(Benzoimidazolylmethyl)amine Zinc(II) 착화합물에 의해 촉매화된 락타이드의 개환 중합: 반응속도, 메커니즘, 그리고 고분자 입체규칙성 연구

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Ring-opening Polymerization of Lactides Catalyzed by (Benzoimidazolylmethyl)amine Zinc(II) Complexes: Kinetics, Mechanism and Polymer Tacticity Studies

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Abstract: Zinc(II) complexes of (benzoimidazolyl)amine ligands, *N*-(1H-benzoimidazol-2-ylmethyl)aniline (**L1**) and *N*-(1H-benzoimidazol-2-ylmethyl)-2-bromoaniline (**L2**), [Zn$_2$(**L1**)$_2$(OBz)$_4$] (**1**), [Zn$_2$(**L2**)$_2$(OBz)$_4$] (**2**) and [Zn(**L1**)$_2$(OAc)$_2$] (**3**) have been employed in the ring-opening polymerization of lactides. The complexes were found to form active catalysts in the polymerization of the D,L-lactide (D,L-LA) and L-lactide (L-LA) monomers. The polymerization kinetics proceeded *via* pseudo-first order mechanism with respect to the monomer. Low molecular weight polymers were obtained with relatively narrow molecular weight distribution of 1.30-1.50. The ligand architecture, the nature of the carboxylate anion and solvent system influenced the rate of lactide polymerization reactions. Polymerization reactions performed in methanol exhibited higher rates of reaction than those in toluene. The activation parameters measured for lactide polymerization using **3** were obtained as ΔH^o=38.4±0.7 kJmol^{-1}, ΔS^o=-167.2±1.8 JK^{-1}mol^{-1} and are consistent with a highly ordered transition state. The polymers produced were mainly atactic and isotactic.

Keywords: ring-opening polymerization, lactides, kinetics, tacticity.

Introduction

The use of biodegradable and biocompatible plastic materials has attracted research interest due to their important applications in the field of tissue engineering, packaging and agriculture.[1-4] Polylactides (PLAs), derived from lactide (LAs) monomers, are one of such materials that are currently receiving considerable attention.[5] Thus the syntheses and structural characterization of PLAs with well controlled stereochemistry has recently witnessed significant growth.[6] The convenient method of synthesizing these polyesters is by ring-opening polymerization (ROP) using metal complexes as catalysts to afford high molecular weight polymers with good molecular weight distribution.[7-10] Examples include metal complexes of tin,[11,12] aluminium,[13,14] titanium,[15,16] zirconium,[17,18] iron,[19,20] zinc,[21-24] copper,[25,26] rare earth,[27,28] alkali,[29,30] and alkaline earth[31,32] metals as catalyst/initiators for the ROP of LAs.

However, the application of these polyesters in health and other biological systems has necessitated the search for virtually non-toxic or biocompatible metal complexes to substitute the currently used toxic tin-based complexes.[4] Among the leading candidates are zinc, copper, calcium, magnesium, and alkali metal complexes which are less toxic and essential elements in living organisms.[31] As part of our ongoing work on the use of zinc(II) complexes as catalysts for ROP of lactides, we report the polymerization of lactides catalyzed by (benzoimidazolyl)amine zinc(II) complexes.[33] The kinetics, mechanistic considerations and polymer stereochemistry have been investigated and are herein discussed.

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Experimental

Materials and Instrumentation. All reactions were carried out under inert atmosphere using standard Schlenk line techniques. The monomers, D,L-lactide and L-lactide, were purchased from Sigma-Aldrich, purified by crystallization from dry toluene and stored under dry conditions. The solvents, $CDCl_3$, toluene, and methanol, were purchased from Merck chemicals. Toluene was distilled from sodium/benzophenone. The complexes used in the polymerization were prepared as described in our recent publication.[33] NMR spectra were recorded on Bruker 400 UltraShield NMR (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer. All the chemical shifts were recorded in δ units relative to tetramethylsilane. The ^{1}H and ^{13}C spectra are referenced using residual $CDCl_3$ solvent peaks. The mass spectra of the polymers were obtained using micromass LCT premier mass spectrometer.

General Procedure for Lactide Polymerization. Polymerization reactions of lactides were carried out in toluene at 110 °C. In a typical polymerization experiment, an equimolar amount of the zinc(II) complex was weighed into a pre-heated Schlenk tube equipped with a magnetic stirrer followed by the addition of toluene (1 mL) and lactide, (0.36 g to give [LA]/[Zn] ratio of 100/1). The Schlenk tube was heated at the desired temperature in an oil bath until completion of the polymerization process. The extent of monomer conversions was monitored by sampling aliquots at regular intervals and percentage conversions determined by ^{1}H NMR spectroscopy using the formula $[PLA]_t/([LA]_t+[PLA]_t)\times100\%$, where $[PLA]_t$ and $[LA]_t$ are the concentrations of the polymer and monomer at time t respectively. These were evaluated by integration of the peaks for LA (5.0 ppm, OCH signal) and PLA (5.2 ppm, OCH signal) according to the equation $[PLA]_t/[LA]_t=I_{5.2}/(I_{5.2}+I_{5.0})$ where $I_{5.0}$ is the intensity of the LA monomer signal at 5.0 ppm, and $I_{5.2}$ is the intensity of the PLA signal at 5.2 ppm for the OCH protons.

Kinetics of Ring-opening Polymerization of Lactides. Kinetic studies were carried out by taking aliquots of the polymer at regular time intervals and quenching the reaction by freezing in liquid nitrogen. The quenched aliquots were dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. The peak intensities at 5.00 ppm (LA) and 5.20 ppm (PLA) determine the reaction kinetics according to eq. (1).

$$\frac{[LA]_o}{[LA]_t} = \frac{I_{5.00}+I_{5.20}}{I_{5.00}} \tag{1}$$
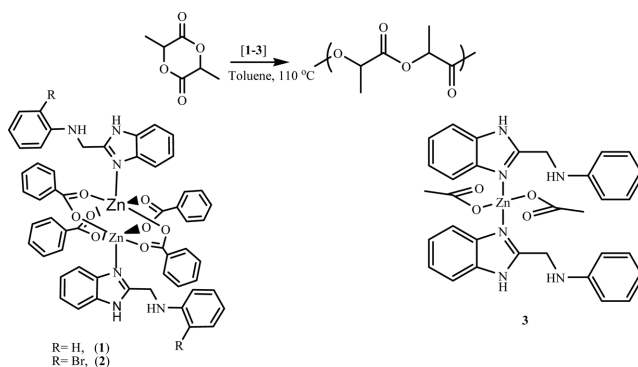
Where $I_{5.00}$=integral of monomer, LA
$I_{5.20}$=integral of polymer, PLA

The apparent rate constants of the reaction were obtain from the gradient of the line of best-fit of the plot of $\ln[LA]_o/[LA]_t$ *versus* time.

Gel Permeation Chromatography. The molecular weight (M_w) and molecular weight distributions (M_w/M_n) of the polymers were determined by size exclusion chromatography (SEC) at Stellenbosch University. The SEC instrument consists of Waters 1515 isocratic HPLC pump, Waters 717 plus autosampler, Waters 600E system controller (run by Breeze version 3.30 SPA), a Waters in-line Degasser AF and a Waters 2414 differential refractometer (operated at 30 °C) in series with a Waters 2487 dual wavelength absorbance UV/Vis detector operating at variable wavelength. The polymers were dissolved in a BHT stabilized THF (2 mgmL^{-1}), filtered through a 0.45 μm nylon filters and eluted through two sets Plgel (polymer laboratories) 5 μm Mixed-C (300×7.5 mm) column and a precolumn (Plgel 5 μm Guard, 50×7.5 mm) at a flow rate of 1 mLmin^{-1}. The column oven was kept at 30 °C and injection volume was 100 μL. THF (HPLC grade stabilized with 0.125% BHT) was used as the eluent. Narrow polystyrene standards ranging from 580 to 2×10^6 gmol^{-1} was used for calibration hence molecular weights were measured as polystyrene equivalents.

Results and Discussion

Polymerization of Lactides. The ring-opening polymerization of the two lactide monomers was investigated using three zinc(II) complexes reported in our recent publication[33] (Scheme 1). The ROP data are summarized in Table 1. From

Scheme 1. Zinc(II) complexes used in the ROP of D,L-LA and L-LA in this study.

Table 1. ROP of D,L-LA and L-LA Catalyzed by Complexes 1-3[a]

Entry	Catalyst	Monomer	Time (h)	Conv. (%)	M_{nNMR}[b]	M_{nGPC}[c]	PDI[c]
1	**1**	D,L-LA	32	95	13 731	1 172	1.45
2	**2**	D,L-LA	50	95	13 532	1 073	1.41
3	**3**	D,L-LA	95	95	13 506	1 186	1.48
4	**3**	L-LA	33	96	13 780	1 815	1.37
5[d]	**3**	L-LA	1	95	13 971	ND	ND
6[e]	**3**	D,L-LA	15	95	13 552	771	1.33

[a]Condition: Temp, 110 °C. [LA]:[Zn]=100; [LA]$_o$=2.5 mmol; solvent, toluene. [b]Calculated from molecular weight of monomer×[M]/[I]×%Conv. [c]Determined by gel-permeation chromatography calibrated with polystyrene standards and, corrected by a factor of 0.58. ND=Not detected. [d]Polymerization in methanol. [e]Polymerization in THF.

the results obtained, all the zinc(II) complexes gave active catalysts in the ROP of D,L-LA and L-LA giving conversions of up to 95% depending on the reaction conditions employed. We thus carried out further mechanistic, kinetics and polymer tacticity studies to have a more detailed account of these polymerization reactions.

Kinetics of Lactide Polymerization. Kinetic studies of the polymerization reactions by catalyst **1-3** were performed using D,L-LA monomer in toluene. ^{1}H NMR spectroscopy was used to monitor the consumption of the monomer and polymer formation as described in the experimental section. A plot of ln[LA]$_o$/[LA]$_t$ *versus* time (Figure 1) gave a straight line consistent with a pseudo-first order reaction kinetics with respect to the monomer as shown in eq. (2). The apparent rate constants of **1-3** in the polymerization reactions were obtained as 0.0934, 0.0582 and 0.0796 h^{-1} respectively. In comparison to the polymerization kinetics we recently reported using ε-capro-
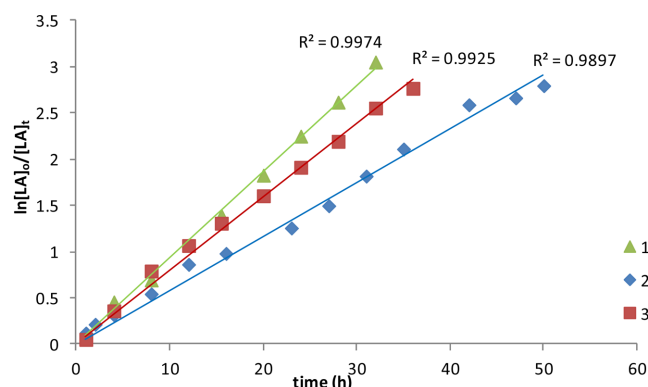
lactone monomer, we did not witness any induction periods in the D,L-LA kinetics.[33] This could be attributed to the presence of two carbonyl groups in the lactide monomer making it more susceptible to coordination to the metal.[34]

$$-\frac{d[\text{LA}]}{dt} = k_{\text{app}}[\text{LA}] \tag{2}$$

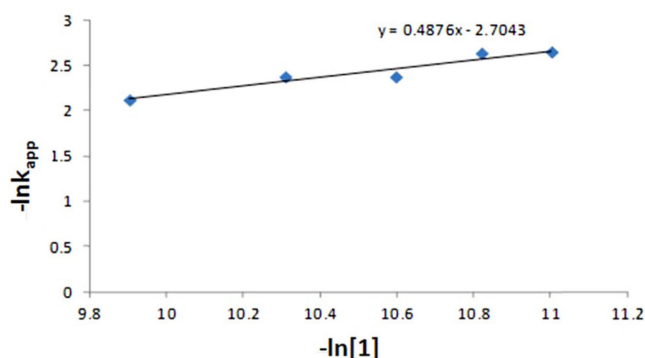where $k_{\text{app}}=k_p[I]^x$, and where k_p is the chain propagation rate constant.

From the apparent rate constants obtained for complexes **1-3**, it is evident that the structure of the complexes showed some influence on their catalytic activities. For instance, catalyst derived from complex **2,** bearing the electron withdrawing bromide on the ligand (**L2**) recorded a lower rate constant compared to the unsubstituted complex **1**. This shows that use of electron-withdrawing substituents on the ligand moiety reduces the catalytic performance of these catalysts. A possible reason could be the low stability of the resultant catalysts due to a more electrophilic zinc(II) metal centre.[35] In addition, the binuclear complex **1** was found to be more active than the corresponding mononuclear complex **3** (Table 1, entries 1 and 3 and Figure 1) and is consistent with a similar literature report where the multinuclear zinc(II) complexes display higher catalytic activities than their mononuclear counterparts.[36] Though the recorded activities of **1-3** are lower than most active zinc(II) alkoxide complexes found in literature,[37-39] their catalytic activities are comparable to other reported zinc(II) alkoxide initiators.[40]

To determine the order of the polymerization reactions with respect to the catalyst, the dependence of k_{app} on the concentration of catalyst **1** was analyzed. A plot of $-\ln k_{\text{app}}$ vs $-\ln[\mathbf{1}]$ gave a linear relationship with a non-integer gradient of 0.49 (Figure 2). Fractional orders of reactions with respect to cat-

Figure 1. Plot of ln[LA]$_o$/[LA]$_t$ *vs* time for D,L-LA polymerization in toluene. The rate constants of the complexes were extracted as 0.0934 h^{-1} (**1**), 0.0582 h^{-1} (**2**) and 0.0796 h^{-1} (**3**). Conditions: temp. 110 °C; [LA]:[Zn]=100; [LA]$_o$=2.5 mmol, solvent, toluene.
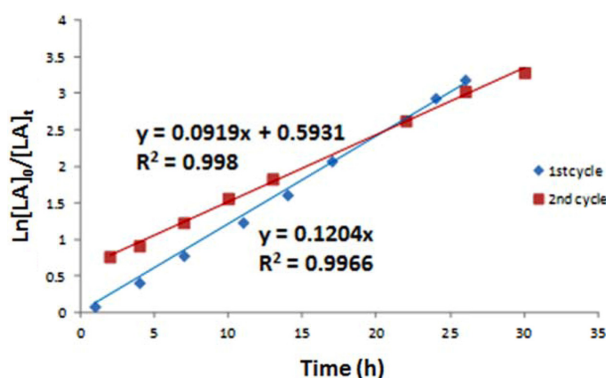
Figure 2. Plot of -lnK_{app} *vs* -ln[**1**] in the ROP of *R,S*-LA for the determination of order of reaction with respect to catalyst **1** at 110 °C; [LA]$_o$=2.5 mmol, solvent, toluene.

alyst initiator have been observed in literature and largely attributed to aggregation of the active species during polymerization.[41,42] The gradient denotes the order of the reaction with respect to **1**, thus the polymerization of *R,S*-LA by **1** follows an overall kinetic law as given in eq. (3).

$$-\frac{d[\text{LA}]}{dt} = k_p[\text{LA}][\mathbf{1}]^{0.49} \tag{3}$$

Initiator Stability. The stability of catalyst **1** was investigated by sequential addition of an equivalent amount of the monomer without addition of the catalyst. This was done after complete consumption of the monomer in the first cycle. The recorded k_{app} for the polymerization reactions in the second cycle was observed as 0.092 h^{-1} compared to 0.120 h^{-1} in the first cycle (Figure 3). This translates to a 24% drop in catalytic activity in the second cycle relative to the first cycle. This result revealed that though the complexes retained appreciable

Figure 3. Kinetic plot for the polymerization of two equivalent amounts of D,L-LA by complex **1** at 110 °C; [LA]:[Zn]=100; [LA]$_o$=2.5 mmol, solvent, toluene.

catalytic activity in the second run, a significant loss of activity occurred. This can be attributed to catalyst deactivation emanating from build-up of impurities or thermal decomposition of the active species.[43]

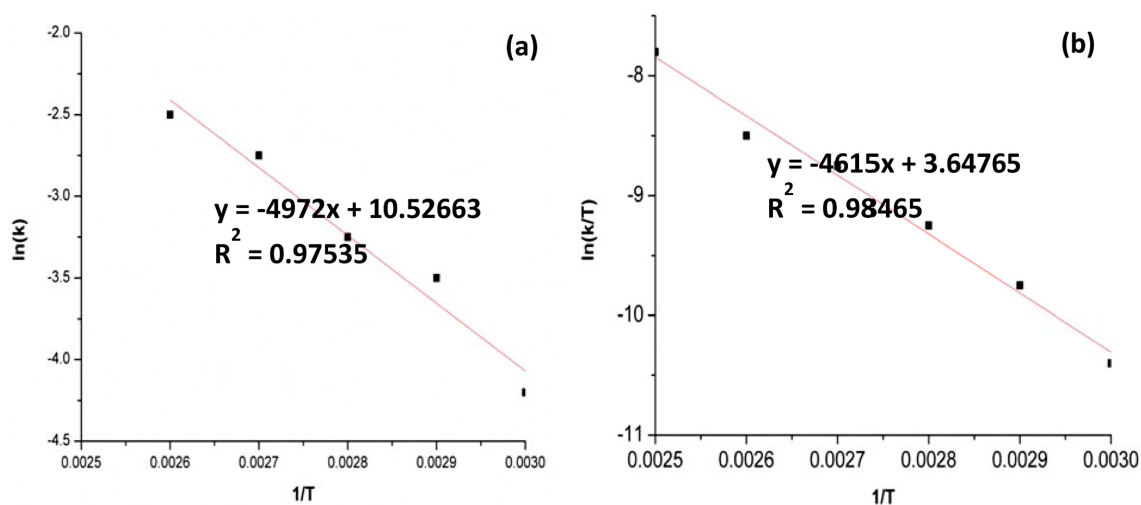**Effects of Temperature and Solvent on the Polymerization.** The influence of temperature on the catalytic activity of complex **3** in the polymerization reaction of D,L-LA was evaluated at reaction temperatures of 60, 90 and 110 °C (Table 2). It was evident that an increase in reaction temperature resulted in an increase in the rate of polymerization reaction. For example, increasing the reaction temperature from 90 to 110 °C was followed by a drastic increase in rate constant from 0.0385 to 0.0796 h^{-1} respectively. The activation parameters calculated from the Arrhenius and Eyrings plots (Figure 4) for the polymerization of D,L-LA by **3** were obtained as ΔH^o=38.4± 0.7 kJmol^{-1}, ΔS^o=-167.2±1.8 JK^{-1}mol^{-1}, E_a=41.3 kJmol^{-1} and ΔG_p^o= 60.7 kJmol^{-1} at 90 °C. These values compare well with those obtained from the polymerization of lactide using tin complexes[44] and are consistent with a highly ordered transition state reaction.[45] The negative value of the entropy, ΔS^o, indicated the ring-opening mechanism is sterically hindered and agrees well with the observations made by Dubois *et al.*[46]

The effect of solvents on the catalytic activity of complex **3** was also investigated using toluene, tetrahydrofuran (THF) and methanol (Table 2, entries 3-5). The apparent rate constants of the kinetics of the polymerization reactions increased from 0.0796 h^{-1} in toluene to 2.9998 h^{-1} in methanol (Figure 5). This increase in the catalytic activity of **3** in the presence of methanol could be due to *in situ* generation of a metal alkoxide which are known to give more active initiators. This observation agrees well with reports of Song *et al.*[47] where addition of isopropanol to zinc ethyl complex resulted in a marked increase in the rate of lactide polymerization at room temperature. The greater rate constant of 0.168 h^{-1} obtained in THF (coordinating solvent) compared to toluene (0.080 h^{-1}) further supports this hypothesis.
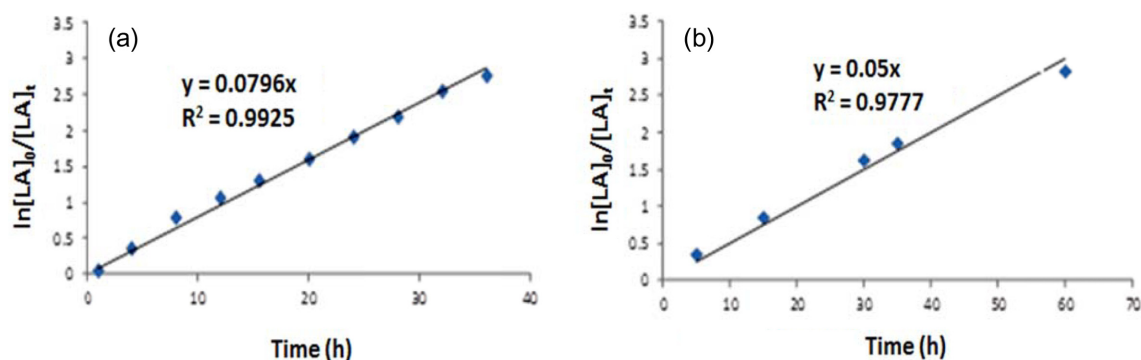
Table 2. Effect of Temperature and Solvent on the Polymerization Kinetics of D,L-LA by Catalyst 3[a]

Entry	[M]	Solvent	Temp. (°C)	K_{app} (h^{-1})
1	D,L-LA	Toluene	110	0.080
2	D,L-LA	Methanol	60	3.000
3	D,L-LA	THF	60	0.168
4	D,L-LA	Toluene	90	0.034
5	D,L-LA	Toluene	60	0.010

[a]Conditions: [M]/[LA]=100, [*R,S*-LA]$_0$=2.5 mmol.

Figure 4. (a) Arrhenius plot of $\ln(k)$ *versus* $1/T$; (b) plot of $\ln(k/T)$ *versus* $1/T$ for complex **3**. The ΔH^o and ΔS^o deduced from the plot were 38.4 kJmol^{-1} and -167.2 JK^{-1}mol^{-1}, respectively. Conditions: [LA]:[Zn]=100; [LA]$_o$=2.5 mmol, solvent, toluene.

Figure 5. Kinetic plot for D,L-LA polymerization in (a) toluene; (b) methanol at 60 ^{o}C; [LA]$_0$/[**3**]=100; [LA]$_o$=2.5 mmol.

Polylactide Molecular Weight and Molecular Weight Distribution. The molecular weight (M_w) and molecular weight distribution (PDI) for PLA synthesized using complexes **1-3** were experimentally determined using GPC and compared to the theoretical values calculated from ^{1}H NMR spectra (Table 2). From the data obtained, molecular weights between 771 to 1 816 Daltons were obtained. This is consistent with the formation of mostly oligomers (5 repeating units) and lower molecular weight polymers. The PDIs of the PLA obtained were relatively narrow ranging from 1.29 to 1.48. The low molecular weights of the polymers obtained were evident of *trans*-esterification reactions occurring concurrently during the polymerization process.[48] In addition, the poor initiating tendencies of carboxylate groups as compared to alkoxides could also account for the low molecular weight of the polymers reported.[48] In deed, at lower conversions, only oligomers

with molecular weights below the detection limit of the instrument were recorded thus it was impossible to determine the living polymerization nature of these catalysts. PLAs obtained from catalysts **1-3** exhibited comparable molecular weights indicating little influence of the ligand motif in controlling polymer molecular weight. Polymer molecular weights of 1816 Daltons and 1185 Daltons were obtained for L-LA and D,L-LA monomers respectively indicating insignificant dependency of polymer molecular weight on the identity of the lactide monomer.

Mechanism of Ring-opening Polymerization of Lactides. Attempts were made to understand the mechanistic pathways of these polymerization reactions catalyzed by complexes **1-3**. This was elucidated using ^{1}H NMR spectroscopy and mass spectrometry techniques. From the previously discussed kinetic data, the linear relationship of $\ln k_{app}$ and $\ln[1]$ (Figure
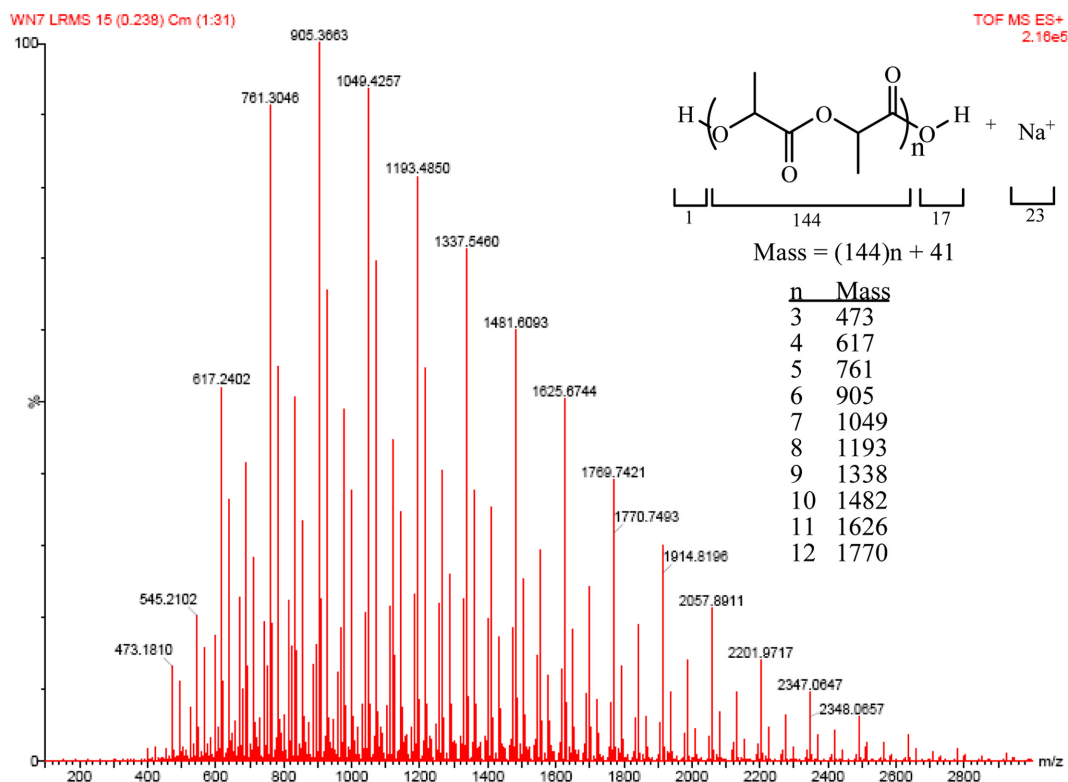
Figure 6. ^{1}H NMR spectrum of poly(D,L-LA) at 95% conversion revealed the absence of any methyl protons associated with the acetate group. Conditions, complex **1**, $[LA]_0/[\mathbf{1}]=100$, $[LA]_0=2.5$ mmol, temp. 110 ^{o}C, bulk polymerization.
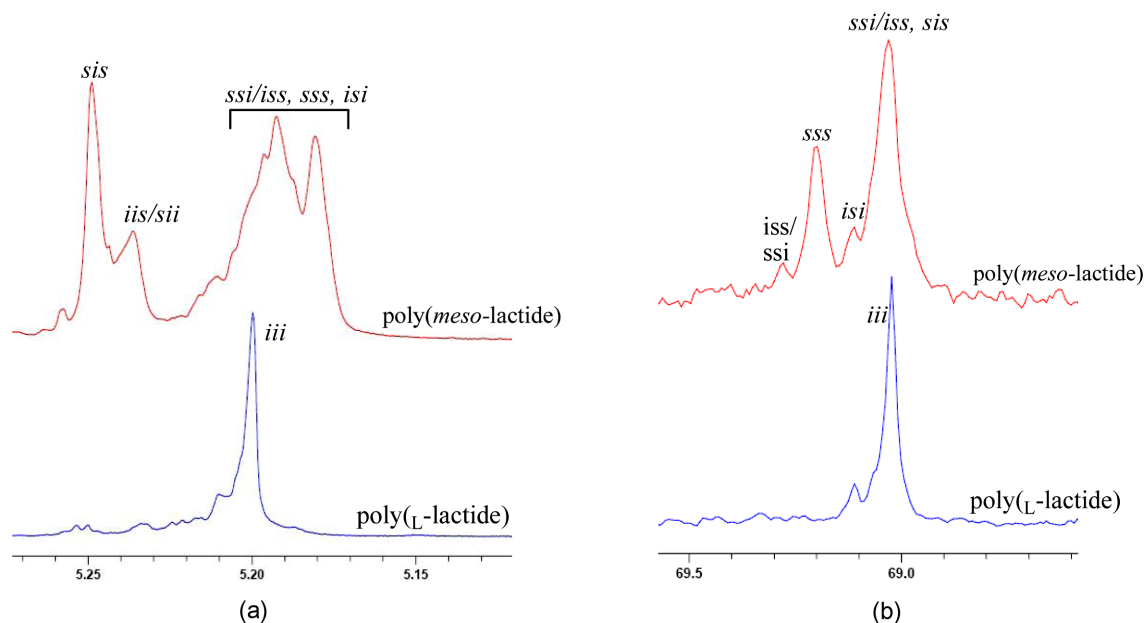
2) pointed to a coordination-insertion pathway. However, the non-integer value of the order of reaction with respect to the catalyst initiator indicates a more complex mechanism. However, both ^{1}H NMR (Figure 6) and mass spectra (Figure 7) of the polymers obtained did not exhibit signals associated with either the ligand backbone or carboxylate end groups typical of

coordination mechanism.[48,49] A careful analysis of the ESI-MS spectra of the polymers revealed the presence of $HO(C_6H_8O_4)_nH \cdot Na^+$ fragments. Hence the hydroxyl anions were observed as the groups in these polymerization reactions. The observation of the -OH end group could be due to the presence of adventitious water molecules that are capable of initiating hydrolysis of the polymer chain.[50,51] Thus it was virtually impossible from these studies to determine the exact mechanistic pathway of these polymerization reactions.

Microstructural Analyses of the Polymers. The stereochemistry and polymer tacticity of the polylactides obtained from catalysts **1-3** were determined by homonuclear decoupled ^{1}H NMR and the ^{13}C NMR spectroscopy. The homonuclear decoupled ^{1}H NMR and ^{13}C NMR of the methine region for poly(D,L-LA) and poly(L-LA) are presented in Figure 8. Both the ^{1}H NMR and ^{13}C NMR spectral data are consistent with the formation of isotactic and atactic poly(D,L-LA) and poly(L-LA) respectively.[52-54] The smaller peaks observed in addition to the main signal in the NMR spectra of the polymers points to some degree of epimerization during the polymerization process.[54]

Figure 7. ESI spectrum of crude PLA ($[D,L-LA]/[\mathbf{3}]=100:1$) polymerized at 110 ^{o}C.

Figure 8. (a) Methine resonance in homonuclear decoupled ^{1}H NMR spectra of PLAs prepared from respective monomer with complex **1** at 110 ^{o}C; (b) Methine carbon signals in the ^{13}C NMR spectra of PLAs prepared from respective monomer with complex **1** at 110 ^{o}C.

Conclusions

In conclusion, we have demonstrated that zinc(II) complexes supported on (benzoimidazolylmethyl)amine ligands form active catalysts in the ring-opening polymerization of lactides to afford low molecular weight polymers. All polymerization reactions follow pseudo-first order kinetics with respect to monomer. Both the complex architecture and monomer stereochemistry influence the reaction kinetics and polymer properties. Coordinating solvents enhance the catalytic activities of the complexes in comparison to non-coordinating solvents. The polymerization reactions proceeded *via* coordination-insertion mechanism to produce both atactic and isotactic polymers. Due to the complex nature of the kinetics of the polymerization reactions and spectral data obtained, it was impossible to conclude on the exact mechanism of the polymerization reactions. We are currently exploiting the N-H functionality in the ligand motif to design Zn-alkoxides expected to exhibit better control of polymer properties.

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