Polyhedron 30 (2011) 405–409

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and X-ray crystal structure of dichloro[*S*-1-phenyl-*N*-(*S*-pyrrolidin-2-ylmethyl)ethanamine]zinc(II) and its catalytic application to *rac*-lactide polymerization

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ARTICLE INFO

Article history:
Received 29 September 2010
Accepted 4 November 2010
Available online 18 November 2010

Keywords:
Polylactide
S-1-phenyl-*N*-(*S*-pyrrolidin-2-ylmethyl)ethanamine
Zinc complex
Ring opening polymerization
Heterotacticity

ABSTRACT

New dichloro zinc(II) complex ligated by the homochiral bidentate ligand *S*-1-phenyl-*N*-(*S*-pyrrolidin-2-ylmethyl)ethanamine (**PPMA**) was synthesized and characterized by X-ray crystallography. The geometry of the (**PPMA**)$ZnCl_2$ is a distorted tetrahedron comprising of zinc metal as a center linked with two N atoms of the **PPMA** in a bidentate coordination mode along with two chloro ligands. The catalytic capacity of the complex was evaluated in ring opening polymerization (ROP) of *rac*-lactide. The active catalyst species was generated *in situ* by treating MeLi to complex (**PPMA**)$ZnCl_2$. The dimethyl derivative of the (**PPMA**)$ZnCl_2$ showed highly activity in ROP of *rac*-lactide and gave preference to heterotactic polylactide.

1. Introduction

Polyesters represent a class of polymers that can serve as promising substitutes for petrochemical-based polymers [1] because of the depleting petrochemical feedstocks and increasing environmental awareness. Polylactides are aliphatic polyesters obtained by polymerizing lactide, a cyclic diester of lactic acid, which is obtained by fermentation of 100% bio-renewable resources such as sugar (beet or cane) or starch (corn, wheat, potatoes) or even from food wastes compared to the most of other polymeric materials. The consumption of petrochemical resources would be significantly reduced by polylactide production, as 150 million tons of these nonrenewable resources are consumed annually for plastic production. These polymeric materials are biodegradable, biorenewable and biocompatible and have great potential to be used as a new class of environmental friendly thermoplast [2–4] and will offer a practical solution to the ecological problems associated with bioresistant wastes.

Ring opening polymerization of lactide to synthesize polylactide has been proven to be the most effective and versatile strategy using homogenous single site metal catalysts. Many different types of metal-based catalysts have been employed for the synthetic protocol of these valuable materials that include non hazardous lithium [5,6], magnesium [7–9], aluminum [10–12], iron [13–15], zinc [16–23] on one hand and highly toxic metals such as tin [24,25], lead [26] and lanthanides [27,28] on the other hand. In particular, the polymerization of lactide by zinc(II) complexes is advantageous due to their unique features, such as lack of color, low-toxicity, low cost, biocompatibility, and environmentally friendly nature. As polylactide is mainly used in biomedical [29], pharmaceuticals, agriculture, and packaging applications [30,31], so it is highly recommended to remove the catalyst residue completely from the polymer. Since the complete removal of the catalytic residues is practically not possible, biocompatible and environmentally friendly metals are preferable.

Stereochemistry is one of the main factors that determine the physical and mechanical properties of a polymeric material [32] and hence, the stereoselective polymerization of lactide, has become a subject of considerable attention in order to elucidate the structure–property relationship. Polylactides can exhibit different microstructures depending both on the monomer (*rac*-lactide, *meso*-lactide, L-lactide) involved and on the course of the polymerization reaction [33,34]. Isotactic polylactides, contain sequential stereocenters of the same relative configuration, while syndiotactic polylactides have sequential stereocenters of opposite relative configuration. By changing the composition and tacticity of the polymers, the physical properties can be tuned and significantly improved. Therefore, the extent of stereocontrol exhibited by catalytic system is very important as the rate of chemical and biological degradation, mechanical and thermal

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0277-5387/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2010.11.002

properties of polylactide depend upon the tacticity of the polymer. With single-site catalysts, the monomer attachment occurs at a metal center that in turn bound to an organic ligand. The metal center reactivity is being modulated by the ancillary ligand, which remains bound throughout the catalytic reaction. Furthermore, the structure of ancillary ligand has a substantial influence on the stereoregularity and hence, the tacticity of the final polymeric material for appropriate applications.

Recently, the zinc-based catalysts for polymerization of lactide have been reported by several groups [35–38]. Additionally, zinc acetate in the presence of BnOH reported by Chakraborty group has been shown the highest catalytic activity with no stereoregularity over the microstructure of the obtained PLA using *rac*-lactide [39].

In this regard zinc based initiators for ROP of *rac*-lactide have been reported by Coates group $[(BDI)Zn(OiPr)]_2$ [(BDI) = 2-((2,6-dialkylphenyl)amido)-4-((2,6-diiso-propylphenyl)imino)-2-pentene] that showed high activity along with high stereoselective for polylactide. The high heterotacticity (P_r) value obtained was found to be 0.94, which is the highest ever reported [40]. Keeping in view these facts, we describe herein, the synthesis, and structural characterization of mononuclear zinc complex (**PPMA**)$ZnCl_2$ and the ability of its dimethyl derivative generated *in situ* to initiate the polymerization of *rac*-lactide, resulted in a high activity and a high stereoselectivity compared to our previous reported initiator $ZnEt_2$(*S*-EPP) [41]. Further included in these studies is the effect of inherent chirality on the tacticity of polylactide afforded from ROP of *rac*-lactide. The X-ray crystal structure of the pre-catalyst, (**PPMA**)$ZnCl_2$, will also be described.

2. Experimental

2.1. Materials

All manipulations involved in the synthesis of ligands and complexes were carried out by the use of bench top techniques in air unless otherwise specified. All polymerizations were carried out by the use of standard schlenk techniques, high vacuum, and 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. EtOH and Et_2O were purchased from high grade commercial supplier and used as received. Starting materials were obtained from high-grade commercial suppliers and used without further purification. 3,6-dimethyl-1-dioxane-2,5-dione (*rac*-lactide) was purchased from Aldrich and stored in glove box and used without further purification. *S*-methylbenzylamine, zinc chloride and methyl lithium (1.6 M in diethyl ether) were purchased from Aldrich and were used without further purification. NMR solvents were purchased from Aldrich and stored over 3 Å molecular sieves.

2.2. Instrumentation

^{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. Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters. Elemental analyses were performed by Fison-EA1108. Gel permeation chromatography (GPC) analyses were carried out on a Waters Alliance GPCV2000, equipped with differential refractive index detectors at the Chemical Analysis Laboratory of the Center for Scientific Instruments of Kyungpook National University. The GPC columns were eluted using THF with 1 ml/min rate at 25 °C and were calibrated with monodisperse polystyrene standards.

2.3. Synthesis and characterization of ligand and complex

2.3.1. 5-Oxo-pyrrolidine-2-carboxylic acid (1-phenyl-ethyl)-amide

To the 2-amino-pentanedioic acid (5.0 g, 33.98 mmol) was added *S*-methylbenzylamine (6 mL, 47.13 mmol) slowly at ambient temperature. The reaction mixture was stirred at 150 °C for 1 day and the progress of the reaction was monitored by TLC. Light brown solid product was obtained after pouring the reaction mixture into dichloromethane and slowly evaporating the solvent at room temperature followed by washing the solid residue several times with diethyl ether (6.52 g, 83.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.00 (m, 1H), 5.12–5.05 (m, 1H), 4.04–4.03 (m, 1H), 2.47–2.06 (m, 5H), 1.47 (d, J = 6.8 Hz, 3H). Analysis calculated for $C_{13}H_{16}N_2O_2$: C, 67.22%; H, 6.94%; N, 12.06%. Found: C, 66.99%; H, 7.01%; N, 12.10%.

2.3.2. S-1-phenyl-N-(S-pyrrolidin-2-ylmethyl)ethanamine (*PPMA*)

To the THF (20 mL) solution of 5-oxo-pyrrolidine-2-carboxylic acid (1-phenyl-ethyl)-amide (2.0 g, 8.6 mmol) was added slowly the THF (20 mL) solution of $LiAlH_4$ (0.65 g, 17.2 mmol) at −78 °C. The reaction mixture was stirred for one day at reflux temperature after warming to room temperature. The progress of the reaction was monitored by TLC. Excess of $LiAlH_4$ was quenched with 2N (10 mL) NaOH. The residue obtained after removing the solvent was dissolved in 30 mL CH_2Cl_2 and washed with distilled water (3 × 20 mL). The CH_2Cl_2 solution of product was dried over anhydrous $MgSO_4$. The solvent was evaporated to give yellow oil (1.30 g, 74.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5H), 3.75 (m, 1H), 3.23–3.12 (m, 1H), 2.90–2.82 (m, 2H), 2.43–2.27 (m, 2H), 1.85–1.60 (m, 5H), 1.34 (d, J = 6.4 Hz, 3H), 1.287–1.20 (m, 1H). Analysis calculated for $C_{13}H_{20}N_2$: C, 76.42%; H, 9.87%; N, 13.71%. Found: C, 75.56%; H, 9.76%; N, 13.82%. IR (solid neat; cm^{-1}): 3060 (m), 2959 (w), 1664 (br, w), 1492 (w), 1450 (br, m),1368 (w), 1351 (w), 1208 (w), 1128 (br, w), 1026 (w), 911 (w), 760 (s), 698 (s), 594 (w).

2.3.3. (*PPMA*) $ZnCl_2$

A 100 mL, one-necked round-bottom flask was charged with $ZnCl_2$ (0.66 g, 4.90 mmol) and EtOH (5 mL) and stirred to make homogenous solution followed by the addition of EtOH solution (5 mL) of **PPMA** (1.0 g, 4.90 mmol). The mixture was stirred at ambient temperature for 12 h and the progress of reaction was monitored by TLC. The solid product was filtered and washed with cold EtOH (3 × 5 mL) and dried *in vacuo* (1.4 g, 84.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 5H), 3.94 (m, 1H), 3.60–3.75 (m, 2H), 3.24 (m, 2H), 3.00–3.16 (m, 2H), 2.32–2.36 (m, 1H), 2.04–2.14 (m, 1H), 1.68–1.95 (m, 4H), 1.60 (d, J = 6.8 Hz, 3H). Analysis calculated for $C_{13}H_{20}Cl_2N_2Zn$: C, 45.84%; H, 5.92%; N, 8.22%. Found: C, 45.80%; H, 5.90%; N, 8.19%. IR (solid neat; cm^{-1}): 3233 (br, w), 3207 (w), 2970 (w), 1464 (w), 1453 (w), 1428 (w), 1382 (w), 1281 (w), 1222 (w), 1197 (m), 1129 (w), 1074 (s), 1047 (s), 1025 (m), 1005 (w), 985 (w), 964 (w), 936 (w),1368 (w), 896 (s),778 (m), 764 (s), 703 (s), 656 (w), 625 (m), 594 (w), 565 (m).

2.4. Polymerization of rac-lactide with in situ generated (*PPMA*)$ZnMe_2$

(**PPMA**)$ZnCl_2$ (0.18 g, 0.5 mmol) and dried THF (7.3 mL) were added to a 100 mL of schlenk flask to make a homogenous solution. To this solution was added MeLi (0.65 mL of 1.6 M solution in diethyl ether, 1 mmol) drop wise at −78 °C. After being stirred for 2 h at room temperature, the resulting solution of (**PPMA**)$ZnMe_2$ was used as a catalyst for polymerization reaction. The general procedure for the polymerization reaction was as follows: a 100 mL of schlenk flask was charged with *rac*-lactide (0.991 g, 6.8 mmol) in the glove box. Dried CH_2Cl_2 (5 mL) was

transferred to the flask via syringe and stirred to make a clear solution. The reaction was initiated by adding the catalyst solution (1.0 mL, 0.0625 mmol) with gas tight syringe under argon. The reaction mixture was stirred at room temperature and −25 °C for 12 h. The polymerization reaction was quenched after prescribed duration by adding water (1 mL). Hexane (2 mL) was added to precipitate the polymer followed by washing with Et_2O. The resultant sticky polymeric material was dried *in vacuo*. A white solid was obtained finally (0.87 g, 97% based on *rac*-lactide). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12–5.25 (m, 1H), 1.51–1.63 (m, 3H).

2.5. X-ray crystallographic analysis

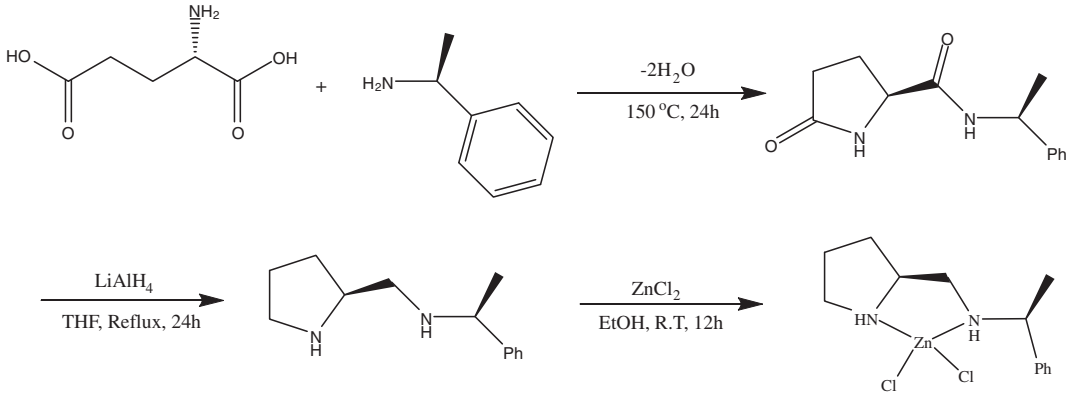
An X-ray quality single crystals were obtained by diffusion of hexane into solution of (**PPMA**)$ZnCl_2$ in CH_2Cl_2. A single crystal was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with MoKα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10° < \theta < 13°$). Intensity data were collected with θ range of 1.79–25.47° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 h during 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 by using Direct method and refined by full-matrix least-squares techniques on F^2 using SHELXS-97 and SHELXL-97 program packages [42]. All non hydrogen atoms were refined anisotropically and all hydrogen atoms of carbon atoms were refined positioned geometrically using riding model with fixed isotropic thermal factors. And amine hydrogen atoms were refined using riding model with 0.87 Å separations and fixed isotropic thermal factors. The final cycle of the refinement converged with R_1 = 0.038 and wR_2 = 0.090.

3. Results and discussion

3.1. Synthesis and X-ray crystal structure of the (*PPMA*)$ZnCl_2$ complex

The synthesis of bidentate ligand **PPMA** has been successfully carried out by two steps process comprising of condensation reaction of *S*-2-aminopentandioic acid and *S*-methylbenzylamine under neat conditions at 150 °C, followed by the reduction of amide to amine analog by treating with stoichiometric amount of $LiAlH_4$ in THF at refluxing temperature. The air and moisture stable dichloro zinc complex of **PPMA** was synthesized by treating $ZnCl_2$ with **PPMA** at ambient temperature for 12 h in EtOH (Scheme 1). The synthesized ligand and complex were characterized by ^{1}H NMR, IR, elemental analysis, and X-ray crystal determination.

The X-ray crystal structure of (**PPMA**)$ZnCl_2$ has two independent molecules per asymmetric unit. The ORTEP drawing of the complex is shown in Fig. 1 with atomic labels. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles are listed in Table 2.



Scheme 1. Synthesis of (**PPMA**)$ZnCl_2$.

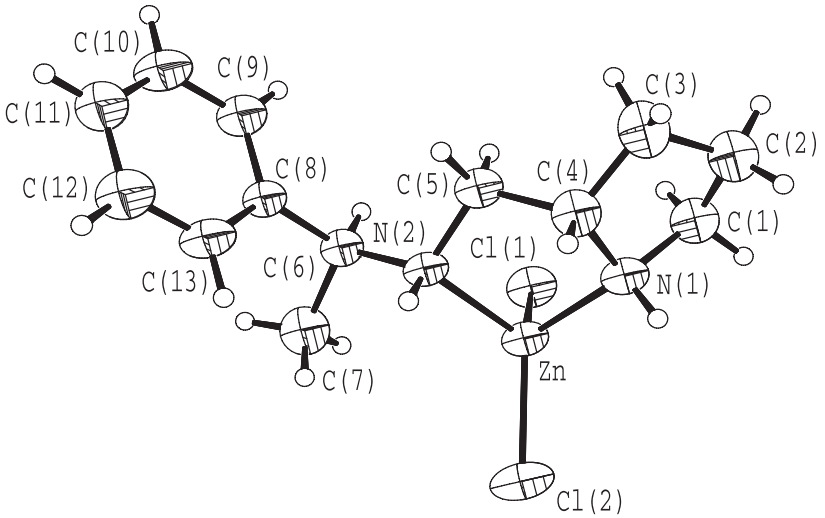


Fig. 1. An ORTEP drawing of (**PPMA**)$ZnCl_2$ with the numbering scheme at 40% probability level.

Table 1
Crystal data and structure refinement of (**PPMA**)$ZnCl_2$.

Empirical formula	$C_{13}H_{20}Cl_2N_2Zn$
Formula weight	681.16
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	10.7971(4)
b (Å)	13.4236(10)
c (Å)	21.5761(11)
V (Å^3)	3127.2(3)
Z	8
D_{calc} (Mg/m^3)	1.447
Absorption coefficient (mm^{-1})	1.897
F(0 0 0)	1408
θ range for data collection (°)	1.79–25.47
Index ranges	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-26 \leqslant l \leqslant 26$
Reflections collected	20650
Independent reflections	5800 [R_{int} = 0.0088]
Reflections observed (>2δ)	4284
Data Completeness	1.000
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5800/0/331
Goodness-of-fit (GOF) on F^2	1.002
Final R indices [$I > 2\delta$ (I)]	R_1 = 0.0383 wR_2 = 0.0899
R indices (all data)	R_1 = 0.0683 wR_2 = 0.1034
Absolute structure parameter	0.006(15)
Largest diff. peak and hole (e Å^{-3})	0.512 and −0.343

Table 2
Selected bond lengths (Å) and angles (°) for (**PPMA**)$ZnCl_2$.

Zn–N(1)	2.046(5)	Zn(1)–N(3)	2.052(4)
Zn–N(2)	2.090(4)	Zn(1)–N(4)	2.108(4)
Zn–Cl(1)	2.227(1)	Zn(1)–Cl(3)	2.238(1)
Zn–Cl(2)	2.209(1)	Zn(1)–Cl(4)	2.218(1)
N(1)–Zn–N(2)	86.6(2)	N(1)–Zn–Cl(2)	113.0(1)
N(2)–Zn–Cl(2)	114.3(1)	N(1)–Zn–Cl(1)	108.0(10)
N(2)–Zn–Cl(1)	109.3(1)	Cl(2)–Zn–Cl(1)	120.42(6)
N(3)–Zn(1)–N(4)	86.1(2)	N(3)–Zn(1)–Cl(4)	126.6(1)
N(4)–Zn(1)–Cl(4)	107.0 (1)	N(3)–Zn(1)–Cl(3)	109.1(1)
N(4)–Zn(1)–Cl(3)	108.1(1)	Cl(4)–Zn(1)–Cl(3)	114.68(5)

The geometry of the (**PPMA**)$ZnCl_2$ complex is a distorted tetrahedron comprising of zinc metal as a center linked with two N atoms of the **PPMA** in a bidentate coordination mode along with two chloro ligands. The planes of two independent molecules between Cl–Zn–Cl and N–Zn–N are 89.9(1)° and 84.5(1)° and the two bite angles for Cl–Zn–Cl and N–Zn–N are 117.55(6)° and 86.4(2)°, respectively. These values are similar with those found in [$ZnCl_2$(*S*-EPP)] complex [41] having similar skeleton to (**PPMA**)$ZnCl_2$. Larger Cl–Zn–Cl than N–Zn–N bite angle is due to the fact that the two binding sites in tetrahedron are occupied by bidentate ligand forming chelate while the other two sites are bounded by large chloride ions.

Two stereogenic N atoms with two chiral centers from the bidentate **PPMA** ligand exist in (**PPMA**)$ZnCl_2$. The induced chirality of N(2) was R_N configuration and C–N single bond was rotated to form head-to-tail configuration of hydrogen atoms of C(6) and N(2). The configuration of N(1) was also R_N and the configuration of hydrogen atoms of C(4) and N(1) was head-to-head, which was thermodynamically favorable resulted from interfering rotation of C–N single bond upon coordination of N(1) atom to mental center. In addition the δ-conformation has been confirmed for the five-membered ring made by Zn–N(1)–C(4)–C(5)–N(2).

3.2. Polymerization of rac-lactide with in situ generated Zn catalyst

Ring opening polymerization of *rac*-lactide employing (**PPMA**)$ZnMe_2$ as an initiator is systematically examined under inert atmosphere. The dimethyl zinc complex (**PPMA**)$ZnMe_2$ was prepared *in situ* from the air stable (**PPMA**)$ZnCl_2$ by treating with two equivalents of MeLi (1.6 M solution in diethyl ether) in THF. The appearance of the resonance for protons of (**PPMA**)$ZnMe_2$ in the high-field region (δ −0.61) demonstrated the formation of the desired complex. Conversion of monomer to polylactide is determined on the basis of ^{1}H NMR spectroscopy. The polymerization was carried out at 25 °C and at −25 °C in CH_2Cl_2 using THF solution of (**PPMA**)$ZnMe_2$ (0.0625 mmol) as initiator. The polymerization results are listed in Table 3. The resultant polymers were isolated and purified using water and hexane followed by Et_2O and dried *in vacuo* for overnight at 40 °C. The well controlled polymerization process indicated from experimental results is shown in Table 3. As the narrow polydispersities over the range of 1.21–1.23 and M_n of the produced polylactides have linear relationship with calculated values predicted from [monomer]/[catalyst], indicated the living polymerization process of single active site. The polymerization was carried out at two different temperatures in order to sort out the relationship between the P_r and polymerization temperature, keeping the [monomer]/[catalyst] constant i.e. [1]/[110]. The fact is revealed that the dimethyl derivative prepared *in situ* is a highly efficient initiator for the polymerization of *rac*-lactide. Viscous solution has been observed within an hour at the desired [monomer]/[catalyst] ratio in dichloromethane at room temperature. Furthermore the polymerization rate at the same [monomer]/[catalyst] ratio at low temperature was slightly decreased.

As described earlier, the physical, mechanical, and degradation properties of the polylactides are dramatically dependent on the tacticity of the polymer. The stereoselectivity of the produced polymer is determined by the Bernoullian statistics based on the data obtained by homonuclear decoupled ^{1}H NMR spectroscopy [43,44] and the calculated values are summarized in Table 3. The representative homonuclear decoupled ^{1}H NMR spectrum of methine proton region of polylactide is shown in Fig. 2 and the calculation of P_r values was carried out from the ratio of the area of (rmr and mrm)/total area of methine proton region from the decoupled spectra. As demonstrated from the table and ^{1}H NMR spectra, the (**PPMA**)$ZnMe_2$ produced high degree of heterotactic polylactides. P_r values [45–48] for polylactides were found to be 0.71 at room temperature compared to 0.55 for the previous complex [$ZnCl_2$(*S*-EPP)]. The inherent chirality at C(6) in complex (**PPMA**)$ZnCl_2$ provides the polylactide with high degree of heterotacticity (P_r = 0.71), since the ligand architecture is expected to play a major role in stereoselectivity [49,50]. These values are higher than those of obtained in the previous work [41] where a chiral center exists but that cannot affect much the microstructure of the polylactide. As mentioned earlier that ligand coordinate to the metal core influence the microstructure of PLA. The study on polymerization of lactide with the zinc acetate complex coupled with the lack of ancillary ligands around the zinc core revealed that

Table 3
Polymerization of *rac*-lactide with *in situ* prepared (**PPMA**)$ZnMe_2$.

Entry	[Monomer]/[catalyst]	Temp. (°C)	Conversion	$M_n \times 10^3$	$M_w \times 10^3$	PDI	P_r
1	110	25	97	15.4	19.0	1.23	0.71
2	110	−25	96	16.4	19.9	1.21	0.75

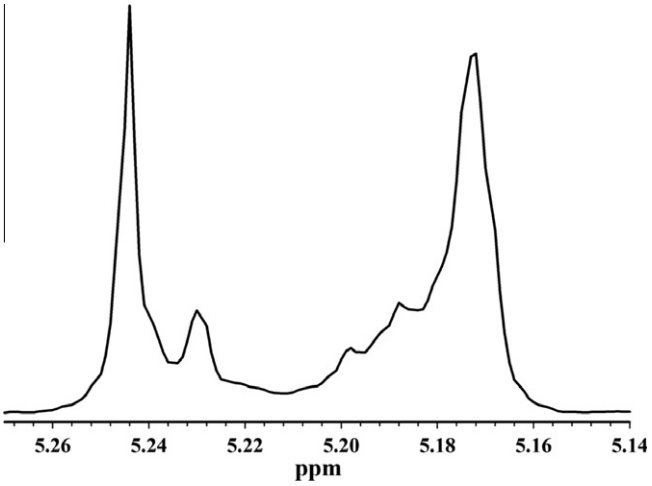


Fig. 2. Homonuclear decoupled ^{1}H NMR spectrum of polylactide (for the preparation conditions, see entry 1 in Table 3).

the zinc complex has exceptionally high catalytic activity at high temperature in the presence of BnOH as an initiator for polymerization but the absence of ancillary ligands leaded to the lack of stereoregularity of PLA [39]. The homo-chiral ancillary ligand in this study may induce relatively high heterotactic PLA. From the experimental results it is significant fact that the temperature has no serious influential effect on the tacticity of the obtained polymer. Decreasing the polymerization temperature from 25 to −25 °C resulted in P_r value increase somewhat from 0.71 to 0.75.

4. Conclusion

In summary, a novel zinc-based pre-catalyst for polylactide, (**PPMA**)$ZnCl_2$, has been successfully synthesized by convenient synthetic procedure. The dimethyl derivative of the (**PPMA**)$ZnCl_2$, generated *in situ*, is found to be active towards ROP of *rac*-lactide. The polymerization appears to be living as depicted by a liner relationship between M_n and percent of conversion, as well as low PDIs. The P_r values were 0.71 and 0.75 at room temperature and −25 °C, respectively.

Acknowledgment

This research was supported by Basic Science Research Programs through the National Research Foundation of Korea (NRF), funded by the Ministry of the Education, Science, and Technology (Grant No. 2009-0075742).

Appendix A. Supplementary data

CCDC 802824 contains the supplementary crystallographic data for (**PPMA**)$ZnCl_2$. 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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