Homo- and heteroleptic zinc aminophenolates as initiators for lactide polymerization†

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The reaction of $ZnEt_2$ with one or two equivalents of aminophenolate ligand *N*-[methyl(2-hydroxy-3, 5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine gives hetero- and homoleptic molecular compounds $[(\mu,\eta^2\text{-}L^2)ZnEt]_2$ and $[Zn(\eta^2\text{-}L^2)_2]$. The later is most probably a mixture of diastereoisomers that in solution shows an interesting dynamic behaviour. Both complexes as well as the BnOH derivative of the latter, $[(\eta^2\text{-}L^2)Zn(\mu\text{-}BnO)]_2$, proved excellent initiators for lactide polymerization.

Introduction

Polyesters derived from renewable sources have attracted considerable attention that results from their biomedical and pharmaceutical applications including implants, sutures and drug delivery devices.[1] Polylactide (PLA) and other aliphatic polyesters are conventionally prepared by ring-opening polymerization (ROP) of cyclic esters through a coordination-insertion pathway involving metal alkoxide initiators.[2] This route has provided rapid and stereoselective conversion to the desired polyesters with exceptional weight control and narrow polydispersity. Alternatively, an activated by catalytic systems based on metal complex/alcohol combinations monomer pathway has also been proposed for ROP of cyclic esters,[3] although this route usually produces low molecular polyesters with broad molecular weight distribution. Nevertheless, a metal complex/alcohol catalytic system offers several advantages such as the ability to cap polyester microstructures with biologically relevant endgroups without catalyst modification. Given that the future commercial use of polyesters relies on understanding of synthetic pathways, we focused on a synthesis of new, well-defined initiators that could be used for mechanistic studies of monomer-activated pathway.

Our primary goal was to prepare Zn(II) complexes supported by aminophenolate ligand, a choice influenced by previous reports indicating that controlled and, in some cases, stereoselective monomer conversion could be achieved with Zn(II) initiators in the presence of donor ligands.[4] For example β-diiminate (BDI)[5] or trispyrazolylhydroborate stabilized zinc complexes[6] have generated active initiators for ROP of lactide (LA). These catalysts polymerize *rac*-LA to mostly heterotactic PLA similarly to recently reported Schiff base ligated zinc alkoxides[4a,7] and *N*,*N*,*O*-multidentate complexes.[4b,8] Additionally, our initial studies on the development of magnesium initiators with aminophenolate ligands indicate that such ligands could play a dual role as the ancillary ligand as well as the initiating group.[9] Moreover, these ligands disfavor ligand dissociation in the presence of added alcohol initiators.

Here we report the synthesis, characterization and lactide polymerization activity of three new zinc complexes with aminophenolate ligand. Detailed structural studies in the solid state and in solution provided insight into the effect of catalyst architecture on lactide polymerization behaviour.

Experimental

General materials and experimental procedures

All the reactions and operations were performed under an inert atmosphere of N_2 using standard Schlenk techniques. Reagents were purified by standard methods: thf, distilled from CuCl, predried over NaOH, and then distilled from Na/benzophenone; toluene, distilled from Na; CH_2Cl_2, CD_2Cl_2 distilled from P_2O_5; hexanes, distilled from Na; methanol, distilled from Mg; C_6D_6, $C_6D_5CD_3$ distilled from CaH_2. L-LA (98%; Aldrich) was sublimed and recrystallized from toluene prior to use. $ZnEt_2$ (Aldrich; 1.0 M solution in hexanes) was used as received. BnOH (Aldrich; >99%) was distilled prior to use. *N*-[Methyl(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine (L^2-H) was prepared according to the literature.[9] ^1H and ^{13}C NMR spectra were recorded at temperature range from 298 to 351 K using a Bruker ESP 300E or 500 MHz spectrometer. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. The weights and number-average molecular weights of PLAs were determined by gel permeation chromatography (GPC) using a HPLC-HP 1090 II with a DAD-UV/Vis and RI detector HP 1047A and polystyrene calibration.

Complex synthesis

$[(\mu,\eta^2\text{-}L^2)ZnEt]_2$ (1). To a solution of L^2-H (0.66 g, 1.99 mmol) in toluene (50 mL) $ZnEt_2$ (2.00 mL, 2.00 mmol) was added dropwise. The reaction mixture was stirred for 3 h and the solution was evaporated to dryness. The resulted white powder was washed with hexanes (20 mL), filtered off and dried in vacuum. Yield: 0.63 g, (0.74 mmol; 74%). Anal. Calc. (found) for $C_{48}H_{82}N_2O_2Zn_2$ (849.95): C 67.83 (67.18), H 9.72 (9.55), N 3.30 (3.17%). ^1H NMR (C_6D_6, 298 K) δ: 7.71 (2H, d, ArH, J_{HH} = 4 Hz), 7.08 (2H, d, ArH, J_{HH} = 4 Hz), 4.68 (2H, d, NCH_2Ar, J_{HH} = 12 Hz), 3.61 (2H, d, NCH_2Ar, J_{HH} = 12 Hz), 2.30 (2H, m, C_6H_{11}), 2.02 (6H, s, NCH_3), 1.89 (18H, s, $C(CH_3)_3$), 1.67 (10H, m, C_6H_{11}), 1.48 (18H, s,

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$C(CH_3)_3$), 1.30 (10H, m, C_6H_{11}), 1.21 (4H, q, CH_2CH_3, J_{HH} = 8 Hz), 0.76 (6H, t, CH_2CH_3, J_{HH} = 8 Hz). ^{13}C NMR (C_6D_6, 298 K) δ: 160.1, 139.6, 138.9, 126.6, 126.4, 125.5 (12C, Ar), 63.3 (NCH_2Ar), 60.1 (2C, C_6H_{11}), 37.3 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 34.3 (NCH_3), 31.7 ($C(CH)_3)_3$), 31.2 ($C(CH)_3)_3$), 26.1, 25.9, 24.3 (10C, C_6H_{11}), 13.2 (CH_2CH_3), 0.7 (CH_2CH_3).

[Zn(L^2)$_2$] (2). To a solution of L^2-H (1.32 g, 3.98 mmol) in toluene (20 mL) $ZnEt_2$ (2.00 mL, 2.00 mmol) was added dropwise. The mixture was stirred at room temperature for 5 h after which time volatiles were removed *in vacuo* to yield a white powder. 10 mL of hexanes were added and the suspension was stirred for 2 h. The white solid was collected by filtration and dried in vacuum. Yield: 1.29 g, (1.77 mmol; 89%). Crystals suitable for X-ray crystallography were grown from toluene at 5 °C. Anal. Calc. (found) for $C_{44}H_{72}N_2O_2Zn$ (726.41): C 72.75 (72.52), H 9.99 (9.94), N 1.96 (1.89%). ^{1}H NMR for major **2a** form (C_6D_6, 298 K) δ: 7.72 (2H, s, ArH), 7.09 (2H, s, ArH), 4.16 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 3.47 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 3.20 (2H, m, C_6H_{11}), 2.48 (6H, s, NCH_3), 1.74 (18H, s, $C(CH_3)_3$), 1.66 (10H, m, C_6H_{11}), 1.59 (18H, s, $C(CH_3)_3$), 1.05 (10H, m, C_6H_{11}). ^{13}C NMR (C_6D_6, 298 K) δ: 164.3, 138.4, 135.5, 125.9, 124.4, 120.5 (12C, Ar), 65.3 (NCH_2Ar), 61.9 (2C, C_6H_{11}), 36.8 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 33.8 (NCH_3), 32.3 ($C(CH)_3)_3$), 30.2 ($C(CH)_3)_3$), 26.9, 26.1, 24.4 (10C, C_6H_{11}). Selected resonances for **2b** form (C_6D_6, 298 K) δ: 7.06 (2H, s, ArH), 4.22 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 3.62 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 2.43 (6H, s, NCH_3), 1.87 (18H, s, $C(CH_3)_3$), 1.78 (18H, s, $C(CH_3)_3$). Selected resonances for **2c** form (C_6D_6, 298 K) δ: 7.03 (2H, s, ArH), 4.68 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 3.77 (2H, d, NCH_2Ar, J_{HH} = 13 Hz), 2.23 (6H, s, NCH_3), 1.82 (18H, s, $C(CH_3)_3$), 1.73 (18H, s, $C(CH_3)_3$).

[(η^2-L^2)Zn(μ-OBn)]$_2$ (3). To a solution of **1** (1.10 g, 1.29 mmol) in toluene (50 mL) BnOH (0.27 mL, 2.60 mmol) was added dropwise and the reaction mixture was stirred for 1 h. After 3 days a white solid precipitated. It was collected by filtration and washed with hexanes and dried *in vacuo*. Yield 0.90 g, (0.90 mmol; 69%). Anal. Calc. (found) for $C_{58}H_{86}N_2O_4Zn_2$ (1006.09): C 69.24 (69.25), H 8.62 (8.63), N 2.78 (2.60%). ^{1}H NMR (C_6D_6, 298 K) δ: 7.75 (2H, s, ArH), 7.07 (10H, m, Ph), 6.91 (2H, s, ArH), 4.77 (4H, CH_2Ph), 3.79 (2H, d, NCH_2Ar, J_{HH} = 12 Hz), 3.52 (2H, d, NCH_2Ar, J_{HH} = 12 Hz), 2.33 (2H, m, C_6H_{11}), 2.12 (6H, s, NCH_3), 2.03 (18H, s, $C(CH_3)_3$), 1.68 (10H, m, C_6H_{11}), 1.55 (18H, s, $C(CH_3)_3$), 1.13 (10H, m, C_6H_{11}). ^{13}C NMR partial (C_6D_6, 298 K) δ: 164.7, 137.0, 144.9, 137.8, 135.4, 127.8, 127.5, 126.4, 125.6, 124.6 (Ar + Ph), 70.1 (CH_2Ph), 64.9 (NCH_2Ar), 64.2 (2C, C_6H_{11}), 36.7 ($C(CH_3)_3$), 36.2 ($C(CH_3)_3$), 34.2 (NCH_3), 32.5 ($C(CH)_3)_3$), 30.4 ($C(CH)_3)_3$), 26.4, 26.0, (C_6H_{11}).

Polymerization

Representative procedure. The monomer L-LA was placed in a Schlenk flask and zinc complex in CH_2Cl_2 was added. The reaction was stirred at the desired temperature for the prescribed time. Next, at certain time intervals about 1 mL aliquots were removed for determination of the conversion using ^{1}H NMR. After reaction was completed it was quenched with methanol, the solution was concentrated in vacuum and the polymer was precipitated with an excess of cold methanol. Filtration and drying in vacuum yielded a white polymer.

Computational details

Full optimization of the geometries was performed at the DFT level with Becke (B3) exchange functional[10] and Lee–Yang–Parr (LYP) correlation functional[11] and the standard 6–31G* basis set. Vibrational frequencies obtained at the same level were used to verify the nature of all stationary points found during optimization. The chemical shielding calculations were performed with the gauge-including atomic orbitals (GIAO) approach at the B3LYP/6–31G** level of theory. The calculated shieldings σ were transformed to chemical shifts in the TMS scale. All the results presented in this paper were evaluated by using Gaussian 03 program.[12]

X-Ray crystallography

X-ray diffraction data were collected using a KUMA KM4 CCD (ω scan technique) diffractometer equipped with an Oxford Cryosystem-Cryostream cooler.[13] The space groups were determined from systematic absences and subsequent least-squares refinement. Lorentz and polarization corrections were applied. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL Package.[14] Non hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined.

Results and discussion

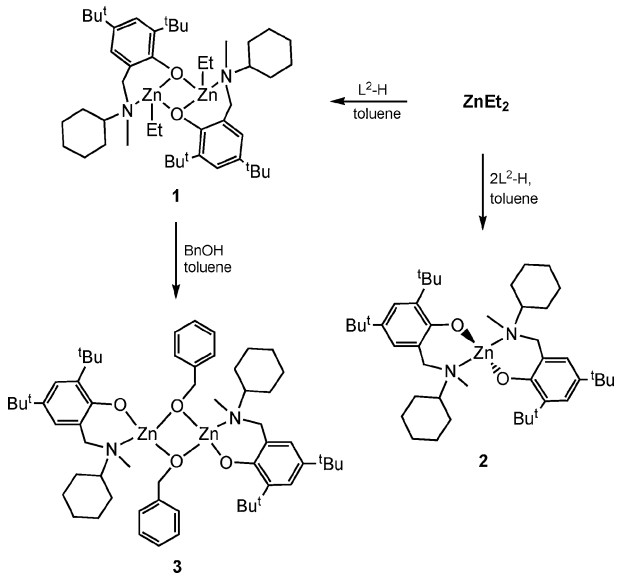
Syntheses

The *N*-[methyl(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine (L^2-H) ligand was readily prepared by Mannich condensation from *N*-cyclohexylmethylamine, paraformaldehyde, and 2,4-di-*tert*-butylphenol in refluxing methanol as described earlier.[9]

Treatment of L^2-H with one or two equivalents of $ZnEt_2$ in toluene at room temperature gave molecular zinc complexes [(μ,η^2-L^2)ZnEt]$_2$ (**1**) and [Zn(η^2-L^2)$_2$] (**2**), respectively, in 74–89% yield as shown in Scheme 1. Compound **1**, due to the presence of ethyl substituent at each Zn centre further reacts with benzyl alcohol (BnOH) in toluene to give dimeric [(η^2-L^2)Zn(μ-OBn)]$_2$ (**3**) in 69% yield (Scheme 1).

All compounds are soluble in polar organic solvents and in toluene and are insoluble in hexanes. Compounds **1** and **3** are moisture sensitive. Interestingly, **2** is stable in air for several hours and according to ^{1}H NMR spectroscopy only slightly decomposes after a few days at room temperature in C_6D_6 in an NMR tube. The complexes were formulated on the basis of NMR spectroscopy, elemental analysis and, in case of **2**, by X-ray crystallography.

The ^{1}H NMR spectra for **1–3** were informative as to formation of dimeric or monomeric species and diagnostic as to stability of the compounds in solution. The methylene protons of the $PhCH_2N$ linker in each complex are diastereotopic giving at room temperature doublets in contrast to the singlet resonance in the free L^2-H ligand. The ^{1}H NMR spectra of **1** and **3** support the existence of only one dimeric species in solution. This is evidenced by the equivalence of the phenyl resonances as well as the presence of two weakly coupled doublets for the diastereotopic $PhCH_2N$ protons.



Scheme 1 Synthesis of **1–3**.

Additionally, ^{1}H NMR for **1** showed signals at 1.21 and 0.76 ppm with integral ratio of 2 : 3 which are attributed to the methylene and methyl protons of the Et group at Zn atom.

Instead, the ^{1}H NMR spectrum of **2** at room temperature indicated the presence of three species in solution, most readily identified by distinctive peaks for the PhCH_2N resonances, appearing as two coupled doublets for each isomer as shown in Fig. 1. The three distinct sets of peaks observed for the isomers showed 1 : 2 : 5 ratio, depending on solution temperature. Variable-temperature (VT) ^{1}H NMR spectroscopy shown in Fig. 2 and the crystal structure of **2** revealed that one isomer (denoted **2a** in the experimental section) was more stable than the others. Entirely different ^{1}H NMR spectra are observed when Lewis base (tetrahydrofuran (thf) or lactide) was added to **2**. The pattern of signals corresponding to diastereotopic methylene signals changed its intensity and additionally the signals of coordinated thf molecule appeared. It suggests stabilization of one form by complexation of a Lewis base.

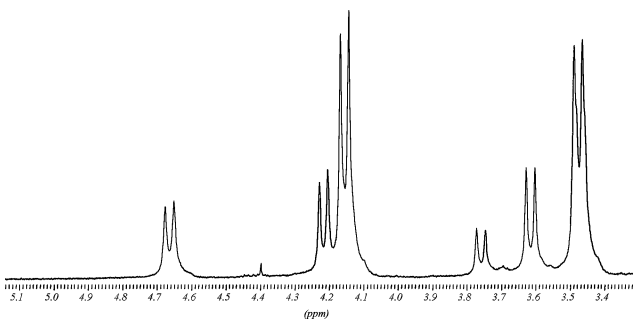


Fig. 1 ^{1}H NMR spectrum of the methylene region of complex **2**.

Solid-state structure determinations

The crystal structures of *N*-[methyl(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine (L^2-H) and **2** were determined as outlined in Table 1 and described in the Experimental section.

Table 1 Crystallographic data for L^2-H and **2**

	L^2-H	**2**
Chemical formula	$C_{22}H_{37}NO$	$C_{44}H_{72}N_2O_2Zn$
M_r	331.53	726.41
T/K	100(2)	100(2)
Space group	$P\bar{1}$	$C2/c$
a/Å	10.306(4)	16.197(4)
b/Å	10.451(4)	12.066(4)
c/Å	10.594(4)	21.147(6)
α/°	91.41(1)	90.0
β/°	112.25(1)	91.51(3)
γ/°	104.86(1)	90.0
V/Å^3	1011.3(7)	4131(2)
Z	2	4
D_c/g cm^{-3}	1.089	1.168
μ(Mo-Kα)/mm^{-1}	0.065	0.631
No. refls measured	15002	14171
No. unique refls	4855	4467
No. observed refls ($>2\sigma$)	3877	3580
R_{int}	0.0344	0.0287
R_1 ($>2\sigma$)	0.0482	0.0370
wR_2 ($>2\sigma$)	0.1076	0.0997
wR_2 (all)	0.1157	0.1054

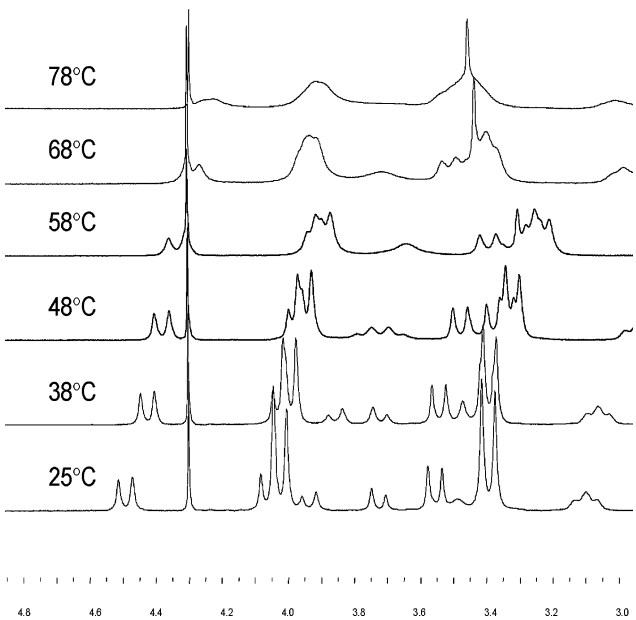


Fig. 2 VT ^{1}H NMR spectrum of the methylene region of **2** in d_8-toluene.

Colourless crystals of L^2-H were obtained by slow evaporation of methanol solution. The compound crystallizes in $P\bar{1}$ space group and the structure is shown in Fig. 3. No internal or external hydrogen bonds were observed in the crystal structure. The cyclohexyl substituent is antiperiplanar (or transoidal according to Michl and West nomenclature)[15] to the phenyl ring with C11–N1–C27–C21 of 163.16(10)°.

The solid-state structure of **2** is shown in Fig. 4 and the key metrical parameters are listed in the figure caption. The X-ray analysis shows **2** to be a molecular monomer. The metal centre is four-coordinated and is surrounded by two pairs of *N*,*O* atoms from two aminophenolate ligands that form a distorted tetrahedron around the zinc atom. Although such coordination is typical for zinc atom to our surprise only one monomeric four-coordinated zinc aminophenolate was found in the CCDC.[16]

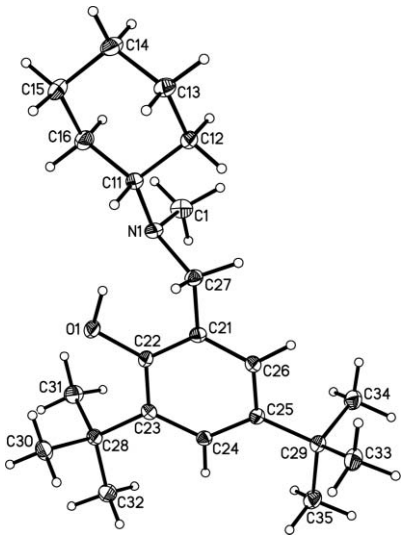


Fig. 3 Structure of *N*-[methyl(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine (L^2-H).

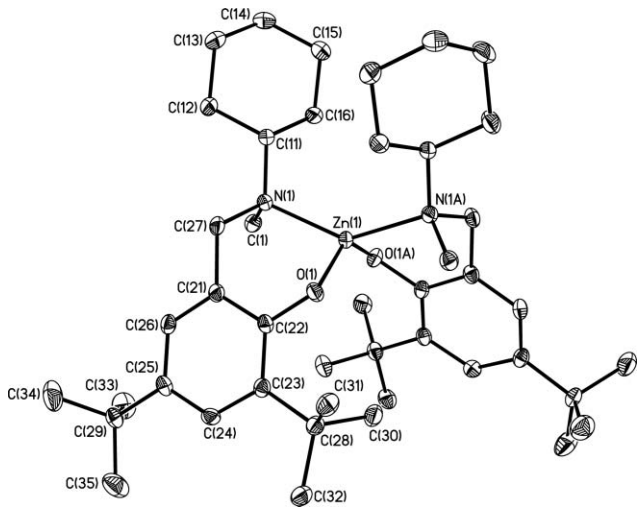


Fig. 4 View of *RR*-**2**. Key bond lengths (Å) and angles (°): Zn(1)–O(1), 1.909(2); Zn(1)–N(1), 2.130(2); O(1)–Zn(1)–O(1A), 129.94(8); O(1)–Zn(1)–N(1), 97.60(6); O(1)–Zn(1)–N(1A), 99.13(6); N(1)–Zn(1)–N(1A), 139.79(8). Symmetry operation for related atoms is: $1 - x$, y, $0.5 - z$.

The distances Zn–N(1) and Zn(1)–O(1) in **2** are 2.130(2) and 1.909(2) Å, respectively, and are similar to those found in $[Zn(L)]\cdot H_2O$ (L = 1-ethyl-4,7-bis(3-*tert*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononane; Zn–O = 1.963(1) and 1.934(1) Å; Zn–N = 2.113(1) and 2.277(1) Å)[17] and $[Zn(L)_2]$ (L = *N*-(2-hydroxy-5-nitrobenzyl)-(*R*)-α-methylbenzylamine; Zn–O = 1.935(2) and 1.933(2) Å; Zn–N = 2.0426(19) and 2.0458(19) Å).[16] Both nitrogen atoms in Fig. 4 have *R* configuration and since the compound crystallizes in the centrosymmetric *C*2/*c* space group the diastereomer S_NS_N is also present in the crystal lattice.

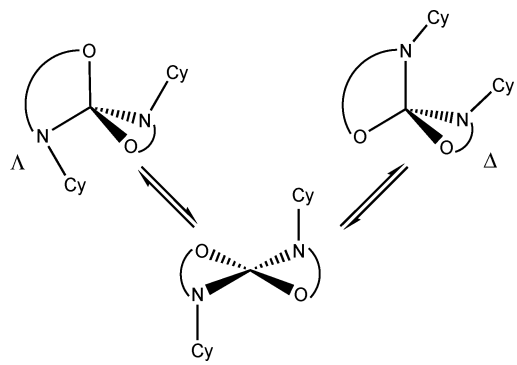
DFT Calculations

We were very curious about the nature of the "isomers" of **2** in solution. In an effort to reveal their origin DFT studies were applied. First, optimization of the single-crystal molecule geometry was performed with a starting geometry based on the X-ray data. Since the free ligand's nitrogen atom is prochiral three different diastereoisomers ($R_NS_N = S_NR_N$) are possible after their coordination to the metal centre. Moreover the tetrahedral complexes of $[M(ab)_2]$ (ab = chelating ligand) formulation can give two stereoisomers (Δ and Λ)[18] what sums up to six different stereoisomers: ΔR_NR_N, ΔS_NS_N, $\Delta R_NS_N = \Delta S_NR_N$, ΛS_NS_N, ΛR_NR_N, and $\Lambda R_NS_N = \Lambda S_NR_N$.

As can easily be noticed, the most recognized difference between isomers is the mutual position of cyclohexyl (or methyl) substituents at nitrogen atoms. In the ΔR_NR_N and ΛS_NS_N isomers they are "aligned" which, at a first glimpse, does not seem to be geometrically preferred. In the $\Delta R_NS_N = \Delta S_NR_N$ and $\Lambda R_NS_N = \Lambda S_NR_N$ isomers the cyclohexyl ligand is coaxial with methyl substituent from the second ligand. Finally, in the Δ*SS* and Λ*RR* isomers the methyls are "aligned".

The geometry optimization for the possible isomers was performed and shielding constants were next calculated. The resulted theoretical ^{1}H NMR spectra for R_NR_N, S_NS_N, and $R_NS_N = S_NR_N$ (all Δ isomers; data for isomer Δ and the corresponding Λ one are equivalent) diastereoisomers showed signals of the diastereotopic protons of the PhCH_2N (linked to C(27) at Fig. 4) linker at: δ 3.29, 3.42, 3.55 and 4.05, 4.08, 4.28 (experimental values: δ 3.48, 3.62, 3.76 and 4.15, 4.22, 4.67).

Although we were quite satisfied with this result we also turned our attention to possible racemization of R_NR_N-**2** through the polytopal isomer as shown is Scheme 2.



Scheme 2 Racemization of **2** through its polytopal square-planar isomer.

Unfortunately, we were not able to stabilize the square-planar isomer but we managed to see changes in shielding constants and chemical shifts in relation with complex deformation that is characterized by changes in the O–Zn–O and N–Zn–N bond angles. Table 2 shows the four most stable structures. They do not significantly differ in Δ*E* values (from 0.63 to 1.55 kcal mol^{-1}), what suggests easy transformation between them, although high barriers between the minima cannot be unambiguously excluded.

As can be noticed the small changes in the complex geometry can cause significant changes in the chemical shift of the diastereotopic protons. This can explain the bigger differences in chemical shift of doublets observed in the experimental spectrum of **2**.

Polymerization of lactide

The focus of our attention was next the verification of the reactivity of **2** and **3** as initiators for lactide polymerization. Both were found

Table 2 Structures, energies and chemical shifts of diastereotopic protons of deformed **2**

	Isomer 1	Isomer 2	Isomer 3	Isomer 4
O–Zn–O/Å	130.8	118.8	124.8	125.4
N–Zn–N/Å	130.4	116.2	138.1	136.6
ΔE/kcal mol^{-1}	0.00	0.63	1.31	1.55
σ (H1)/ppm	3.35	5.09	3.22	4.92
σ (H2)/ppm	3.98	3.23	4.22	3.46
σ (H1′)/ppm	3.35	5.09	3.22	4.92
σ (H2′)/ppm	3.98	3.23	4.22	3.46

Primed protons are diastereotopic CH_2 ones from the second ligand at the same metal center.

to ring-open L-lactide to produce isotactic poly-L-lactide (PLLA) in toluene or CH_2Cl_2 at room temperature with the expected molecular weight and low polydispersity. The results are collected in Table 3.

All of the initiator systems exhibit molecular weights in close agreement with calculated values and narrow PDI, characteristic for well controlled living propagation. The high level of control afforded by these initiators was exemplified by linear correlations between M_n and conversion shown in Fig. 5. The heteroleptic complex **3** is notably more reactive than **2**. These initiators polymerized 100 equiv. of L-lactide within 2 h and 6 days, respectively. The ^{1}H NMR spectrum of PLLA prepared using a [L-LA] : [**3**] ratio of 20 : 1 shoved one benzyl ester and one hydroxy chain end suggesting that the initiation occurred through the insertion of the benzyloxy group into L-lactide (Fig. 6, Scheme 3).

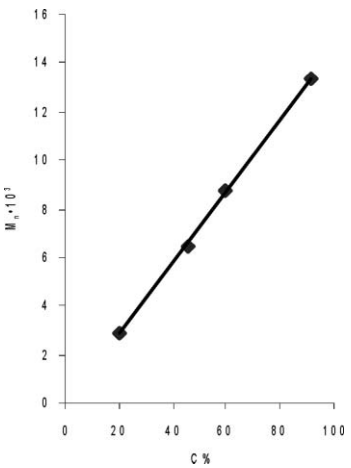


Fig. 5 Plot of PLLA M_n as a function of monomer conversion for the polymerization initiated by **3**.

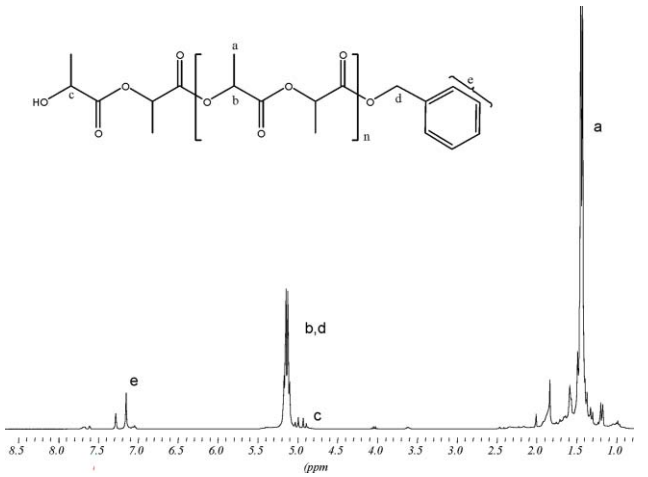
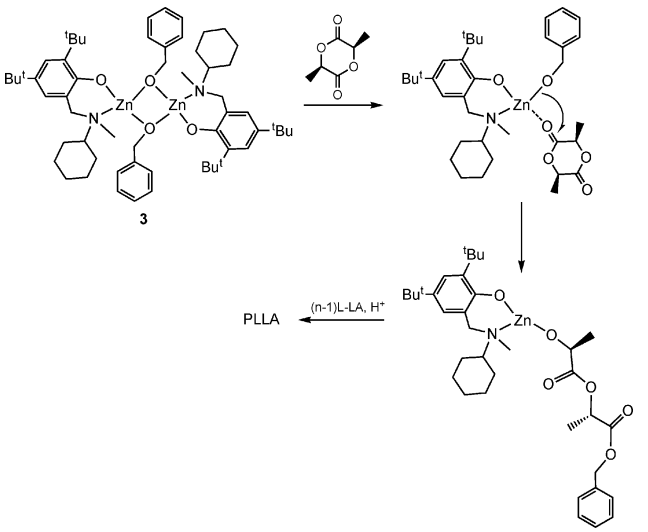


Fig. 6 ^{1}H NMR of PLLA prepared with **3** ([L-LA] : **3** = 20 : 1).



Scheme 3 Proposed mechanism for the ring-opening polymerization of L-LA initiated by **3**

As it was already pointed out, the ^{1}H NMR spectrum of compound **2** in CD_2Cl_2 exhibits three sets of doublets for the diastereotopic methylene hydrogens but when benzyl alcohol and lactide were added to a CD_2Cl_2 solution of **2**, the pattern of

Table 3 Polymerization of L-lactide with initiators (I) **2**, **3** and **2**–BnOH[a]

Entry	I	Solvent	[I] : [L-LA] : BnOH	t/min	$10^{-3}M_n$[b]	$10^{-3}M_n$[c]	Conv.[d] (%)	PDI[b]
1	**3**	CH_2Cl_2	1 : 100 : 0	120	15.38	14.23	98	1.09
2	**3**	Toluene	1 : 50 : 0	60	6.98	6.59	90	1.11
3	**2**	CH_2Cl_2	1 : 100 : 0	6 days	16.38	11.19	76	1.47
4	**2**	Toluene	1 : 100 : 1	80	15.98	13.37	92	1.20
5	**2**	CH_2Cl_2	1 : 100 : 1	60	16.73	14.38	99	1.16
6	**2**	CH_2Cl_2	1 : 50 : 1	20	7.80	6.95	95	1.12
7	**2**	CH_2Cl_2	1 : 100 : 2	40	8.42	7.24	99	1.16

[a] General polymerization conditions: solvent 10 mL, T = 25 °C, [I] = 0.025 M. [b] Determined by GPC, PDI calibrated with polystyrene standards. [c] Calculated value. [d] Conversion determined by ^{1}H NMR spectroscopy.

ArCH_2N signals disappeared and only one singlet at 3.8 ppm was observed (signal e in Fig. 7).

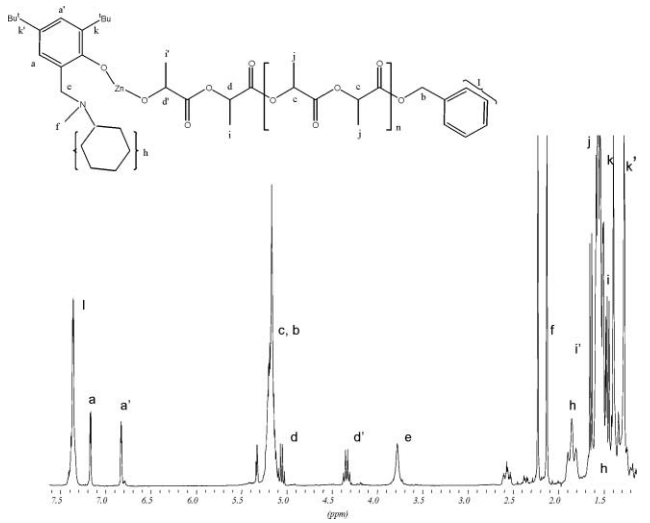
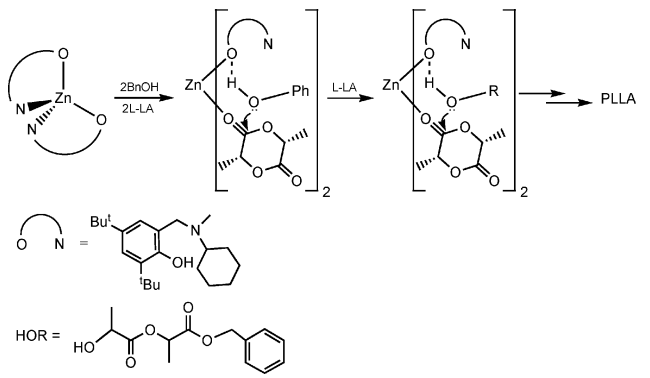


Fig. 7 ^{1}H NMR of PLLA prepared with **2** ([L-LA] : **2** = 20 : 1) prior to quenching.

This data suggests that benzyl alcohols coordinate to zinc metal centre and form hydrogen bonds with oxygen atom of neighbour aminophenolate ligands what is followed by dangling of –NCy fragments. Next, an insertion of benzyloxo ligand to the carbonyl group of lactide takes place what leads to ring-opening polymerization (Scheme 4).



Scheme 4 Proposed mechanism for the ring-opening polymerization of L-LA initiated by **2** in the presence of 2 equiv. of BnOH.

Although alcohol initiators are commonly added to precatalysts in ROP, to our knowledge this is the first example of well-defined pre-coordinated system. Such strategy may have advantages in that the initiator : metal stoichiometry is precisely controlled at the molecular level.

Conclusion

In conclusion, three zinc complexes supported by aminophenolate ligand have been prepared and characterized. The compound **3** demonstrates high activity in initialization of ROP of L-lactide to give at room temperature polymers with narrow PDIs. The most effective for the controlled catalytic polymerization of lactides was complex **2** in the presence of BnOH. Overall, the data support a monomer-activated mechanism that involves dangling of aminophenolate ligand. The work will be continued to understand the origin of stereocontrol in these new lactide polymerization initiators.

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