

SYNTHESIS OF β -DIKETIMINATE DERIVATIVES OF ZINC ALKOXIDES: CATALYTIC PROPERTIES FOR RING OPENING POLYMERIZATION

TAIMUR ATHAR*, ABDUL HAKEEM, NEHA TOPNANI

Indian Institute of Chemical Technology, Hyderabad (A.P.), India

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ABSTRACT

A series of zinc (II) complexes has been prepared based on a β -diketiminato ligand framework and exhibits the highest rate of polymerization with better stereoselectivity in the formation of poly(lactide) from the rac-lactide with aggregation and narrow polydispersities. Degree of aggregation and their reactivity's depends on the nature of alkoxy groups, the role of metal ion, solvent and their structural properties. The nature of substituent group on β -diketiminato ligand exerts a significant change affecting both the degree of selectivity and the rate of polymerization. The polymerizations are living, as evidenced by the narrow polydispersities and with their linear nature and average molecular weight.

Keywords: β -diketiminato Zinc alkoxides, PLA and PCL, Ring opening polymerization

1. INTRODUCTION

The remarkable advances have been reported for olefin polymerization by using single – site catalysts. The stereochemical properties of Poly(lactide) (PLA) and polycaprolactone (PCL) depends on the efficiency of a catalyst. The mechanical and physical properties, as well as their chemical and biological degradation depend on the single site interaction of catalyst. Poly(lactide) (PLA) and polycaprolactone (PCL) are used as biopolymer due to their biocompatibility, permeable and biodegradability properties since many years.¹⁻³ In last one decade, many efforts have been devoted for improving ROP with the help of alkoxy based initiators. In alkoxy based catalyst the metal-oxygen bonds play an important role for the ring-opening polymerizations-copolymerizations and transesterification reactions. The rate of polymerization depends on the following three parameters: nature of OR groups, the role of central metal ion and the nature of solvent in their coordinative aggregates. It is worth pointing that ROP of lactides can be initiated by alkoxy group in two-step (1) an anionic-type insertion mechanism of the monomer at the rate of propagation step without any transfer or termination reactions. Therefore the knowledge of the catalyst behaviors along with their mechanistic approach are essential at the molecular scale to better understand the conversion of monomer into poly product with better controls in molecular weight with narrow polydispersity. Ring-opening polymerization of lactides has been initiated by various metal alkoxides (Al, Li, Mg, Fe, Sn, Zr Zn or Ti) since last one decade.⁴⁻¹⁰ So, it is important to analyze and discuss in detail the dependence of the kinetic course of the reactions with catalyst in the solution state.

Monoanionic β -diketiminato ligand have been considered to be one of the most versatile ligands in coordination chemistry and helps in fine tuning the ligand properties with functional groups which leads to the formation of strong metal –ligand bond which is capable to control stereo chemical properties via a chain –end control mechanism.¹¹⁻¹²

Bulky substituents on the nitrogen atoms play an important role as a catalyst for the activation of small molecule and polymerization.¹³⁻¹⁶

The formations of β -diketiminato derivatives of Zinc alkoxides such as dinuclear or trinuclear take place by changing the functional groups at the molecular level.¹⁵

The role of alkoxy group with different substituents has been investigated for their activity towards the formation of dinuclear and trinuclear zinc complexes.

Herein we report the synthesis, structure of β -diketiminato Zn alkoxide complexes along with their solid-state molecular structures, their dynamic behavior and their reactivity towards ROP based on β -diketiminato ligand by using the concepts of molecular recognition within architectural properties of macromolecules.

2. EXPERIMENTAL PART

General Procedure

The reaction was performed in an inert atmosphere by using Schlenk

line. Solvents were distilled under nitrogen prior to use. Starting materials were purchased from Aldrich and used as such. Ligands were synthesized as reported in the literature.¹⁴

Rac –Lactide was sublimed under vacuum at 50°C. ¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova-600 (600 MHz for ¹H and 150 MHz for ¹³C) or a Varian Mercury-400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer by using TMS as an internal standard for (¹H) or the central line of CDCl₃ (¹³C). Microanalyses were performed by using a Heraeus -RAPID instrument Results within \pm 0.4% with the theoretical value. GPC measurements were performed on Postnova PN1122 by using THF as solvent delivery system with TriSEC GPC software at 35°C. Molecular weight and polydispersity indexes were calculated by using polystyrene as a standard.

Ligand Synthesis: The ligands with same N-aryl substituents in β -diketiminato was prepared by using 2.0 equiv of ArNH₂ in 2, 4-pentanedione in toluene by using *p*-toluenesulfonic acid as catalyst and then refluxed for 2 days. The ligands with different N-aryl substituents in β -diketiminato was prepared by using 1.0 equiv of ArNH₂ with 2,4-pentanedione in toluene with *p*-toluenesulfonic acid as catalyst and then refluxed for 1 day by using the same equivalent aniline (ArNH₂) was added into the solution and refluxed again for 2 days

Synthesis of [(BDI-2)Zn(m-OBn)]₂Zn(m-OBn)₂

The synthesis of 2-(2-Methoxyphenylimino)-4-(2,6-diisopropylphenylamido)-pent-2-ene (BDI-2) and [(BDI-2)ZnEt] was carried out as reported by Gibson¹⁴ (BDI-2) ZnEt (2 g , 4.37 mmol) was dissolved in 20 ml hexane, followed by dropwise addition of benzyl alcohol (0.55 mL , 5.24 mmol) at 0°C with continuous stirring for 30 minutes .The solution was warmed to room temperature and then stirred for 12 hours till white solids precipitated out. The mixture was filtered through celite .The filtrate was concentrated and white solid was crystallized from dried toluene solids at 0°C. Yield: 2.2 g (1.62 mmol , 37%). ¹H NMR (CDCl₃ , ppm) at room temperature: δ 7.10-6.45 (17H, m, ArH), 4.69 (1H, s, 1H, s, HC{C(Me)NAr}), 4.14 (4H, br s, OCH₂Ar), 3.44 (3H, s, OCH₃), 2.87 (2H, br s, CHMe₂), 1.64 (3H, s, HC{(CH₃)C=N(^o-MeAr)}), 1.56 (3H, s, (CH₃)C=N(^{2,6}-Di^{ipr}Ar)), 0.94 (6H, d, J_{H-H} = 6.8 Hz, ArCH(CH₃)₂), 0.77 (6H, s, ArCH(CH₃)₂). ¹³C NMR (CDCl₃ , ppm) at room temperature: δ 168.10 (HC{C(CH₃)NAr}), 167.92 (HC{C(CH₃)NAr}), 152.63 (MeOCCN), 144.41 (NCCCMe₂), 142.46 (NCCCMe₂), 138.77 (MeOCCN), 127.74, 127.02, 125.73, 124.86, 124.64, 123.35, 120.74, 111.70 (Ph), 94.51 (HC{C(CH₃)NAr}), 68.30 (PhCH₂O), 55.207 (CH₃O), 27.45 (ArCH(CH₃)₂), 24.14 (ArCH(CH₃)₂), (ArCH(CH₃)₂), 23.71 (HC{C(CH₃)NAr}), 22.89 (HC{C(CH₃)NAr}). Elemental analysis calc. for C₇₆H₉₀N₄O₆Zn₃C₆H₅CH₃: C: 69.04, H: 6.84, N: 3.88%, Found: C: 68.82, H: 6.71, N: 3.81%.

Synthesis of 2-(2-methoxyphenylimino)-4-(pentafluorophenylamido)-2-pentene(L,-H). A toluene solution of pentafluoroaniline (21 g, 110 mmol) with catalytic amount (0.1 g) of *p*-toluenesulfonic acid was added with 2, 4-pentanedione (12 mL, 120 mmol). After being refluxed for 24 h with water being continuously removed by using a Dean-Stark trap. Volatile materials were removed under vacuum the resulting to the formation of slurry .Slurry was

suspended in toluene (100 ml) followed by an addition of 2-methoxyaniline (14 mL, 120 mmol). The solution was refluxed for 48 h with water being removed by using a Dean-Stark trap again. The product was purified by column chromatography. The filtrate was dried in vacuum to give a yellow solid. Yield: 29 g (71%). ¹H NMR (CDCl₃, 400 MHz) at room temperature: *d* 12.38 (1H, s, NH), 7.15–6.89 (4H, m, ArH), 5.00 (1H, s, *b*-CH), 3.81 (3H, s, ArOCH₃), 2.12 (3H, s, CH₃CNArF₃), 1.93 (3H, s, CH₃CNArOMe). ¹³C NMR (CDCl₃, 400 MHz): at room temperature *d* 171.45 (CH₃CNArF₃), 155.87 (CH₃CNArOMe), 152.31 (MeOCCN), 140.53, 139.09, 138.92, 137.55, 136.74, 136.46, 128.95, 126.08, 125.36, 124.19, 120.28, 111.22 (Ph), 97.54 (*b*-C), 55.64 (OCH₃), 22.23 (CH₃CNArOMe), 20.60 (CH₃CNHFF₃). Anal. Calc. (Found) for C₁₈H₁₅F₃N₂O: C 58.38 (58.73), H 4.08 (4.12), N 7.56 (7.57) %.

Synthesis of [(L₁)₂Zn₂(μ-OBn)]₂. A L₁-H (0.37 g, 1.00 mmol) was taken in hexane followed by the addition of diethyl zinc (1.2 mL, 1.2 mmol). After being stirred at 0°C for 8 hrs, a light yellow solution was obtained. Volatile materials were removed in vacuum to yield yellow oil. Oil was taken in hexane (20 mL) followed by the addition of BnOH (0.11 mL, 1.0 mmol), the mixture was stirred for 8 hrs. Volatile materials were removed to yield a light yellow powder. The solid was recrystallized from toluene at 0°C to yield colorless crystals. Yield: 0.34 g (31%). ¹H NMR (CDCl₃, 400 MHz) at room temperature: *d* 7.28–6.51 (9H, m, ArH), 4.75 (1H, s, *b*-CH), 4.57 (2H, br s, PhCH₂O), 3.61 (3H, s, ArOCH₃), 1.61 (3H, s, CH₃CNArF₃), 1.38 (3H, s, CH₃CNArOMe). ¹³C NMR (CDCl₃, 400 MHz) at room temperature: *d* 171.93 (CH₃CNArF₃), 166.72 (CH₃CNArOMe), 152.02 (MeOCCN), 145.00, 143.29, 140.78, 139.09, 138.50, 137.56, 136.65, 136.03, 129.02, 128.21, 127.91, 125.45, 125.29, 119.65 (Ph), 95.90 (*b*-C), 68.85 (PhCH₂O), 55.03 (OCH₃), 23.16 (CH₃CNArOMe), 20.56 (CH₃CNHFF₃). Anal. Calc. (Found) for C₅₂H₄₈F₁₀N₄O₂Zn₂ [(L₁)₂Zn₂(μ-OBn)]₂·C₂H₆: C 56.08 (56.76), H 4.34 (4.98), N 5.03 (5.48) %.

Synthesis of 2 - (2, 6 - diisopropylphenylimino) - 4 - (4 - chlorophenylimino) - pent - 2 - ene (BDI-DiiPr-^pCl-H).

2, 6-Diisopropylaniline (5.5 g, 31 mmole) was taken in toluene in the presence of catalytic amount of para-toluenesulfonic acid, the 2, 4-pentadione (3.1 mL, 30 mmol) was added. The mixture was refluxed for 36 hrs by using Dean-Stark trap.

Volatile materials were removed in vacuum followed by the addition of 4-chloroaniline (3.95 g, 30.8 mmol) in 20 ml toluene and then refluxed for 36 hrs to remove of water completely by using a Dean-Stark trap. A clear solution was dried in vacuo after extracting with toluene to yield black solid. Recrystallization of the complex takes place in 24 hours at -18°C in ethanol to yield light yellow crystals. Yield: 8.52 g (23 mmol, 75%). ¹H NMR (CDCl₃, ppm) at room temperature: δ 12.55 (1H, s, NH), 7.23-7.14 (5H, m, ArH), 6.82 (2H, d, ArH), 4.88 (1H, s, HC{C(Me)NAr}₂), 3.00 (2H, sept, J_{H-H} = 6 Hz, CH(Me)₂), 2.01 (3H, s, H₃CC=N(^pClAr)), 1.56 (3H, s, H₃CC=N(^{2,6}-DiiPrAr)), 1.21 (6H, d, J_{H-H} = 6.8 Hz, ArCH(CH₃)₂), 1.12 (6H, d, J_{H-H} = 6.6 Hz, ArCH(CH₃)₂). ¹³C NMR (CDCl₃, ppm) at room temperature : δ 161.39 (HC{C(CH₃)NAr}), 159.31 (HC{C(CH₃)NAr}), 144.80, 142.20, 140.44, 128.75, 127.88, 125.31, 123.40, 123.03 (Ph), 95.82 (HC{C(CH₃)NAr}), 28.31 (ArCH(CH₃)₂), 24.28 (ArCH(CH₃)₂), 22.55 (ArCH(CH₃)₂), 20.77 (H₃CC=N(^pClAr)), 20.66 (H₃CC=N(^{2,6}-DiiPrAr)). Mass spectrum (EI, m/e) : 368.4 [M]⁺. Elemental analysis calc. for C₂₃H₂₉ClN₂: C: 74.88, H: 7.92, N: 7.59%. Found: C: 74.50, H: 7.68, N: 7.24%.

Synthesis of [(BDI-DiiPr-^pCl)Zn(m-^{OPr})]₂

(BDI-DiiPr^pCl-H) (5 g, 13.5 mmol) was dissolved in hexane, ZnEt₂ (1M in hexane, 16 ml, 16 mmol) was added drop wise at 0°C. The reaction mixture was stirred for 12 hours at ambient temperature.

A volatile material was removed by vacuum followed by recrystallization to takes place within 12 hours at 0°C in ethanol to yield white crystal. Yield: 3.52 g (3.575 mmole, 65%). ¹H NMR (CDCl₃, ppm) at room temperature: δ 7.27-7.16 (3H, m, ArH), 6.62 (2H, d, ArH), 6.46 (2H, t, ArH), 4.81 (1H, s, HC{C(Me)NAr}₂), 3.73 (1H, sept, OCH(Me)₂), 3.18 (2H, sept, CH(Me)₂), 1.80 (3H, s, HC{C(CH₃)NAr}₂), 1.58 (3H, s, HC{C(CH₃)NAr}₂), 1.11 (6H, d, J_{H-H} = 6.4 Hz, ArCH(CH₃)₂), 1.07 (6H, d, J_{H-H} = 7.2 Hz, ArCH(CH₃)₂), 0.74 (3H, d, J_{H-H} = 7 Hz, OCH(CH₃)₂), 0.66 (3H, d, J_{H-H} = 7 Hz, OCH(CH₃)₂). ¹³C NMR (CDCl₃, ppm) at room temperature: δ 169.47 (HC{C(CH₃)NAr}), 165.82 (HC{C(CH₃)NAr}), 148.14, 146.09, 142.47, 128.23, 127.90, 126.39, 125.64, 123.90 (Ph), 96.69 (HC{C(CH₃)NAr}), 65.59 (OCHMe₂), 27.76 (ArCH(CH₃)₂), 27.37 (OC(CH₃)₂), 27.02 (OC(CH₃)₂), 24.62 (ArCH(CH₃)₂), 24.47 (ArCH(CH₃)₂), 24.37 (HC{C(CH₃)NAr}), 23.82 (HC{C(CH₃)NAr}). Elemental analysis calc. for C₅₂H₇₀Cl₂N₄O₂Zn₂: C: 63.19, H: 6.74, N: 5.76%. Found: C: 63.42, H: 7.16, N: 5.69%.

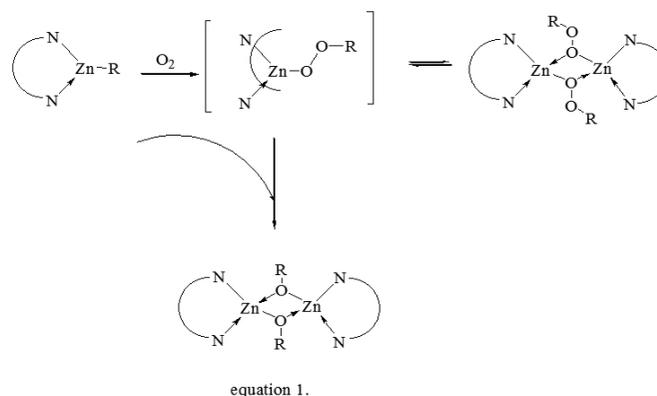
Polymerization procedure: A typical polymerization procedure was carried out by the synthesis of PLA at room temperature with the conversion yield (94%) as supported by ¹H NMR spectroscopic studies. A mixture of

catalyst (0.0506 g, 0.05 mmol) and L-lactide (0.72 g, 20 mmol) in toluene (20 mL) was stirred at room temperature for 2 min. Volatile materials were removed and the residue was redissolve in THF (10 mL). The mixture was quenched with an aqueous acetic acid solution (0.35N, 10 mL) and the polymer was precipitated out in *n*-hexane (40 mL) to give white crystalline solids. Yield: 0.52 g (72%).

3. RESULTS AND DISCUSSION

Effect of functional group in N-aryl positions on the structure of β-diketiminato Zn complexes:

The utility of above synthetic methodology for the preparation of zinc complexes with a dinuclear and trinuclear complexes takes place with the help of alkoxy ligands has been investigated. These complexes have wide range potential applications. These studies show the effect of β-diketiminato Zn alkoxide complexes with the help polar interactions. All dinuclear complexes obtained by substitution with an electron donating groups at the N-aryl positions. However the trinuclear complexes were obtained with the help of electron withdrawing groups at the 1 or 3 positions in pentene along with iso-propyl group at the 2,6 N -aryl positions. With the presence of an electronegative substitution the polar interaction helps to overcome the p-resonance effect leads to formation of trinuclear complex with the help of s-electron withdrawing effect. Spectroscopic and elemental analysis data are consistent with the representative compound. The mechanism for the formation of these complexes is shown in equation 1.



Ring Opening Polymerization of Lactides Initiated by β-diketiminato Zn complex:

Alkoxides are considered as a potential precursor as a single-site catalyst due to their high electropositive nature of elements which are stabilized by the electronegative oxygen atoms, which will leads to a decrease in the reactivity towards a acid-base side interaction which will leads to an anionic polymerization in lactones. The slow activity in the alkoxide-bridged dimer with different initiating groups leads to the difference in the catalytic action.

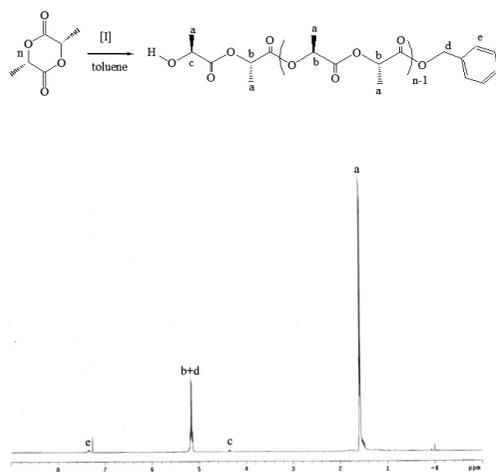
A preliminary experiment was conducted to investigate the utility of the β-diketiminato ligands as a catalysts towards polymerization of rac-lactide by using different functional groups at N-aryl position. These catalysts show the good ROP to yield PLA with narrow polydispersities and good molecular weight control and stereoselectivity. With the help of electrons donating group at the N-aryl positions the polymerization reactions takes less than 10 mins. The rate of polymerization differs with functional groups depending in the position at the N-aryl substitution. It is concluded that Lewis acidity character increases at the Zinc center due to the presence of an electron withdrawing groups and lead to the formation of strong bond between Zinc and BnO⁻ thereby affecting the rate of ROP.

Ring opening polymerization (ROP) of L-lactide (LLA) with complexes 1 -3 was systematically examined in an inert atmosphere. These experimental results show the complex 1 act as an efficient initiator for the polymerization of LLA. More than 90% conversion takes place within 3 min in toluene at ambient temperature and with narrow PDIs (1.09-1.18) as illustrated in Table 1.¹⁵ All four BnO⁻ groups could be used as initiators on trinuclear Zn complex. The *M_n* versus [LLA]₀/[1] ratio plot as shown in Figure 1.

Table 1 Polymerization of L-lactide using complex 1 as an initiator.

Entry	[M]/[Zn]	Temp.	Time(min)	Mn(GPC) ^a	Mn(cal.) ^b	Conv.(%) ^c	PDI
1	40	r.t	3	3299	1600	>99	1.15
2	60	r.t	3	5100	2300	>99	1.18
3	80	r.t	3	8000	3000	>99	1.10
4	100	r.t	3	10483	3700	>99	1.09

^aObtained from GPC analysis and calibrated by polystyrene standard. ^bCalculated from the molecular weight of L-lactide x [M]₀/4[1]₀ x conversion yield plus Mw(BnOH). ^cObtained from ¹H NMR analysis.



¹H NMR spectrum of PLA-50 catalyzed by compound 3 at 50 °C

Figure 1. Synthesis of poly lactide ¹H NMR spectrum of PLA-50 catalyzed by compound 3 at 50 °C

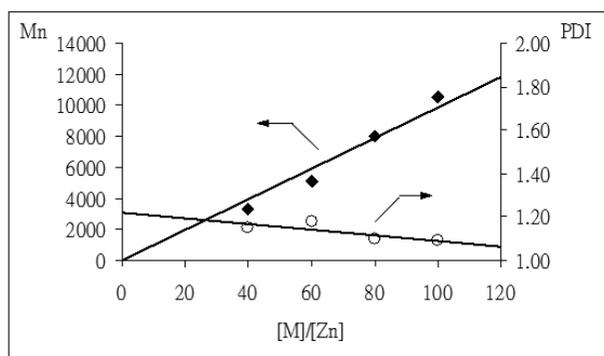


Figure 2. Plot of Mn (GPC) vs. [M]/[Zn] with polydispersity indices indicated by closed circles (GPC).

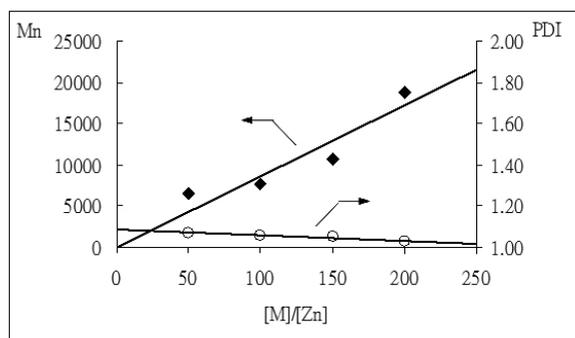


Figure 3. Plot of Mn (GPC) vs. [M]/[Zn] with polydispersity indices indicated by closed circles (GPC).

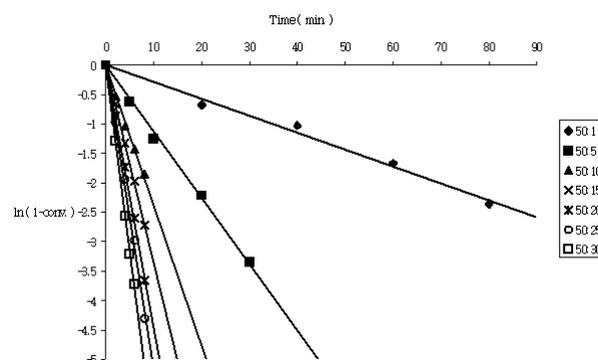


Figure 4. First-order kinetic plots for L-lactide polymerizations with time in toluene with different concentration of complex 4 as an initiator.

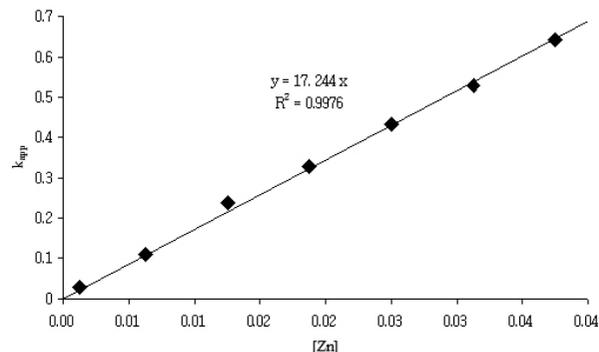


Figure 5. Linear plot of k_{obs} versus [1] for the polymerization of L-lactide with [LA]₀ = 0.5 M in toluene. $k = 17.24 \text{ M}^{-2} \text{ s}^{-1}$

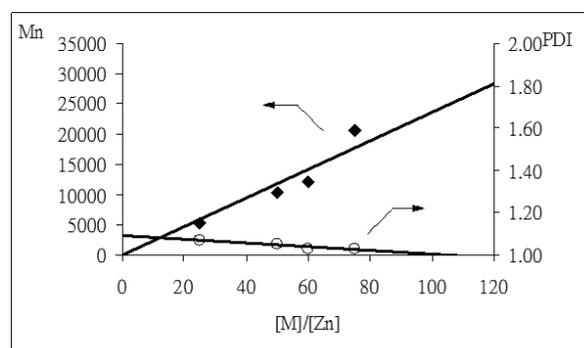


Figure 6. Plot of Mn (GPC) vs. [M]/[Zn] with polydispersity indices indicated by closed circles (GPC).

Table 2 Polymerization of L-lactide using complex 2 as an initiator.

Entry	[M]/[Zn]	Temp.	Time(h)	Mn(GPC) ^a	Mn(cal.) ^b	Conv.(%) ^c	PDI
1	50	r.t.	2	6500	3700	>99	1.07
2	100	r.t.	2	7700	7300	>99	1.06
3	150	r.t.	2	10700	10900	>99	1.05
4	200	r.t.	2	18800	14500	>99	1.03

^aObtained from GPC analysis and calibrated by polystyrene standard. ^b Calculated from the molecular weight of L-lactide $\times [M]_0/4[1]_0$, \times conversion yield plus Mw(BnOH). ^c Obtained from ¹H NMR analysis.

Table 3 Polymerization of L-lactide using complex 3 as an initiator.

Entry	[M]/[Zn]	Temp.	Time(min)	Mn(GPC) ^a	Mn(cal.) ^b	Conv.(%) ^c	PDI
1	25	r.t.	20	5200	3650	>99	1.07
2	50	r.t.	20	10300	7250	>99	1.05
3	60	r.t.	20	12050	8300	96	1.03
4	75	r.t.	20	20700	10850	>99	1.03

^aObtained from GPC analysis and calibrated by polystyrene standard. ^b Calculated from the molecular weight of L-lactide $\times [M]_0/4[1]_0$, \times conversion yield plus Mw(BnOH). ^c Obtained from ¹H NMR analysis.

The ROP reaction was carried out with complex 2; the results are given in Table 2. When the $[LLA]_0/[2]$ ratio was increased, *Mn* of PLLA was increased linearly, supporting the living property of polymerization with complex 2. PDI (1.03-1.07) as illustrated in table 2. The *Mn* versus $[LLA]_0/[2]$ ratio plot shown as Figure 4. Electron withdrawing group attack the carbonyl group of lactide by increasing Lewis acidic character of alkoxy group. More than 90% conversion takes place within 2 hrs at room temperature in toluene, and their kinetic studies¹³⁻¹⁴ reveals the catalytic process follows the first order reaction and with a kinetic constant $k = 17.24 \text{ M}^{-2} \text{ s}^{-1}$ which are independent of type of monomer used along its and complex concentration. (Figure 3 and 4). More than 90% conversion takes place within 20 min at room with complex 3 at a desired $[LLA]_0/[3]$ ratio in toluene and with PDIs in the range of (1.09-1.18) as shown in Table 3. These results support the living property before the reaction was quenched. The *Mn* versus $[LLA]_0/[3]$ ratio plot was shown as Figure [5,6]

These results show that stereoselectivities with *Pr* values are mostly syndiotactic structure with high *Pm* value.¹⁵

4. CONCLUSIONS

Binuclear and trinuclear β -diketiminato Zinc complexes were reported and act as single, living initiators for the polymerization of rac-lactides to form heterotactic PLA with new architectural properties. The ligand framework is flexible with limited role to provide steric bulk for heterotactic chain –end control. Micro structural analyses of the polymer exert a significant influence to control the stereochemistry of monomer with the tacticity with growing polymer chains and with good PDIs thereby reducing the rate of degradation. Kinetic analysis further supports that the polymerization follows the first order behavior in monomer. Much work needs to be done to fully understand the factors responsible for molecular design of single-site catalyst for stereoselective ROP of lactides based on fine tuning the steric and electronic factor of ligand framework to enhance polymerization activity restricting the transesterification reactions.

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