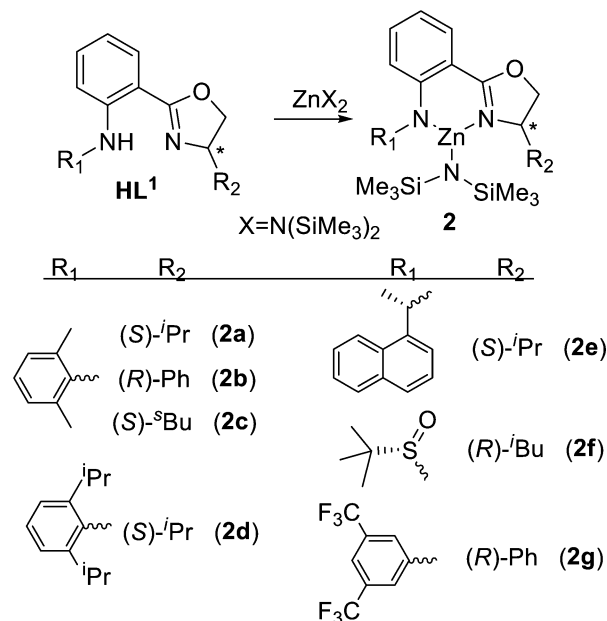


As one of the leading sustainable materials, polylactides (PLAs) have attracted considerable interest due to their outstanding properties such as biodegradability, biocompatibility, and renewability.¹ Synthetically, PLAs can be produced from lactic acids through condensation polymerization; or more preferably, from the ring opening polymerization (ROP) of lactide (LA), because the latter approach offers advantages such as higher molecular weight, narrower distribution, and better stereocontrol. Depending on the stereochemistry of the LA monomer, the selectivity of catalysts, and the reaction conditions, an array of microstructures can be obtained. Among them, the isotactic PLA is the most valuable due to its high melting point.² In principle, polymerization of homochiral lactides (L-LA or D-LA) can produce isotactic polymers in the absence of epimerization; however, the use of *rac*-lactide is advantageous because it opens up the possibility that stereoblock PLA or stereoblock copolymer of PLA may be obtained, resulting in a melting point higher than PLLA or PDLA alone.³ Therefore, intensive efforts have been devoted to the discovery of new stereoselective initiators, particularly those that can produce isotactic PLAs from *rac*-LA.

Since the pioneering work that demonstrated a chiral salen aluminum complex exhibits high isolelectivity for *rac*-LA,⁴ a number of stereoselective initiators have been developed.⁵ Compared to the available heteroselective catalysts, isolelective catalysts are relatively scarce, and most of them are derived from aluminum complexes supported by salen-type ligands and their derivatives.⁶ However, Al catalysts often suffer from low activity in ROP of LA, typically requiring a prolonged time (24 h or longer) at elevated temperatures (70–100 °C).^{5,6} Other examples include those based on heavier group 13 elements,⁷ particularly indium,⁸ group 3 and lanthanides,⁹ and group 4 elements.¹⁰

We have been interested in the amido-oxazolinates ligands (HL¹, Scheme 1) as a chiral variation of the conventional

Scheme 1. Chiral Zinc Amido–Oxazolinates Complexes



β -diketiminate ligands, because they allow opportunity for facile introduction of stereogenic groups.¹¹ In analogy to the zinc-diketiminates complexes in alternating copolymerization of CO₂ and epoxides, we have shown the zinc complexes 2 are viable initiators for asymmetric alternating copolymerization of CO₂ and cyclohexene oxide with modest stereocontrol.¹²

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Table 1. ROP of *rac*-Lactide by Catalysts 2a–g^a

run	cat	<i>T</i> (°C)	<i>t</i> (min)	conv. ^b (%)	<i>M_n</i> ^c (kg/mol)	<i>M_{n,calcd}</i> ^d (kg/mol)	<i>D</i> ^e	<i>P_m</i> ^e	<i>T_m</i> ^f (°C)
1	2a	23	13 h	91	49.0	13.1	1.29	0.81	189
2	2a	50	30	98	30.0	14.1	1.30	0.77	176
3	2a	75	15	93	3.6	13.4	1.14	0.76	179
4	2a	0	3 d	94	59.2	13.5	1.19	0.90 (0.87)	214
5 ^g	2a	50	30	95	40.1	27.4	1.13	0.80	208
6 ^h	2a	130	8	91	45.5	13.1	1.15	0.77	
7 ⁱ	2a	50	125	91	34.5	13.1	1.12	1.0	168
8	2b	50	30	96	18.0	13.8	1.07	0.76 (0.76)	184
9	2c	50	30	96	30.2	13.8	1.10	0.80	195
10	2d	50	30	97	28.0	14.0	1.18	0.67 (0.70)	170
11	2e	50	30	80	29.4	11.5	1.05	0.72	194
12	2f	50	30	95	21.2	13.7	1.37	0.78	196
13	2g	50	30	93	37.4	13.4	1.23	0.86 (0.82)	204
14	2g	23	44 h	96	52.2	13.8	1.32	0.91 (0.89)	212

^aReactions were carried out using 1 mol % of catalyst at 50 °C in toluene, unless noted otherwise. ^bDetermined by ¹H NMR. ^cExperimental molecular weight determined by GPC, corrected by a factor of 0.58. ^dCalculated molecular weight based on conversion and catalyst loading. ^eProbability of *meso* enchainment, determined by the integration of methine region of the homonuclear decoupled ¹H NMR. The *P_m* values in the parentheses were determined on the basis of ¹³C NMR. ^fDetermined from the second heating cycles of DSC. The values are averages of three duplicates. ^g1:200 ratio of catalyst/monomer was used. ^hBulk conditions without solvent. ⁱL-Lactide was used.

Herein we report their application for ROP of *rac*-lactide, in which they exhibit fast rates and high isoselectivity. Although zinc compounds have been extensively studied,^{5,13} to our knowledge, these are the highest isoselectivity achieved by zinc-based catalysts from *rac*-LA to date. In contrast, analogous zinc complexes supported by conventional β -diketiminato ligands induce high level of heterotacticity (*P_r* up to 0.94).¹⁴ Very recently, moderate to high preference toward isoselectivity has been obtained with zinc-based catalysts.¹⁵ However, the highest *P_m* (0.84) was achieved at very low temperature (−38 °C).^{15a}

We initially examined compound 2a for ROP of *rac*-lactide under various conditions, which were conveniently monitored by ¹H NMR spectroscopy. Selected results are summarized in Table 1. The reaction was first carried out in toluene at ambient temperature with 1 mol % catalyst, leading to a 91% conversion after 13 h. At 50 °C, the conversion was nearly complete within 30 min. At higher temperature (75 °C), low molecular weight PLA was produced (run 3). The reactions could be carried out in other solvents such as THF or dichloromethane with slightly lower conversions or without solvent under melt conditions (run 6). The catalyst loading can be decreased to 0.5 mol % without much change in conversion. No epimerization of lactide was observed during the catalysis, as L-LA was polymerized to a purely isotactic PLA (run 7).

The molecular weights of the resulting PLAs appear to be significantly higher than the theoretical *M_n* calculated from the initial catalyst loading and conversion, assuming a single chain for each initiator. This can be attributed to a slow initiation step vs propagation, possibly due to the bulky initiating group N(SiMe₃)₂.^{9a} However, in the presence of an alcohol, benzyl alcohol (BnOH, 1 equiv vs Zn), the polymerization became slower and low molecular weight PLA was produced (entry 9, Table S1). We attribute this lowered activity to the deactivation of Zn complex by alcohols, which is supported by the observation that stoichiometric reaction of BnOH and 2a leads mostly to free ligand. On the other hand, despite the slow initiation with 2a, the molecular weights increase with the progress of the reaction, and the dispersities are relatively narrow (1.03–1.30), suggestive of controlled behavior of the polymerization. Investigation by MALDI TOF mass spectrom-

etry of a PLA sample (Figure S3) revealed the presence of a N(SiMe₃)₂ end group, as well as transesterification indicated by the cluster of peaks separated by 72 mass units.

The microstructure of the PLA was evaluated by the homonuclear-decoupled ¹H NMR spectra, and the tetrad peaks were assigned according to the literature.¹⁶ The most notable feature is that catalyst 2a exhibits a high level of isoselectivity, as indicated by the dominant peak around 5.17 ppm attributed to the *mmm* tetrad (Figure 1a). A *P_m* value of 0.81 was achieved at

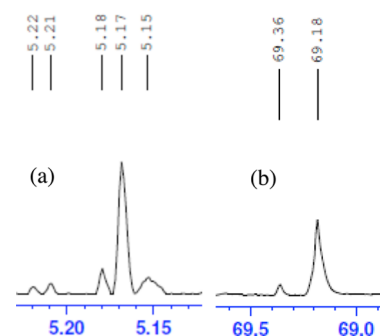


Figure 1. Methine region of (a) the homonuclear decoupled ¹H NMR (500 MHz) and (b) ¹³C NMR (125 MHz) spectra of PLA generated with 2a (Table 1, run 4).

ambient temperature for 2a, which was further improved to 0.90 at 0 °C. The observed tetrads distribution for the methine carbon in the ¹³C NMR of the resulting PLA (Figure 1b) confirmed the high isotacticity.¹⁷ This represents the highest isoselectivity obtained with a zinc based initiator from ROP of *rac*-lactide thus far.¹⁵ Under bulk conditions (130 °C), the isotactic preference by 2a was maintained (*P_m* = 0.77). It is noted that a number of aluminum systems maintain high stereoselectivity under solvent-free conditions, which is often preferred in order to minimize generation of waste.^{6h,k,l}

The reaction progress was monitored with compound 2a by periodically taking samples for ¹H NMR determination. The conversion–time profile indicates approximately first order kinetics in monomer, as linear plot of ln([LA]₀/[LA]_t) versus time was observed with up to 85% conversion. The dependence on catalyst concentration was determined to be 0.93 (±0.14) from

the plot of $\ln(k_{\text{obs}})$ versus $\ln[2\mathbf{a}]$ (Figure S10), thus, the overall rate law can be written as $\text{rate} = k[\text{cat}][\text{LA}]$. Activation parameters of the polymerization were obtained from the Eyring plot (Figure S11) at 23–55 °C: $\Delta H^\ddagger = 54 (\pm 7) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -112 (\pm 21) \text{ J mol}^{-1} \text{ K}^{-1}$. These values are comparable with the literature reports¹⁸ and suggest an ordered transition state that is in agreement with a coordination–insertion mechanism.

With established reaction conditions, we next examined a series of related zinc amido-oxazolinates complexes (**2b–g**) with varying steric and electronic substituents. At 50 °C in toluene with 1 mol % catalyst, the conversion of *rac*-lactide reacted >93% within 20–30 min for most of the catalysts tested. All of them showed good control of the polymerization process, as judged by the narrow molecular weight dispersities despite the molecular weight being higher than the theoretical values. Invariably this series of zinc catalysts exhibited a distinct preference for isotactic PLAs, and the highest P_m value of 0.86 (at 50 °C) was obtained with catalyst **2g** that incorporates strong electron withdrawing groups ($-\text{CF}_3$). At 23 °C, the selectivity was improved to $P_m = 0.91$. The high isotacticity was further verified by the observed tetrads distribution for the methine carbon in the ¹³C NMR of the resulting PLA (Figures S6–7).

The thermal properties of the resulting PLAs were further investigated with differential scanning calorimetry (DSC). Distinctive melting transitions (T_m) abstracted from the second heating cycle were observed in a range of 170–215 °C. This can be roughly correlated with the P_m values of the polymers (Figure S16), in agreement with the literature report.¹⁹ In particular, the T_m value for PLA prepared from **2a** at 0 °C with $P_m = 0.90$ (run 4, Table 1) was determined to be 214 °C (Figure 2), representing one of the highest T_m for PLA derived

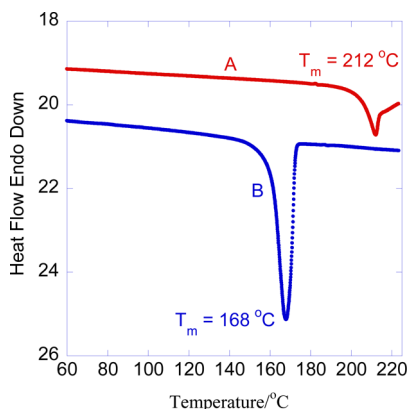


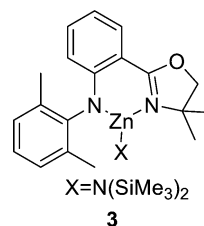
Figure 2. DSC thermograms of the second heating cycles of PLA samples from run 4 (A) and run 7 (B) of Table 1.

directly from *rac*-LA. As a comparison, T_m of a purely isotactic PLA is determined to be 168 °C (Table 1, run 7), in line with the literature value.⁵ The unusually high T_m may be attributed in part to the high molecular weights and supports the formation of stereoblock or stereocomplex PLAs due to the cocrystallization of isotactic segments of opposite configuration, which is expected from highly isoselective ROP of *rac*-LA.

As noted earlier, the iso-selectivity of ROP of *rac*-LA is mostly observed with Al-based catalysts, and their analogues in group 13 and group 3. It is worth noting that the metal alone is not the only factor determining the stereoselectivity, and the steric and electronic features of the supporting ligands may have a major effect on the stereo outcome. For example, with a slight modification of ligands, Al compounds have been tuned from

highly isospecific ($P_m = 0.79$) to highly heterotactic ($P_r = 0.96$) in ROP of *rac*-LA.²⁰ In this context, we also note that use of chiral catalysts does not necessarily ensure stereocontrol in ROP of *rac*-LA, as a number of chiral zinc catalysts have demonstrated.²¹

For metal-catalyzed ROP of cyclic esters, two pathways are often invoked to explain the observed stereoselectivity: chain end control and enantiomorphic site control. Since the present zinc catalysts are chiral, we thought that it may entail an enantiomorphic site control mechanism, that is, the chirality of the catalyst determines which monomer gets inserted favorably. This seems to agree with the result of an analogous, nonchiral Zn catalyst **3**, in which only atactic PLA was produced for the ROP of *rac*-LA. However, the tacticities of the PLA obtained with **2a**, as judged by P_m , remained essentially unchanged versus conversion during the ROP of *rac*-LA (Figure S12). Though *rac*-LA reacted faster than *L*-LA under the same conditions with **2a**, the rate difference, $k_{\text{rac-LA}}/k_{\text{L-LA}} \sim 1.6$ (Figure S13), is not large enough to account for the observed high isotacticity. The roughly first order dependence on *rac*-LA monomer also indicated little supposed differentiation between the two stereoisomers of *rac*-LA. Furthermore, the tetrad signals (particularly *rrmm* and *rmr*; Figure S5) resulting from the stereoerrors showed unusual relative intensities that are not easily accounted for by a purely enantiomorphic site control or chain end control mechanism alone.²² A possible explanation is that there are significant contributions of chain end control mechanism after a chain transfer/transesterification event leading to stereoerrors. This gives rise to an isotactic multiblock stereocopolymer. The presence of both mechanisms has been proposed in other systems to account for the stereoselectivity during the ROP of *rac*-LA.^{15a,23}



In summary, we have described a family of amido-oxazolinates zinc catalysts that show fast rate and high isoselectivity for ROP of *rac*-lactide, producing isotactic PLA with P_m up to 0.91, the highest so far by a zinc-based system. These findings demonstrate the ability of zinc catalysts to produce highly isotactic PLA from *rac*-lactide by proper selection of ancillary ligands. Given that zinc catalysts are generally more active than the aluminum catalysts in ROP of lactides and the present catalysts feature an easily modifiable ligand framework for improvement and interrogation, it is reasonable to expect that more active and stereoselective catalysts would be discovered. Efforts aimed at improving the stereocontrol and understanding the origin of isoselectivity and detailed reaction mechanisms are underway in our lab.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, representative NMR, GPC, MALDI MS, and DSC data and figures, and kinetic plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +1-701-777-2241. Fax: +1-701-777-2331. E-mail: gdu@chem.und.edu.

Notes

The authors declare no competing financial interest.

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