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Synthesis and structural characterization of a dichloro zinc complex of *N,N′*-bis-(2,6-dichloro-benzyl)-(*R,R*)-1,2-diaminocyclohexane: Application to ring opening polymerization of *rac*-lactide

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ABSTRACT

A novel dichloro zinc complex $(L^1)ZnCl_2$, where L^1 is *N,N′-bis-(2,6-dichloro-benzyl)-(R,R)*-1,2-diaminocyclohexane, has been synthesized and characterized. The dimethyl derivatives, generated *in situ* from the well characterized dichloro zinc complexes $(L^1)ZnCl_2$ and $(L^2)ZnCl_2$, where L^2 is *N,N′-bis-(benzyl)-(R,R)*-1,2-diaminocyclohexane, were employed as initiators for the ring opening polymerization (ROP) of *rac*-lactide (*rac*-LA). The complexes were found to be highly efficient initiators yielding the polylactide (PLA) with a narrow molecular weight distribution. The catalytic activity and heterotactic selectivity of the Zn(II) complexes were affected by the substituents on the phenyl groups of benzyl moieties in (*R,R*)-1,2-diaminocyclohexane. The dimethyl derivative of $(L^2)ZnCl_2$ produced highly stereocontrolled PLA with $P_r = 0.75$ at −25 °C.

1. Introduction

Polylactide (PLA), a biorenewable, biocompatible and biodegradable polymer, has been a subject of considerable attention in academic as well as in industrial research over the past few decades [1]. The physical features, such as gas permeability, low haze, transparency, flavor-resistance, high mechanical strength and easy processibility, make PLA a practical alternative to traditional petrochemical based polymeric materials [2]. The synthesis of PLA can be accomplished either by polycondensation of lactic acid or ROP of lactide (LA). LA, the cyclic dimer of lactic acid, can be derived from inexpensive and annually renewable resources, such as corn, molasses, starch, sugars as well as dairy products, and hence this reduces the environmental load on the fossil fuel required to produce PLA. Furthermore, PLA is degradable to carbon dioxide and water, and thus emerges as an environmentally friendly material [3]. Furthermore, PLA based bioplastics have been increasing its utility in a wide range of pharmaceutical, biomedical [4,5], agriculture [6] as well as industrial and microelectronic fields [7].

ROP is undeniably, the most desirable and convenient method to produce PLA in terms of its greater degree of control over the molecular parameters of the subsequent polymeric materials. This significant regulatory effect of the polymerization process leads to polymers being obtained with lower polydispersities, higher molecular weights and high stereoregularity compared to the polycondensation route [8]. The use of a single site homogenous metal catalyst is the most effective and versatile approach towards the synthesis of PLA *via* ROP, as their steric and electronic environments and Lewis acidity can be tuned effectively. Many metal species, such as calcium [9], magnesium [10], zinc [11,12], aluminum [13], tin [14], lead and bismuth [15], lanthanides [16], group 4 elements [17], iron [18], germanium [19] and indium [20], have been utilized extensively for the ROP of *rac*-LA. However, zinc based initiators are much preferred for PLA synthesis, especially for resorbable biomaterials [21], food packaging [22] and pharmaceutical applications [23] due to their biocompatibility, coupled with their lower toxicity. Representative zinc complexes, comprising mostly of achiral supporting ligand specimens including β-diketiminate [24], tris(pyrazolyl)hydroborate [25], amidinate [26], phenolates [27], amino-bis(pyrazolyl) [28], oxazolinate [29], salen type ligand [30], Schiff's bases [31] and recently neutral N-heterocyclic carbenes [32], oxabispidine [33] and guanidine [34], have been synthesized and their successful application towards the ROP of *rac*-LA has been extensively reviewed recently [35]. Especially, zinc acetate in the presence of BnOH, reported by the Chakraborty group, has shown the highest catalytic activity and no stereoregularity for the obtained PLA using *rac*-LA [36].

The research results showed that the mechanical and physical properties, as well as biological degradation behaviors, of polymers rely dramatically on the tacticity of the obtained polymers, which in turn is influenced by the initiator's architecture. Therefore, chiral catalysts are considered to be highly versatile in terms of stereoregularity and increased tacticities [37,38]. The most important

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breakthrough, reported by Spassky, was for chiral salen-based aluminum initiators, resulting in excellent isotactic stereospecificity for the ROP of *rac*-LA [39–43]. However, these catalytic systems suffered from inherently low activities and the polymerization runs had to be carried out at high temperatures over a relatively long period of time to obtain affordable conversions. Achiral zinc complexes supported by β-diiminates are found to be highly active and heterospecific (P_r = 0.94) towards the ROP of *rac*-LA [44]. Chiral zinc catalysts for *rac*-LA polymerization are rare [45–47]. Recently, the C_2 symmetric chiral ligands (*R,R*)-1,2-diaminocyclohexane derivatives are arising as attractive auxiliaries to serve as a powerful stereoregulating system for the ROP of LA [48,49]. Herein, we reported the synthesis and characterization of a dichloro zinc complex incorporating *N,N′*-bis-(2,6-dichloro-benzyl)-(*R,R*)-1,2-diaminocyclohexane. The dimethyl derivatives of $(L^1)ZnCl_2$ and $(L^2)ZnCl_2$ [50], generated *in situ*, were evaluated as initiators for the ROP of *rac*-LA.

2. Experimental

2.1. General considerations

All manipulations involved in the synthesis of the ligands and the complexes were carried out by the use of bench top techniques in air, unless otherwise specified. All polymerizations were carried out using standard Schlenk techniques, high vacuum and a glove box under argon. THF was dried over Na/benzophenone ketyl, while CH_2Cl_2 was dried over CaH_2. These solvents were deoxygenated by distillation under argon prior to use. The starting materials, (±)-trans-1,2-diaminocyclohexane, *L*-(+)-tartaric acid, 2,6-chlorobenzaldehyde (98%), $NaBH_4$, $ZnCl_2$, methyl lithium (MeLi) (1.6 M in diethyl ether) and 3,6-dimethyl-1-dioxane-2,5-dione (*rac*-LA), were purchased from Aldrich and were used without further purification. L^1 [51] and $(L^2)ZnCl_2$ [50] were prepared by the reported procedure.

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Advance Digital 400-NMR spectrometer and chemical shifts were recorded in ppm units using $SiMe_4$ as an internal standard. Coupling constants are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters. Elemental analyses were determined using an EA 1108-Elemental Analyzer at the Chemical Analysis. Gel permeation chromatography (GPC) analyses were carried out on a Waters Alliance GPCV2000, equipped with differential refractive index detectors. The GPC columns were eluted using THF with a 1 ml/min rate at 25 °C and were calibrated with monodisperse polystyrene standards.

2.2. Synthesis

2.2.1. Dichloro [N,N-bis-(2,6-dichloro-benzyl)-(R,R)-1,2-diaminocyclohexane] Zn(II) complex, $(L^1)ZnCl_2$

An EtOH (7 mL) solution of L^1 (1.48 g, 3.42 mmol) was treated with $ZnCl_2$ (0.46 g, 3.42 mmol) in EtOH (5 mL) at ambient temperature overnight to give a solid precipitation. Washing the precipitate after filtration with Et_2O afforded a white solid as the final product (1.67 g, 87%). *Anal.* Calc. for $C_{20}H_{20}Cl_6N_2Zn$: C, 42.40; H, 3.56; N, 4.95. Found: C, 42.36; H, 3.60; N, 5.00%. ^{1}H NMR (400 Hz, $CDCl_3$) δ: 7.37 (m, 4H, ArH), 7.29 (m, 2H, ArH), 4.45 (m, 4H, N(CH_2)$_2$), 2.85 (m, 2H, CHA), 1.98 (m, 2H, (NH)$_2$CHA), 1.71 (m, 2H, CHA), 1.22 (m, 2H, CHA), 1.11 (m, 2H, CHA). IR (solid neat; cm^{-1}): 2931 (m), 2860 (m), 2360 (m), 2341 (w), 1580 (m), 1560 (m), 1435 (s), 1191 (m), 1156 (w), 1089 (s), 1042 (w), 1004 (w), 960 (m), 935 (m), 841 (w), 818 (w), 779 (s), 764 (s), 725 (m), 701 (m), 636 (m), 619 (w), 566 (w).

2.3. Polymerization of rac-LA with the in situ generated dimethyl zinc complexes

The active catalyst, the dimethyl zinc complex, was prepared as follows. $(L^1)ZnCl_2$ (0.28 g, 0.50 mmol) and dried THF (7.30 mL) were added to a 100 mL Schlenk flask under argon to make a homogenous solution. To this solution was added MeLi (0.65 mL of a 1.6 M solution in diethyl ether, 1 mmol) dropwise at −78 °C. After being stirred for 2 h at room temperature, the resulting solution of $(L^1)ZnMe_2$ was used as a catalyst for the polymerization reaction. The general procedure for the polymerization reaction was as follows. A 100 mL Schlenk flask was charged with *rac*-LA (0.901 g, 6.25 mmol) in a glove box. Dried CH_2Cl_2 (5 mL) was transferred to the flask *via* a syringe and stirred to make a homogenous solution. The polymerization reaction was initiated by slowly adding the catalyst solution (1 mL, 0.0625 mmol) *via* a gas tight syringe under argon at 25 °C. The reaction mixture was stirred at 25 and then −25 °C for 12 h. All the volatiles were removed and the obtained crude polymeric material was dissolved in CH_2Cl_2 (5 mL), followed by the addition of water (1 mL) and then hexane (2 mL) to yield the resultant sticky polymeric material, which was then washed with Et_2O (5 mL × 2). The polymer was dried completely *in vacuo* for 12 h at 40 °C. A white solid was obtained as the final polymeric material (0.89 g, 98.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14–5.25 (m, 1H), 1.54–1.63 (m, 3H).

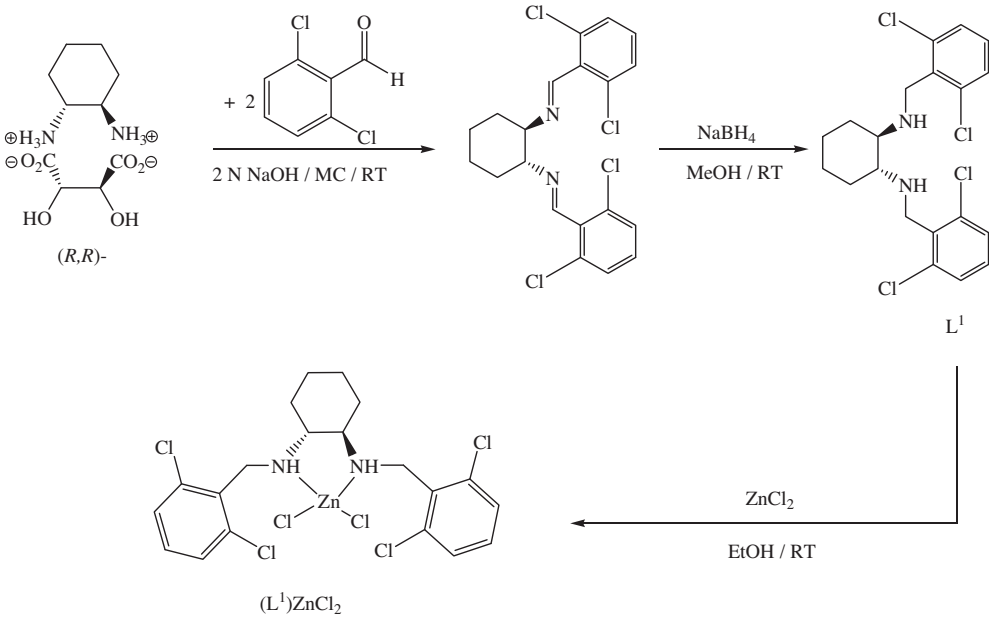
2.4. X-ray crystallography

An X-ray quality single crystal, which was obtained from a hot EtOH solution, was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with MoKα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with a θ range of 1.59–25.47° in the $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during the data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with ψ-scans were applied to the data. The structure was solved using the direct method and refined by full-matrix least-squares techniques on F^2 using SHELXL-97 and SHELXS-97 program packages [52]. All non hydrogen atoms were refined anisotropically, except for the disordered Cl atoms on the phenyl groups of the benzyl moieties and all non hydrogen atoms of solvated EtOH, which were refined isotropically. All hydrogen atoms were refined positioned geometrically using the riding model with fixed isotropic thermal factors. The final cycle of the refinement converged with R_1 = 0.045 and wR_2 = 0.125.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of the ligand involved the use of the (*R,R*)-1,2-diaminecyclohexane-*L*-tartrate salt to resolve free pure (*R,R*)-1,2-diaminocyclohexane, which in turn undergoes a condensation reaction with 2,6-dichlorobenzaldehyde to produce the diimine product. The diimine moiety was further reduced using $NaBH_4$ in MeOH at ambient temperature to obtain the *N,N′*-disubstituted C_2 symmetric diamine. The corresponding dichloro Zn(II) complex was synthesized *via* the reaction of the ligand precursor with $ZnCl_2$ in a 1:1 molar ratio in dried EtOH at ambient temperature (Scheme 1). The white analytically pure dichloro zinc complex was obtained in 85–87% yield after washing the solid with cold EtOH and Et_2O followed by drying *in vacuo*. The newly synthesized ligand and zinc complex were characterized by ^{1}H NMR, IR and elemental analysis.



Scheme 1. Synthesis of the L^1 supported mononuclear dichloro zinc complex.

The crystal structure of $(L^1)ZnCl_2$ was determined by X-ray crystallography.

The crystallographic data and the results of the refinement for $(L^1)ZnCl_2$ are summarized in Table 1. Selected bond angles and lengths for $(L^1)ZnCl_2$ are tabulated in Table 2. An ORTEP drawing of $(L^1)ZnCl_2$ with the atomic labeling is shown in Fig. 1. The X-ray structure revealed that the zinc atom is coordinated by two nitrogen atoms of a bidentate chiral ligand and two chloro ligands adopting a nearly tetrahedral geometry. The Zn–N bond lengths for $(L^1)ZnCl_2$ are 2.102(5) Å for Zn–N1 and 2.081(5) Å for Zn–N2. The bond distances for Zn–Cl are 2.186(2) and 2.239(2) Å for Zn–Cl1 and Zn–Cl2, respectively. The bond angles for Cl1–Zn–Cl2 and N1–Zn–N2 are 122.31(9)° and 85.5(2)°, respectively. These numerical parameters are very similar to those in $(L^2)ZnCl_2$ [50]. The data reflect that a much smaller bite angle is observed for N1–Zn–N2 compared to Cl1–Zn–Cl2. This is a common structural feature for $(L)ZnX_2$ type complexes, where L is a bidentate ligand forming a five-membered ring with Zn and X is a halide, with the ligands forming a distorted tetrahedral geometry around the zinc centre.

The crystal structure of $(L^1)ZnCl_2$ revealed a relatively rigid framework, where the chloro substituted phenyl groups of the benzyl moieties are arranged in a "back and forth" manner to the five-membered ring comprising the Zn atom (Fig. 2a) and this lead to less bulk around the metal center. However, the two unsubstituted phenyl groups of the benzyl moieties in $(L^2)ZnCl_2$ lie above and below the plane of corresponding five-membered ring and resulted in bulkiness in either side of the metal center (Fig. 2b).

Moreover, $(L^1)ZnCl_2$ has two chiral centers, R_C and R_C, derived from the (*R,R*)-1,2-diaminocyclohexane fragment, while the hydrogen atoms of the chiral carbon and nitrogen are found to be in head-to-tail conformation (Fig. 1). The resulting X-ray structure also shows that the two stereogenic nitrogen atoms are R_N and R_N. Furthermore, the chelate formation by the homochiral bidentate diaminocyclohexane ligand leads to stabilization of the divalent zinc centre and the resultant five-membered chelate ring made up of N1–C1–C6–N2 atoms with Zn is found to be in the λ-conformation.

Table 1
Crystallographic data of $(L^1)ZnCl_2{\cdot}CH_3CH_2OH$.

Empirical formula	$C_{20}H_{22}\ Cl_6\ N_2\ Zn{\cdot}CH_3CH_2OH$
Formula weight	614.53
Crystal system	Orthorhombic
Space group	$P2_12_12$
Unit cell dimensions	
a (Å)	16.914(1)
b (Å)	19.552(2)
c (Å)	8.3217(6)
V (Å^3)	2752.0(7)
Z	4
D_{calc} (mg/m^3)	1.483
Absorption coefficient (mm^{-1})	1.493
F(000)	1256
θ range for data collection (°)	1.59–25.47
Index ranges	$-20 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 23$, $0 \leqslant l \leqslant 10$
Reflections collected	3006
Independent reflections (R_{int})	2911 (0.0087)
Reflections observed (>2δ)	2077
Data completeness	1.000
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2911/0/286
Goodness-of-fit (GOF) on F^2	1.099
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0452$, $wR_2 = 0.1247$
R indices (all data)	$R_1 = 0.0741$, $wR_2 = 0.1337$
Absolute structure parameter	0.00 (3)
Largest difference peak and hole (e/Å^3)	0.543 and −0.545

3.2. Ring opening polymerization of rac-LA using the dimethyl zinc complexes

The synthesis of a high molecular weight polymer generally depends upon the controlled ROP of *rac*-LA using well-defined metal

Table 2
Selected bond lengths (Å) and bond angles (°) of $(L^1)ZnCl_2{\cdot}CH_3CH_2OH$.

Zn–N1	2.102(5)	N1–C1	1.474(8)
Zn–N2	2.081(5)	N1–C14	1.480(8)
Zn–Cl1	2.186(2)	N2–C6	1.500(8)
Zn–Cl2	2.239(2)	N2–C7	1.473(8)
N1–Zn–N2	85.5(2)	N1–Zn–Cl2	102.2(2)
N2–Zn–Cl2	105.3(2)	N1–Zn–Cl1	111.1(1)
N2–Zn–Cl1	122.6(2)	Cl1–Zn–Cl2	122.3(9)

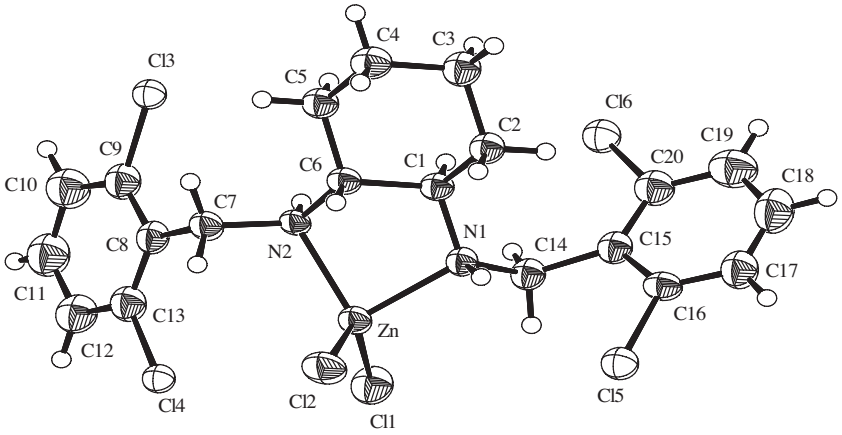


Fig. 1. An ORTEP drawing of $(L^1)ZnCl_2$ with the atomic numbering scheme; ellipsoids are drawn at the 40% probability level.

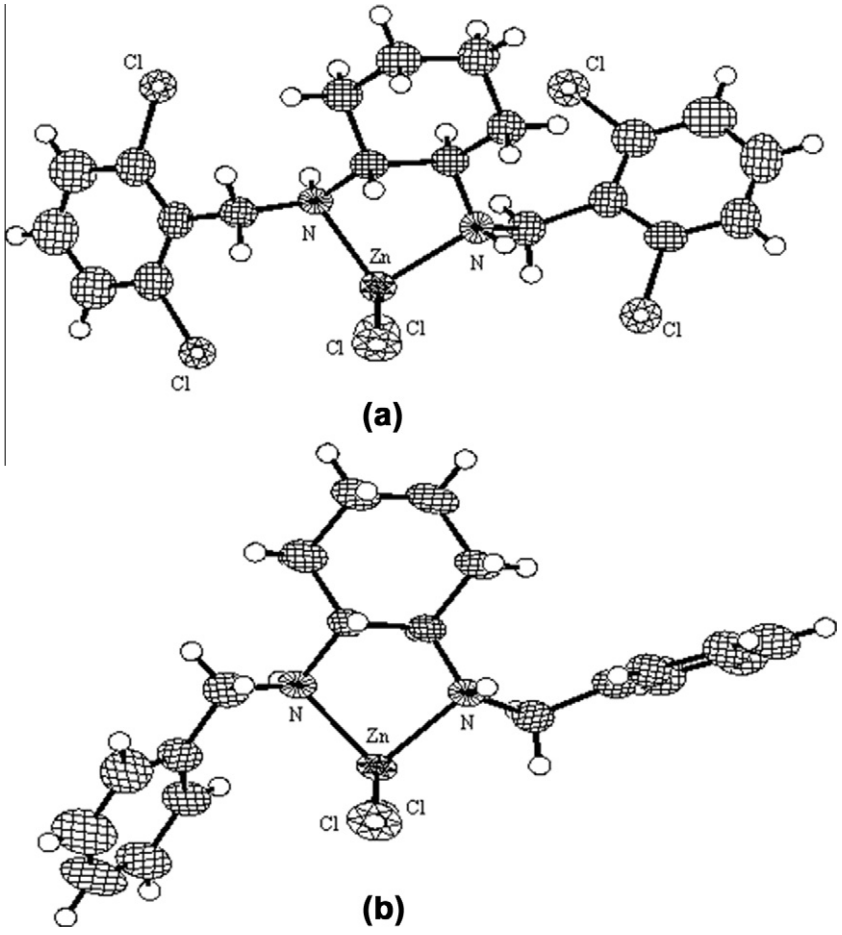


Fig. 2. Comparative views of the X-ray structures (a) $(L^1)ZnCl_2$ and (b) $(L^2)ZnCl_2$, which demonstrates the imparted coordination sphere around the Zn atoms by the substituted and unsubstituted phenyl groups of the benzyl moieties.

complexes. The dichloro Zn(II) complexes did not show any activity towards the polymerization of *rac*-LA at room temperature or −25 °C. The active dimethyl derivatives of the complexes $(L^1)ZnCl_2$ and $(L^2)ZnCl_2$ have been generated *in situ* by treating these dichloro complexes with two equivalents of MeLi in THF. The THF solutions of the dimethyl complexes were systematically examined under argon atmosphere for their catalytic activities toward the ROP of *rac*-LA, and the results are summerized in Table 3. Conversion of the *rac*-LA monomer to PLA has been determined on the basis of ^1H NMR spectroscopic studies. These dimethyl derivatives of the zinc complexes, $(L^1)ZnMe_2$ and $(L^2)ZnMe_2$, were found to be highly efficient initaitors for the ROP of *rac*-LA at room temperature as well as at low temperature in CH_2Cl_2. The monomer was quantitatively ($\leqslant$97%) converted to the polymeric species within 12 h by using the dimethyl zinc complexes as initiators. The active catalyst species formation was confirmed by ^1H NMR analysis, with the

corresponding peaks for the methyl groups appearing at δ −0.57 and −0.62 ppm in $CDCl_3$ for $(L^1)ZnMe_2$ and $(L^2)ZnMe_2$, respectively. The M_n and molecular weight distribution (M_w/M_n) of the obtained polymers are given in Table 3. The well controlled living polymerization is evidenced by the narrow PDIs and the linear relationship between the measured M_n values, % conversion and monomer/initiator ratio (Table 3).

The experimental results indicate that the chloro substituents on the phenyl groups of benzyl moieties of the (*R*,*R*)-1,2-diaminocyclohexane fragment in the complex $(L^1)ZnCl_2$ play a major role in tuning the tacticity of the the obtained polymer. The heterotacticities of the PLAs obtained at two different temperatures (Table 3) were assigned using the methine proton region of the homodecoupled ^{1}H NMR spectra, as described by Hillmyer and co-workers [53,54]. Fig. 3 represents a homodecoupled ^{1}H NMR spectrum of the obtained PLA from polymerization of *rac*-LA using $(L^2)ZnMe_2$. The microstructures of PLA derived from *rac*-LA can exhibit five tetrad sequences, i.e. *sis*, *sii*, *iis*, *iii*, *isi*, for describing its tacticites. The degree of heterotactic PLA can be represented by the parameter P_r, which represents the probability of forming new racemic diad [35]. P_r values were calculated using the equation $P_r = 2I_1/[I_1 + I_2]$ from the homodecoupled ^{1}H NMR spectra, where $I_1 = (sis + sii/iis)$ and $I_2 = (iis/sii + iii + isi)$ [45,55]. As illustrated from the polymerization data (Table 3), the unsubstituted $(L^2)ZnCl_2$ complex gives a high heterotactic preference compared to the chloro substituted complex $(L^1)ZnCl_2$. The beneficial effect on sterocontrol can be attributed to the greater flexibility imparted by the unsubstituted benzyl moiety to the metal coordination sphere and improved accommodation of the geometric requirments of the transition states associated with the polymerization process, as is evident from the crystal structure of $(L^2)ZnCl_2$ (Fig. 2b) [50]. The decrease in heterotacticity of the PLA obtained using the chloro substituted complex $(L^1)ZnCl_2$ might be the result of the rigidity of the chloro substituted benzyl moieties in comaprison to the flexible free benzyl units in $(L^2)ZnCl_2$ (Fig. 2a).

Furthermore, the experimental results demonstrate that temperature has no major influence on the tacticity of the obtained PLAs, as lowering the temperature from 25 to −25 °C resulted in a P_r value increase from 70% to 75% for $(L^2)ZnCl_2$ under same experimental conditions. The high heterotactic PLA could be obtained mainly by a chain end control mechanism [56] using $(L^1)ZnMe_2$ and $(L^2)ZnMe_2$ as initiators. As stated earlier, the chirality of the ancillary ligand bound to the metal atom is also crucial in determining the stereochemical selectivity [45]. However, recent studies have highlighted some complex aspects, namely the nature of metal, size of ancillary ligand, chirality of the ligand framework, the chirality of the end group of the growing polymer chain as well as solvent seem to play unpredictable roles for chiral complexes in influencing the stereo-preference in a racemic monomer mixture [57].

Table 3
ROP of *rac*-LA initiated by the *in situ* generated dimethyl zinc complexes supported by homochiral (*R*,*R*)-1,2-diaminocyclohexane based ligands.

Catalyst	Temp. (°C)	[a]Conversion (%)	[b]$M_n \times 10^3$	[b]$M_w \times 10^3$	[b]PDI	[c]P_r
$(L^1)ZnMe_2$	25	98.7	14.98	18.47	1.2	0.63
$(L^1)ZnMe_2$	−25	98.3	14.32	18.26	1.2	0.67
$(L^2)ZnMe_2$	25	97	15.07	18.22	1.2	0.70
$(L^2)ZnMe_2$	−25	97	14.27	18.27	1.2	0.75

The monomer/catalyst ratio was fixed at 100 in all cases. Solvent for polymerization = 5 mL CH_2Cl_2. Time = 12 h.

[a] Determined by ^{1}H NMR.

[b] Determined by gel permeation chromatography (GPC) in THF, relative to a polystyrene standard.

[c] Probability of heterotactic enchainment P_r values were calculated on the basis of homonuclear decoupled ^{1}H NMR spectra according to the literature [45,55].

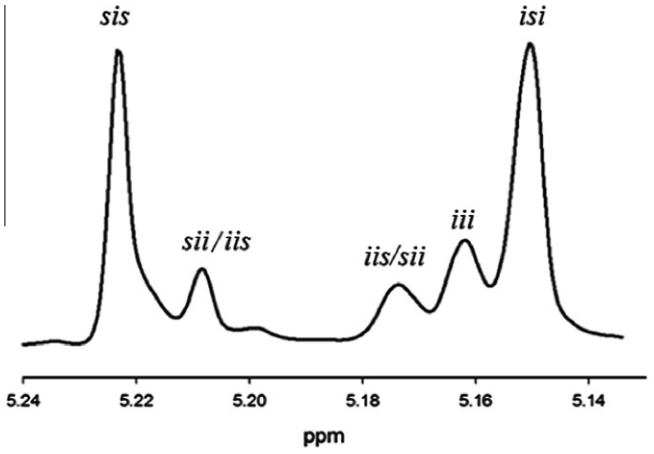


Fig. 3. Homonuclear decoupled ^{1}H NMR spectrum of the methine region of PLA produced by $(L^2)ZnMe_2$ at −25 °C, in CH_2Cl_2.

4. Conclusion

In conclusion, the present investigation has demonstrated that dimethyl zinc complexes supported by the homochiral ligands L^1 and L^2, which were generated *in situ*, were found to be highly efficient initiators for the ROP of *rac*-LA. The polymerization of *rac*-LA catalyzed by these zinc initiators is demonstrated in a living fashion with narrow PDIs. The M_n of the obtained PLAs is close to the monomer/initiator molar ratio in the polymerization process. Moreover, the decrease in stereoregularity of the PLA obtained using the dimethyl zinc complex bearing the ligand with chloro substituents on the phenyl groups of the benzyl moieties towards the ROP of *rac*-LA may be explained by the lack of flexibility of the substituted benzyl units, which would either hamper the monomer attack or create a significant transition state associated with the polymerization process around the coordination sphere of the zinc center.

Acknowledgement

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Appendix A. Supplementary data

CCDC 838450 contains the supplementary crystallographic data for compound $(L^1)ZnCl_2$. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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