Polym. Bull. (2012) 68:1789–1799
DOI 10.1007/s00289-011-0647-0

ORIGINAL PAPER

Polymerization of *rac*-lactide catalyzed by group 4 metal complexes containing chiral N atoms

Minggang Hu · Mei Wang · Peili Zhang · Kun Jin · Yuee Chen · Licheng Sun

Received: 10 August 2011 / Accepted: 4 October 2011 / Published online: 12 October 2011

Abstract The hydroxyl- and phenoxy-bridged dinuclear zirconium and hafnium complexes, **1** and **2**, containing a chiral N atom in the N_2O_2 ligand (H_2L = 2-(((2-pyridylmethyl)(2-hydroxyphenyl)amino)methyl)-4,6-di(*tert*-butyl)phenol) were used as catalysts for the ring-opening polymerization of *rac*-lactide. Experiments prove that **1** and **2** are living and controlled catalytic systems with activity up to 3.25 g_{pol} $mmol_{ini}{}^{-1}$ h^{-1}. The isotactic-rich polylactides in a narrow polydispersity ($M_w/M_n = 1.01$–1.13) were produced with enantiomeric complexes **1** and **2** ($P_m = 0.65$–0.73). The kinetic studies show a first-order dependency in both monomer and initiator. The initiation mechanism is discussed on the basis of the MALDI-TOF MS and ^1H NMR spectra of the *rac*-LA oligomer prepared by **1**.

Keywords Hafnium · Isoselectivity · Lactide · Polymerization · Zirconium

---

Electronic supplementary material The online version of this article (doi: 10.1007/s00289-011-0647-0) contains supplementary material, which is available to authorized users.

M. Hu · M. Wang (✉) · P. Zhang · K. Jin · Y. Chen · L. Sun (✉)
State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Centre on Molecular Devices, Dalian University of Technology, Dalian 116012, China
e-mail: symbueno@dlut.edu.cn

L. Sun
e-mail: lichengs@kth.se

M. Hu
College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar 161005, China

L. Sun
Department of Chemistry, Royal Institute of Technology, 10044 Stockholm, Sweden

Introduction

Development of Lewis acid catalysts for controlled polymerization of lactide (LA) is a lasting interest over past two decades as polylactide (PLA) is a biodegradable and biocompatible polyester derived from biorenewable feed stocks [1]. The stereoregular PLA with improved physical and mechanical properties is an attractive polymeric material of high quality. A promising and practical strategy for the convenient production of the stereoregular PLA is the stereoselective ring-opening polymerization (ROP) of *rac*-LA [2–7]. Hence, many efforts have been made to develop discrete, well-characterized single-site catalysts for the stereoselective ROP of *rac*-LA. Most known catalysts do not bias toward different enantiomers in the ROP of *rac*-LA, thereby furnishing atactic amorphous PLA. In the last decade, many complexes of Ca [8], Mg [9, 10], Zn [11, 12], Sn [13], Al [5, 6], Sc [14], Y [15, 16], Ge [17], Ti [18, 19], and Zr [20], have been found to be good initiators for the ROP of *rac*-LA to heterotactic-rich PLA, while the reports on efficient catalysts to isotactic-rich PLA are limited to salen and salan aluminum complexes [2, 3, 21–24].

Group 4 metal complexes have attracted considerable attention, generally in the drive for the fundamental new coordination chemistry of group 4 metals and their potential applications as Lewis acid catalysts. In recent years, group 4 metal complexes were successfully used as initiators for the ROP of *rac*-LA. However, most reported Ti, Zr, and Hf complexes display good catalytic activity with no stereoselectivity or with heteroselectivity [18–20, 25, 26]. So far, only a salan zirconium complex was reported with isoselectivity in the ROP of *rac*-LA to give a stereoblock PLA [27]. In our earlier work, we prepared the enantiomeric dinuclear zirconium and hafnium complexes (**1** and **2**) from the reactions of MCl_4 (M = Zr, Hf) and an unsymmetric N_2O_2 ligand (Fig. 1) [28]. The coordination of the prochiral tertiary amine to the metal center leads to the formation of the complex with a chiral N atom. It would be interesting if we can successfully transfer the chirality at an N atom of a complex to polymers, because in this way the stereoselectivity of polymerization can be approached without using any chiral auxiliary in the preparation of catalysts. The catalytic properties of complexes **1** and

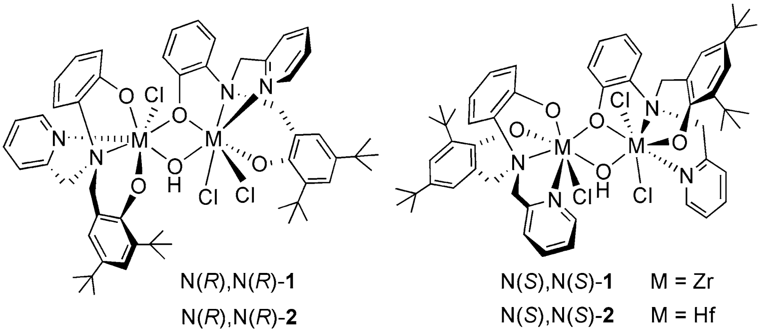


Fig. 1 Dinuclear complexes **1** and **2** containing chiral N atoms

2 for the polymerization of *rac*-LA and the initiation mechanism of the reaction were studied.

Experimental section

General procedures

All reactions and manipulations related to organometallic compounds were carried out under dinitrogen atmosphere using standard Schlenk techniques. Toluene was distilled under nitrogen with sodium/diphenyl ketone and ethyl acetate was distilled with calcium hydride prior to use. *rac*-LA and L-LA (both from Aldrich) were recrystallized three times from ethyl acetate. Zirconium chloride was purchased from Aldrich. Other commercially available chemical reagents were used without further purification. Unsymmetric amine-pyridine-bis(phenolate) ligands (H_2L) was prepared according to modified literature procedures [29] (see Supplementary material). Complexes **1** and **2** were prepared as the procedure previously reported [28].

^{1}H NMR Spectra were recorded on a Varian 400 and 600 NMR spectrometers. Mass spectra were recorded on an ESI-Q-TOF MS (Micro) instrument. Molecular weight and molecular weight distribution were determined by gel permeation chromatography (PL-GPC 220). The GPC column was eluted with THF at 40 °C at a rate of 1 mL/min and the data were calibrated with polystyrene standards. The M_n values have been corrected by a Mark–Houwink factor of 0.58 [30].

Typical procedure for polymerization of *rac*-LA

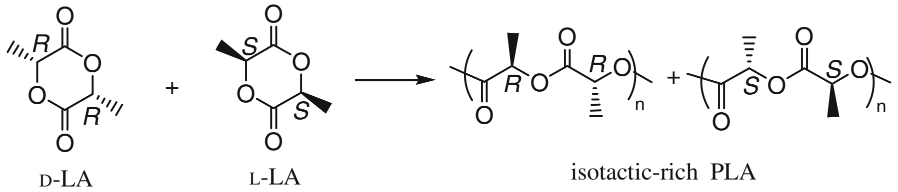
A toluene solution (10 mL) of the racemic initiator **1** (0.057 g, 0.05 mmol) and *rac*-LA (1.44 g, 10 mmol) was stirred at 130 °C for 10 h. The reaction was stopped by cooling the tube quickly with an ice-water bath. A sample was taken from the resulting solution for determination of the conversion of *rac*-LA by ^{1}H NMR spectroscopy. The volatiles were evaporated under reduced pressure and the residue was dissolved in a minimum amount of CH_2Cl_2. The polymer was precipitated with addition of cold methanol. The resulting solid was washed with methanol (3 × 20 mL) and dried under high vacuum.

Results and discussion

Influence of temperature on the ROP of *rac*-LA

The ROP of *rac*-LA catalyzed by **1** and **2** was initially explored at 130 °C in toluene with a 100:1 molar ratio of monomer to catalyst. The conversions of *rac*-LA are 94–97% in 8 h with activities of 3.05–3.25 $g_{pol}\ mmol_{ini}^{-1}\ h^{-1}$ (Table 2, entries 1 and 5). The M_n values are in the range of 15300–16100 with narrow polydispersities (M_w/M_n = 1.09–1.13). The enantiomeric dinuclear complexes **1** and **2** play an

Table 1 Effect of temperature on the ROP of *rac*-LA initiated by **1** and **2**



Entry	Initiator	T (°C)	Time (h)	Conv[a]	M_n[b]	M_w/M_n[b]	P_m[c]
1	**1**	90	48	80	12800	1.01	0.73
2	**1**	110	48	94	15900	1.03	0.72
3	**1**	130	8	97	16100	1.09	0.65
4	**2**	90	48	43	6300	1.02	0.73
5	**2**	110	48	94	15500	1.02	0.70
6	**2**	130	8	94	15300	1.13	0.66

Conditions: [*rac*-LA] = 1 M, [*rac*-LA]/[Ini] = 100:1, toluene 10 mL

[a] Determined by ^{1}H NMR

[b] Determined by GPC in THF and calibrated with polystyrene standards. The M_n values have been corrected by a Mark–Houwink factor of 0.58, due to the use of polystyrene standards [30]

[c] P_m is the probability of isotactic enchainment calculated by analysis of the homonuclear-decoupled ^{1}H NMR spectra [11]

isotactic selectivity in the ROP of *rac*-LA. The homonuclear-decoupled ^{1}H NMR spectra of the methine region of the PLA sample derived from **1** and **2** suggest the formation of the isotactic-rich PLA (Supplementary Figs. S1, S2). The P_m values are 0.65 and 0.66 for the ROP of *rac*-LA initiated by **1** and **2**, respectively.

The conversion of *rac*-LA apparently went down when the reaction temperature was decreased from 130 to 90 °C while keeping the molar ratio of *rac*-LA to catalyst in 100:1. The conversion of *rac*-LA was reduced from 97% with **1** as initiator in 8 h at 130 °C to 80% in 48 h at 90 °C (Table 1, entry 3 vs. 1). The catalytic results show that the hafnium complex **2** is somewhat less active than the analogous zirconium complex **1**. The conversion of *rac*-LA decreased from 94% in 8 h at 130 °C to 43% in 48 h at 90 °C with **2** as initiator (Table 1, entry 6 vs. 4). It was noticed that the polydispersities of PLA are further narrowed to 1.01–1.03 with decrease of the reaction temperature to 110 and 90 °C, together with gradual decrease in the M_n value. The narrow polydispersities (M_w/M_n = 1.01–1.13) and the linear correlation between the observed M_n and the conversions of monomer imply a living polymerization system with **1** and **2** as initiators (Supplementary Figs. S3, S4).

An increase of isotactic selectivity (P_m) of PLA was observed with decrease of the reaction temperature. The P_m was up to 0.73 when polymerization of *rac*-LA was carried out at 90 °C with **1** or **2** as initiator (Table 1, entries 1 and 4), indicating that introduction of the chiral N atom to the initiator does play a role in stereoselective polymerization. The isotactic selectivities of **1** and **2** are higher than the P_m values (0.5–0.6) reported for the ROP of *rac*-LA initiated by the mononuclear zirconium and hafnium complexes containing an analogous symmetric amine-pyridine-bis(phenolate) ligand [27]. To the best of our knowledge, among group 4 metal complexes used as initiators for polymerization of *rac*-LA, only a salan zirconium complex was found to be an efficient initiator for the stereoselective polymerization of *rac*-LA to stereoblock PLA with isoselectivity up to 0.75.

Influence of the molar ratio of monomer to initiator on the ROP of *rac*-LA

The influence of the molar ratio of monomer to initiator on the ROP of *rac*-LA was studied with **1** and **2** as initiators in toluene at 130 °C. As the molar ratio of *rac*-LA to initiator was increased from 100:1 to 200:1, the conversions of monomer maintained 91–97%, but the M_n values are almost doubled (Table 2, entries 2 vs. 1 and 6 vs. 5). Further increase of the molar ratio of *rac*-LA to initiator to 300:1 resulted in an apparent decrease of the conversions of monomer to 75% for **1** and 67% for **2**, with gradual increases of the M_n values and slight decreases of the polydispersities from 1.13 to 1.04. Variation of the molar ratio of *rac*-LA to **1** or **2** does not influence the isotactic selectivity (P_m) of the ROP of *rac*-LA, which varies in the range of 0.65–0.71.

Kinetic and thermodynamic studies of the ROP of *rac*-LA with complexes **1** and **2**

The kinetics of the ROP of *rac*-LA initiated by **1** and **2** at different molar ratios of monomer to initiator in toluene at 130 °C was studied by ^{1}H NMR spectroscopy. Semilogarithmic plots for these polymerizations are shown in Figs. 2 and 3. In each figure, the linear relationship between $\ln([LA]_0/[LA]_t)$ and time (h) reveals a first-order kinetics in monomer. The ROP of *rac*-LA with **1** and **2** proceeds according to the rate equation: $-d[LA]/dt = k_{app}[LA]$, where $k_{app} = k_p[Ini]^x$ (k_{app} and k_p are the apparent propagation and propagation rate constants). The polymerization rate of *rac*-LA increases with decrease of the molar ratio of monomer to initiator. The k_{app}

Table 2 The ROP of *rac*-LA in different molar ratios of monomer to initiator

Entry	Initiator	Mon:Ini	Time (h)	Conv^a	M_n^{b}	M_w/M_n^{b}	P_m^{c}	Activity^d
1	**1**	100:1	8	97	16100	1.09	0.65	3.25
2	**1**	200:1	10	94	30100	1.08	0.71	2.47
3	**1**	250:1	10	85	32500	1.06	0.67	2.75
4	**1**	300:1	10	75	33700	1.04	0.67	2.97
5	**2**	100:1	8	94	15300	1.13	0.66	3.05
6	**2**	200:1	10	91	28000	1.07	0.66	2.38
7	**2**	250:1	10	80	30800	1.05	0.68	2.63
8	**2**	300:1	10	67	31000	1.04	0.67	2.64

Conditions: [*rac*-LA] = 1 M, 130 °C, toluene 10 mL

[a−c] The same as those in Table 1

[d] $g_{pol}\ mmol_{ini}^{-1}\ h^{-1}$

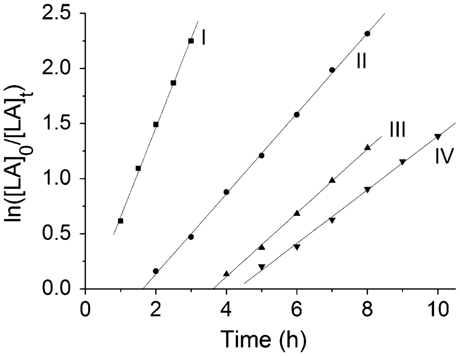


Fig. 2 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ versus time for the ROP of *rac*-LA in toluene at 130 °C with **1** as initiator and [*rac*-LA] = 1.0 M (*I* [*rac*-LA]/[**1**] = 100:1, *II* 200:1, *III* 250:1, *IV* 300:1)

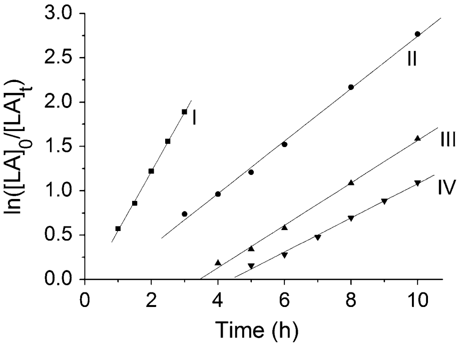


Fig. 3 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ versus time for the ROP of *rac*-LA in toluene at 130 °C with **2** as initiator and [*rac*-LA] = 1.0 M (*I* [*rac*-LA]/[**2**] = 100:1, *II* 200:1, *III* 250:1, *IV* 300:1)

for **1** changes from 0.243 to 0.809 h^{-1} when the [*rac*-LA]/[**1**] ratio is varied from 300 to 100. The similar k_{app} values are calculated for the ROP of *rac*-LA using **2** as initiator. They are 0.192, 0.296, and 0.667 h^{-1} with [*rac*-LA]/[**2**] = 300, 200, and 100, respectively, which are somewhat slower than the rates of polymerization of *rac*-LA by complex **1** under the same condition.

The kinetic dependence on the initiator was also studied with the concentration of the initiator (**1** or **2**) varying from 0.0033 to 0.01 M. The apparent propagation rate constants versus the concentrations of the initiator are plotted in Figs. 4 and 5. The linear relationship of $\ln k_{app}$ versus ln[Ini] reveals a first-order dependency of the rate

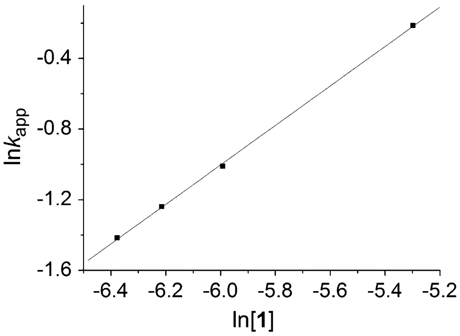


Fig. 4 Plot of $\ln k_{app}$ versus ln[**1**] for the ROP of *rac*-LA in toluene at 130 °C with [*rac*-LA] = 1.0 M

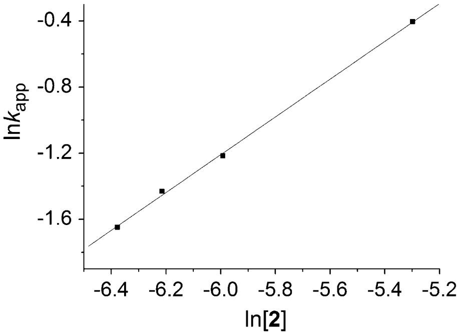


Fig. 5 Plot of $\ln k_{app}$ versus ln[**2**] for the ROP of *rac*-LA in toluene at 130 °C with [*rac*-LA] = 1.0 M

on initiator ($x = 1.1 \pm 0.04$). Therefore, the ROP of *rac*-LA initiated by **1** or **2** follows the overall rate equation: $-d[LA]/dt = k_p[LA][Ini]$.

Furthermore, the kinetics of the ROP of L-LA was also studied to make a comparison. The polymerization performed with an enantiopure L-LA resulted in an entirely isotactic PLA (Supplementary Fig. S5). Therefore, the epimerization in this catalytic system can be ruled out [31]. The k_{app} of 0.491 h^{-1} for the ROP of L-LA with **1** in toluene at 130 °C is apparently higher than that (0.364 h^{-1}) determined for the polymerization of *rac*-LA under the same conditions (Fig. 6). Similarly, the k_{app} values for the ROP of *rac*-LA and L-LA with **2** are 0.296 and 0.372 h^{-1},

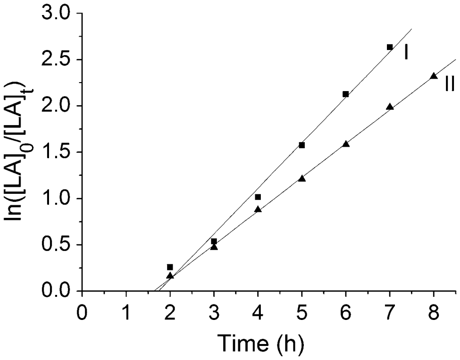


Fig. 6 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ versus time for the polymerizations of L-LA and *rac*-LA in toluene at 130 °C with **1** as initiator and [LA] = 1.0 M (*I* [L-LA]/[**1**] = 200:1, *II* [*rac*-LA]/[**1**] = 200:1)

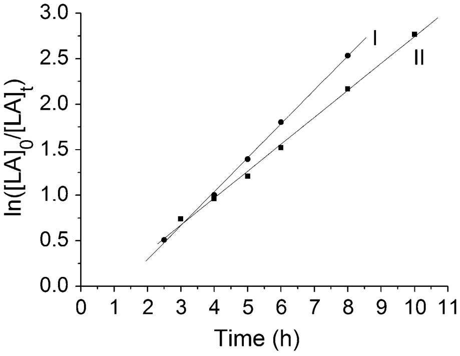


Fig. 7 Semilogarithmic plots of $\ln([LA]_0/[LA]_t)$ versus time for the polymerizations of L-LA and *rac*-LA in toluene at 130 °C with **2** as initiator and [LA] = 1.0 M (*I* [L-LA]/[**2**] = 200:1, *II* [*rac*-LA]/[**2**] = 200:1)

respectively (Fig. 7). The lower polymerization rates of *rac*-LA than those of L-LA indicate that the isoselective polymerization occurs with complexes **1** and **2** as initiators. The predominant formation of isotactic PLA from *rac*-LA polymerization implies that the homopropagation rate ($k_{\mathrm{D/D}}$ or $k_{\mathrm{L/L}}$) is higher than the cross-propagation rate ($k_{\mathrm{D/L}}$ or $k_{\mathrm{L/D}}$). These kinetic results are consistent with the observed isotactic selectivity in the ROP of *rac*-LA with **1** and **2**.

Thermodynamic studies on the ROP of *rac*-LA using **1** and **2** as initiators were conducted to get activation parameters of the reaction. The polymerization of *rac*-LA speeded up with increase of the reaction temperature (Supplementary Figs. S6, S7). The k_{app} values are 0.034, 0.157, and 0.809 h^{-1} for **1** and 0.012, 0.078, and 0.667 h^{-1} for **2** at 90, 110, and 130 °C, respectively. The activation parameters of the polymerization of *rac*-LA using **1** and **2** as initiators are calculated according to the following equation: $\ln(k_{\mathrm{app}}/T) = -(\Delta H^{\neq}/\mathrm{R}T) + \ln(K_{\mathrm{b}}/h) + \Delta S^{\neq}/R$ using the k_{app} values determined at different temperatures (Supplementary Figs. S8, S9). The activation enthalpy ($\Delta H^{\neq}$) for the *rac*-LA polymerization with **1** is 93.2 kJ mol^{-1} and the entropy ($\Delta S^{\neq}$) is -86.33 J K^{-1} mol^{-1}. The activation enthalpy ($\Delta H^{\neq} = 119.1$ kJ mol^{-1}) and entropy ($\Delta S^{\neq} = -23.9$ J K^{-1} mol^{-1}) for the ROP of *rac*-LA initiated by **2** are computed in the same way.

Studies on the mechanism of the ROP of *rac*-LA with complex 1

To gain some insights into the initiation mechanism, short oligomers of *rac*-LA were prepared. The oligomerization of *rac*-LA was performed with complex **1** (0.1 mmol) in a molar ratio of 20:1 for monomer to initiator in toluene (2 mL) at 130 °C for 4 h. The resulting solution was quenched by a drop of methanol. Two sets of peaks are found in the MALDI-TOF mass spectrum of the oligomer (Fig. 8).

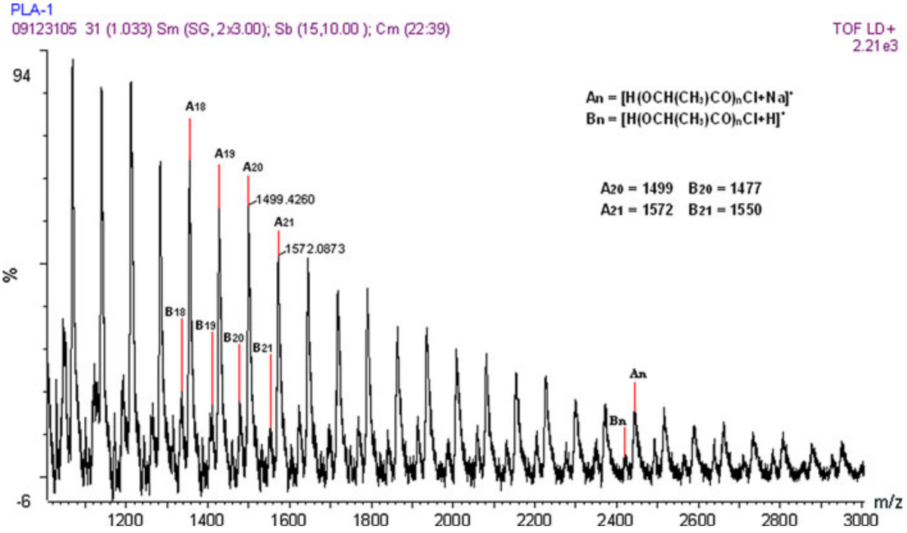


Fig. 8 A MALDI-TOF mass spectrum of the oligomer obtained from the ROP of *rac*-LA with **1** after the resulting solution is quenched with a drop of methanol

The regular mass intervals of the two sets of peaks are well consistent with the species of $[H(OCH(CH_3)CO)_nCl+Na]^+$ (An) and $[H(OCH(CH_3)CO)_nCl+H]^+$ (Bn), respectively, both with an acyl chloride terminal end cap.

Moreover, the ^{1}H NMR spectrum of the oligomer does not show any signals for aromatic protons, which suggests that the groups of the amine-pyridine-bis-(phenolate) ligand do not attend the polymerization process. In addition to the strong signals at δ 5.15–5.21 (m, OCH(CH$_3$)) and 1.55–1.59 (m, CH(CH_3)) for the protons of the oligomer chains, the ^{1}H NMR spectrum of the oligomer, obtained after the resulting solution is quenched with an excess of methanol, shows the signals at δ 4.36 (q, OCH(CH$_3$)), 2.76 (br, OH), and 1.49 (d, CH(CH_3)) for the end group HOCH(CH$_3$)C=O, and a small singlet at δ 3.76 (OCH_3) for the methyl ester, derived from alcoholysis of the acyl chloride terminal (–COCl) (Fig. 9). Both the MALDI-TOF MS and the ^{1}H NMR spectra of the oligomer support that the chloride ion acts as the initiating group in the ROP of *rac*-LA with complex **1**. The initiation may occur through the insertion of a molecule of *rac*-LA into the Zr–Cl bond of complex **1** and the ROP of *rac*-LA proceeds exclusively via an acyl-oxygen cleavage of the monomer. This mechanism is further supported by the observation of only one methine peak in the homonuclear-decoupled ^{1}H NMR spectrum of PLLA (Supplementary Fig. S5). According to all spectroscopic evidence and the catalytic results, a coordination-insertion mechanism is proposed for the ROP of *rac*-LA initiated by complexes **1** and **2**.

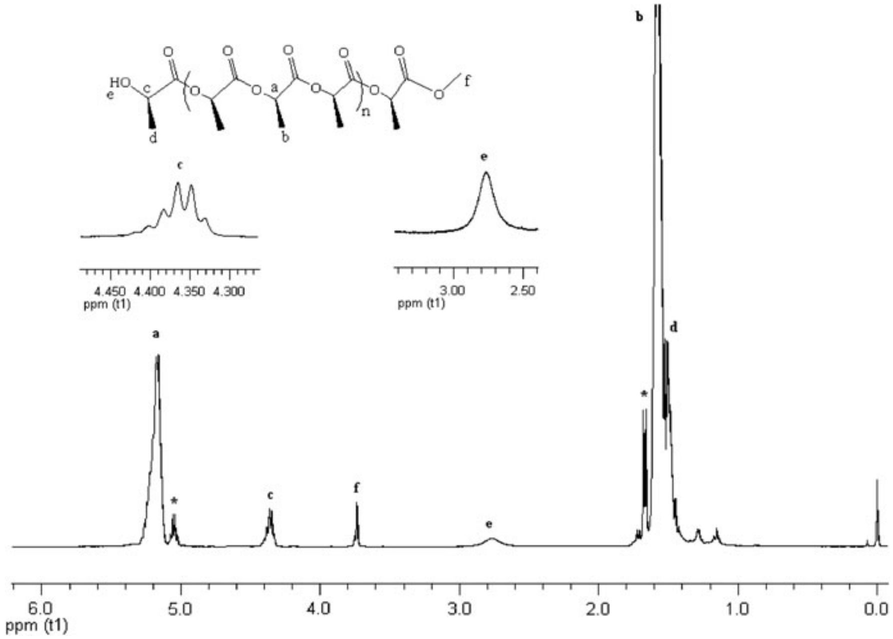


Fig. 9 ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of the oligomer obtained from the ROP of *rac*-LA with **1** after the resulting solution is alcoholized with an excess of methanol (The signals marked with an *asterisk* are attributed to the monomer)

Conclusions

The experimental results show that complexes **1** and **2** are efficient initiators for the ROP of *rac*-LA. The polymerization proceeds in a well-controlled manner, giving isotactic-rich PLA in a narrow polydispersity. Although the stereocontrol mechanism for the ROP of *rac*-LA initiated by these group 4 metal complexes is not clearly understood currently, it is assumed that the asymmetric coordination environment around the metal center, resulting from the chirality of the tertiary amine N atom in the ligand, may play a role in governing the stereoselective ROP of *rac*-LA. The MALDI-TOF MS and the ^{1}H NMR spectra of the *rac*-LA oligomer with **1** suggest that the initiating group is a chloride ion, thus the initiation process may occur through the insertion of a molecule of *rac*-LA into the M–Cl bond of the complex. Further studies are under way to improve the stereoselectivity of the ROP of *rac*-LA by modifying the substituents and structures of the unsymmetric N_2O_2 ligands and to enhance the activity by adjusting the metal center and the initiating group of the complex.

Acknowledgments This study was supported by the National Natural Science Foundation of China (Grant no. 20973032), and the K & A Wallenberg Foundation of Sweden.

References

1. Platel RH, Hodgson LM, Williams CK (2008) Biocompatible initiators for lactide polymerization. Polym Rev 48:11–63
2. Radano CP, Baker GL, Smith MR III (2000) Stereoselective polymerization of a racemic monomer with a racemic catalyst: direct preparation of the polylactic acid stereocomplex from racemic lactide. J Am Chem Soc 122:1552–1553
3. Ovitt TM, Coates GW (2002) Stereochemistry of lactide polymerization with chiral catalysts: new opportunities for stereocontrol using polymer exchange mechanisms. J Am Chem Soc 124:1316–1326
4. Nomura N, Ishii R, Akakura M, Aoi K (2002) Stereoselective ring-opening polymerization of racemic lactide using aluminum-achiral ligand complexes: exploration of a chain-end control mechanism. J Am Chem Soc 124:5938–5939
5. Hormnirun P, Marshall EL, Gibson VC, Pugh RI, White AJP (2006) Study of ligand substituent effects on the rate and stereoselectivity of lactide polymerization using aluminum salen-type initiators. Proc Natl Acad Sci USA 103:15343–15348
6. Du H, Pang X, Yu H, Zhuang X, Chen X, Cui D, Wang X, Jing X (2007) Polymerization of *rac*-lactide using Schiff base aluminum catalysts: structure, activity, and stereoselectivity. Macromolecules 40:1904–1913
7. Hormnirun P, Marshall EL, Gibson VC, White AJP, Williams DJ (2004) Remarkable stereocontrol in the polymerization of racemic lactide using aluminum initiators supported by tetradentate aminophenoxide ligands. J Am Chem Soc 126:2688–2689
8. Chisholm MH, Gallucci JC, Phomphrai K (2004) Well-defined calcium initiators for lactide polymerization. Inorg Chem 43:6717–6725
9. Chisholm MH, Huffman JC, Phomphrai K (2001) Monomeric metal alkoxides and trialkyl siloxides: (BDI)Mg((OBu)-Bu-*t*)(THF) and (BDI)Zn(OSiPh$_3$)(THF). Comments on single site catalysts for ring-opening polymerization of lactides. J Chem Soc Dalton Trans 222–224
10. Chisholm MH, Gallucci J, Phomphrai K (2002) Coordination chemistry and reactivity of monomeric alkoxides and amides of magnesium and zinc supported by the diiminato ligand CH(CMeNC6H3–2, 6-Pr-i(2))(2). A comparative study. Inorg Chem 41:2785–2794

11. Chamberlain BM, Cheng M, Moore DR, Ovitt TM, Lobkovsky EB, Coates GW (2001) Polymerization of lactide with zinc and magnesium beta-diiminate complexes: stereocontrol and mechanism. J Am Chem Soc 123:3229–3238
12. Chen HY, Tang HY, Lin CC (2006) Ring-opening polymerization of lactides initiated by zinc alkoxides derived from NNO-tridentate ligands. Macromolecules 39:3745–3752
13. Nimitsiriwat N, Gibson VC, Marshall EL, Elsegood MRJ (2008) The reversible amination of tin(II)-ligated imines: latent initiators for the polymerization of *rac*-lactide. Inorg Chem 47:5417–5424
14. Ma H, Spaniol TP, Okuda J (2006) Highly heteroselective ring-opening polymerization of *rac*-lactide initiated by bis(phenolato)scandium complexes. Angew Chem Int Ed 45:7818–7821
15. Amgoune A, Thomas CM, Roisnel T, Carpentier J-F (2006) Ring-opening polymerization of lactide with group 3 metal complexes supported by dianionic alkoxy-amino-bisphenolate ligands: combining high activity, productivity, and selectivity. Chem Eur J 12:169–179
16. Amgoune A, Thomas CM, Carpentier J-F (2007) Yttrium complexes as catalysts for living and immortal polymerization of lactide to highly heterotactic PLA. Macromol Rapid Commun 28:693–697
17. Chmura AJ, Chuck CJ, Davidson MG, Jones MD, Lunn MD, Bull SD, Mahon MF (2007) A germanium alkoxide supported by a C_3-symmetric ligand for the stereoselective synthesis of highly heterotactic polylactide under solvent-free conditions. Angew Chem Int Ed 46:2280–2283
18. Kim Y, Jnaneshwara GK, Verkade JG (2003) Titanium alkoxides as initiators for the controlled polymerization of lactide. Inorg Chem 42:1437–1447
19. Russell SK, Gamble CL, Gibbins KJ, Juhl KCS, Mitchell WS III, Tumas AJ, Hofmeister GE (2005) Stereoselective controlled polymerization of DL-lactide with $[\mathrm{Ti(trisphenolate)O}\text{-}i\text{-}\mathrm{Pr}]_2$ initiators. Macromolecules 38:10336–10340
20. Chmura AJ, Davidson MG, Frankis CJ, Jones MD, Lunn MD (2008) Highly active and stereoselective zirconium and hafnium alkoxide initiators for solvent-free ring-opening polymerization of *rac*-lactide. Chem Commun 1293–1295
21. Spassky N, Wisniewski M, Pluta C, Borgne AL (1996) Highly stereoelective polymerization of rac-(D, L)-lactide with a chiral Schiff's base/aluminium alkoxide initiator. Macromol Chem Phys 197:2627–2637
22. Jhurry D, Bhaw-Luximon A, Spassky N (2001) Synthesis of polylactides by new aluminium Schiff's base complexes. Macromol Symp 175:67–80
23. Zhong Z, Dijkstra PJ, Feijen J (2002) [(salen)Al]-mediated, controlled and stereoselective ring-opening polymerization of lactide in solution and without solvent: synthesis of highly isotactic polylactide stereocopolymers from racemicD,L-lactide. Angew Chem Int Ed 41:4510–4513
24. Zhong Z, Dijkstra PJ, Feijen J (2003) Controlled and stereoselective polymerization of lactide: kinetics, selectivity, and microstructures. J Am Chem Soc 125:11291–11298
25. Frediani M, Semeril D, Mariotti A, Rosi L, Frediani P, Rosi L, Matt D, Toupet L (2008) Ring opening polymerization of lactide under solvent-free conditions catalyzed by a chlorotitanium calix[4]arene complex. Macromol Rapid Commun 29:1554–1560
26. Lee J, Kim Y, Do Y (2007) Novel chlorotitanium complexes containing chiral tridentate Schiff base ligands for ring-opening polymerization of lactide. Inorg Chem 46:7701–7703
27. Chmura AJ, Davidson MG, Jones MD, Lunn MD, Mahon MF, Johnson AF, Khunkamchoo P, Roberts SL, Wong SSF (2006) Group 4 complexes with aminebisphenolate ligands and their application for the ring opening polymerization of cyclic esters. Macromolecules 39:7250–7257
28. Hu MG, Wang M, Zhu HJ, Zhang L, Zhang H, Sun LC (2010) Preparation and structures of enantiomeric dinuclear zirconium and hafnium complexes containing two homochiral N atoms, and their catalytic property for polymerization of *rac*-lactide. Dalton Trans 39:4440–4446
29. Pascaly M, Duda M, Schweppe F, Zurlinden K, Müller FK, Krebs B (2001) The systematic influence of tripodal ligands on the catechol cleaving activity of iron(III) containing model compounds for catechol 1,2-dioxygenases. Dalton Trans 828–837
30. Kowalski A, Duda A, Penczek S (1998) Polymerization of L,L-lactide initiated by aluminum isopropoxide trimer or tetramer. Macromolecules 31:2114–2122
31. Thakur KAM, Kean RT, Hall ES, Doscotch MA, Munson EJ (1997) A quantitative method for determination of lactide composition in poly(lactide) using ^{1}H NMR. Anal Chem 69:4303–4309