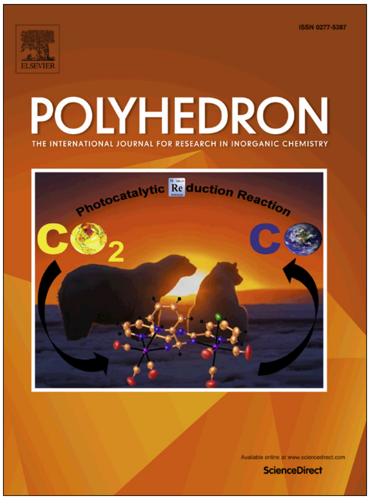

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Nickel(II) Complex Catalyzed Ring-Opening Polymerization of Lactide

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Abstract

The present manuscript is focused on the synthesis of a series of nickel complexes [Ni-HMBED, Ni-HMBPD and Ni-HMBBD] based on Salen-type Schiff-base ligands and a study of their reactivity for the ring-opening polymerization (ROP) of lactide. These nickel complexes were prepared by the reactions of a nickel solution with one molar equivalent of the Salen-type Schiff-base ligands in methanol under a nitrogen atmosphere. Characterization of these nickel complexes have been carried out by different analytical techniques, which showed a square planar geometry for the Ni atom. The nickel complexes have shown high activity towards the ring-opening polymerization of lactide, with variation in the diamine group. The linear relationship established between the percentage conversion and the number-average molecular weight has confirmed the controlled ROP by the use of the nickel complexes as a catalyst. Finally, a mechanism for the ROP of lactide has been proposed.

Keywords: Ring opening polymerization, Lactide, Schiff base, Nickel complex, PLA.

1. Introduction

In the last two decades, polymer scientists have been putting their efforts to search and find new polymeric systems with new structures and promising properties. Poly(lactic acid) (PLA) is an important biodegradable and biocompatible polyester, [1-3] which is mainly synthesized by the ring-opening polymerization (ROP) of lactide (LA), and as it degrades to non-toxic components it very useful for biomedical applications [4-7]. PLAs are also used in orthopedic applications, tissue engineering and biodegradable internal fixation devices [8-9]. However, to be used in a biomedical field, it is necessary to know the extent to which the metal residues are removable. Further, removal of metal up to a zero level does not happen in reality, thus, non-cytotoxic metals should be preferred. Thus, environmentally benign metals with no harmful effects towards living beings should be considered [10]. However, different metal catalysts, such as complexes of aluminum [11-13], lithium [1,14-16], magnesium [17-21], copper [22-23], iron [24], tin [25-26], titanium [27-28] or zinc [19, 29-33] etc., have been used towards the ROP of lactide. In recent times, Ca, Mg, Fe and Zn based initiators or catalysts has received great attention because of their metabolic action in the body [34-35]. Nowadays, nickel complexes, with high electron transfer ability and stability of reactive intermediates, should also be considered as a part of in-depth investigations.

Furthermore, nickel initiators having nitrogen-containing polydentate ligands have not been discussed much to date for their application in the ROP of lactide [36-40]. Nowadays, FDA-approved stannous octanoate is also being used commercially for the synthesis of PLAs. Nickel complexes [41] are less toxic and have almost similar catalytic characteristics as stannous octanoate, which has been used for synthesis of PLA. Recently, our research group has synthesized Schiff base copper complexes which resourcefully catalyzed the ROP of *L*-lactide

[22-23]. Although, nickel Schiff base complexes have been widely studied for various chemical transformations, their application in the ROP of *L*-lactide is still unexplored. Thus, in the current context, study of the nickel complexes based on Salen type ligands, such as HMBED (N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)ethylenediamine, HMBPD (N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)propylenediamine and HMBBD (N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)benzylenediamine), as initiators for ROP has been carried out. The main advantages of these complexes are their stability in air and their ease of preparation. In the later part, a kinetic study of the ROP of lactide was carried out to propose a reaction mechanism.

2. EXPERIMENTAL

2.1 Materials

The combination of a glove box and standard Schlenk techniques were used for the syntheses of the Schiff bases, their nickel complexes and PLA. All syntheses were executed in dry nitrogen ambiance. All solvents were of analytical grade and were dried and distilled prior to use. Toluene and dichloromethane were dried and distilled from sodium benzophenone and P_2O_5 respectively. Anhydrous nickel chloride, ethylene diamine (ED), propylene diamine (PD) and benzylene diamine (BD) were purchased from HiMedia Laboratories Pvt. Ltd., Mumbai, India. 2-Hydroxy-3-methoxybenzaldehyde (HMB) and benzyl alcohol were procured from E. Merck, India. *L*-Lactide (LA) was obtained from Sigma Aldrich and was used as received. Other chemicals were of analytical grade (>99.0 wt %) and were used as received.

2.2 Characterization of the Schiff bases and their nickel complexes

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. A Shimadzu 1601 PC UV–Vis spectrophotometer was used for determination of the electronic spectra. TGA was carried out under a nitrogen atmosphere using a Perkin-Elmer Pyris, Diamond thermal analyzer at a heating rate of 10ºC min^{-1}. AAS was carried out with a Perkin-Elmer 3100 atomic absorption spectrometer at λ_{max} of the nickel ion. Analyses of compositions of the Schiff bases and their nickel complexes were done on a Haraeus Carlo Ebra 1108 elemental analyzer. An FT-NMR-Brucker 300 MHz spectrometer was used to record the NMR spectra of the samples, using DMSO-d^6 as a solvent and tetramethylsilane (TMS) as an internal reference. The room temperature magnetic moment (μ) of the nickel complexes was measured with a Vibrating Sample Magnetometer-155. Merck VAPRO 5600, Germany, A vapor pressure osmometer was used to determine the molecular weights of the Schiff bases, their nickel complexes and PLA. The crystal structure of the ligand was determined with a Bruker Kappa Apex-II diffractometer.

2.3 Synthesis of Characterization of Schiff bases and their nickel complexes

The N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)ethylenediamine (HMBED), N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)propylenediamine (HMBPD) and N,N'-bis(2-hydroxy-3-methoxybenzaldehyde)benzene-1,2-diamine (HMBBD) Schiff bases have been synthesized by modification of a synthetic route reported in the literature [35]. A mixture of 2-hydroxy-3-methoxybenzaldehyde (20.00 mmol, 3.04 g) and the diamine (10.00 mmol; 0.6g for ED, 0.74g for PD and 1.08g for BD) in methanol were refluxed at 60 ºC for about 2 h. Upon cooling the reaction mixture and recrystallizing with chloroform, colored crystals (yellow, light yellow and orange colored for the ED, BD and PD ligands respectively) were obtained. Yield: 92.6, 91.2 and 94.4 % for ED, PD and BD respectively. The nickel complexes (Ni-HMBED, Ni-HMBPD and Ni-HMBBD) were synthesized by refluxing a 100 ml methanolic solution of the respective Schiff base (20.00 mmol; 6.56g for ED, 6.85g for PD and 7.53 g for BD) and 20.00 mmol (2.59

g) of nickel chloride in a round bottom flask at 60 ºC for 5 h. All the reactions were carried out under a nitrogen atmosphere. Finally, the nickel complexes were recovered in methanol and dried in a vacuum desiccator. Yield: 86.1, 84.3 and 88.8 % for Ni-HMBPD, Ni-HMBED and Ni-HMBBD, respectively

The thermal stabilities of the Ni-HMBED, Ni-HMBPD and Ni-HMBBD catalysts were analyzed to provide proof for the complexation and also to study their applications in high-temperature reactions. The TGA of HMBED, HMBPD and HMBBD Schiff bases showed a weight loss of 50.4, 46.3 and 40.1 wt% at 500 ºC, but their nickel(II) ion complexes showed a weight loss of 39.5, 38.4 and 35.5 wt%, which indicates that the Ni-HMBED, Ni-HMBPD and Ni-HMBBD complexes were more stable in comparison to the free ligands, and among all the complexes Ni-HMBPD was found to be the most stable (Figure 1) [42]. FTIR and UV techniques for the HMBED, HMBPD and HMBBD Schiff bases and their nickel complexes have provided evidence for the formation of Ni-HMBED, Ni-HMBPD and Ni-HMBBD, and their structures and geometries were also confirmed by elemental analysis and a magnetic property study.

The absorption bands for the >C=N and >C–O phenolic groups and a broad band for the phenolic OH group were observed at 1613, 1256 and 3100-2800 cm^{-1} for HMBED, 1634, 1258 and 3000-2850 cm^{-1} for HMBPD and 1609, 1260 and 3050-2850 cm^{-1} for HMBBD, respectively. Elemental analysis data for HMBED showed (wt %): C 66.13, N 8.42, H 6.21; Calcd(%): C 65.84, N 8.53, H 6.14; for HMBPD (wt %): C 66.35, N 7.89, H 6.70; Calcd (%): C 66.65, N 8.18, H 6.48; for HMBBD (wt %): C 70.35, N 7.02, H 5.70; Calcd (%): C 70.20, N 7.44, H 5.36, which correspond to the formula $C_{18}H_{20}N_2O_4$, $C_{22}H_{22}N_2O_4$ and $C_{22}H_{20}N_2O_4$, respectively [43-44]. The molecular weights of the HMBED, HMBPD and HMBBD Schiff bases were 329.23

(Calcd 328.36), 340.63 (Calcd 342.39) and 377.68 g mol^{-1} (Calcd 376.41 g mol^{-1}), respectively. The absorption bands at 264 and 330 nm for HMBED, 262 and 330 nm for HMBPD and 260 and 330 nm for HMBBD (Figure 3), represent $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively (Figure S1-S3) [22-23,45-47].

The complexation of the nickel ion with the HMBED, HMBPD and HMBBD Schiff bases was carried out by refluxing a mixture of the Schiff bases and nickel chloride at 60 °C for 5 h (Scheme 1) in methanol. The elemental analysis for the Ni-HMBED complex showed (wt %): C 56.64, N 7.21, H 4.81; Calcd(%): C 56.15, N 7.18, H 4.71; for Ni-HMBPD (wt %): C 57.71, N 7.09, H 5.19; Calcd(%): C 57.18, N 7.02, H, 5.05; for Ni-HMBBD (wt %): C 60.51, N 6.19, H 4.13; Calcd(%): C 61.01, N 6.47, H 4.19, which correspond to the formula $C_{18}H_{18}NiN_2O_4$, $C_{19}H_{20}NiN_2O_4$ and $C_{22}H_{18}NiN_2O_4$, respectively. The observed molecular weights of Ni-HMBED, Ni-HMBPD and Ni-HMBBD were 385.47, (Calcd 385.04), 399.34, (Calcd 399.07) and 434.10 g mol^{-1}, (Calcd 433.08 g mol^{-1}).

A considerable difference in the IR bands for the >C=N and >C–O groups were observed due to complexation and also two new absorption bands at 520 and 421 cm^{-1} for Ni-HMBED, 513 and 429 cm^{-1} for Ni-HMBPD and 525 and 422 cm^{-1} for Ni-HMBBD were observed due to the formation of Ni–O and Ni–N bonds (Table S1 and Figure S4-S6). Further, the phenolic OH band between 2800 and 3100 cm^{-1} for HMBED, 2850 and 3000cm^{-1} for HMBPD and 2850 and 3050 cm^{-1} for HMBBD disappeared, which provides proof for the formation of the complexes Ni-HMBED, Ni-HMBPD and Ni-HMBBD [43].

The Ni-HMBED, Ni-HMBPD and Ni-HMBBD complexes showed a hypsochromic shift in the $\pi \rightarrow \pi^*$ transition from 264 to 251, 262 to 251, 260 to 246 nm respectively and for the $n \rightarrow \pi^*$ transition from 330 to 300, 330 to 278 and 330 to 292 nm, respectively. Two additional bands at

331 and 424nm for Ni-HMBED, 301 and 381nm for Ni-HMBPD, and 312 and 403nm for the Ni-HMBBD complex were observed for the C→T and d→d transitions (Table S1). These electronic transitions correspond to t_{2g}^{6} e_{g}^{2} configuration for the nickel(II) ion in these complexes. The magnetic moments (μ) of the Ni-HMBED, Ni-HMBPD and Ni-HMBBD complexes were found to be 0.69, 0.67 and 0.84 BM, which indicates the occurrence of a low-spin nickel(d^8) center and the slight variation from diamagnetism may be due to the presence of small amounts of paramagnetic impurities [48-50]. All the nickel complexes have a square planar geometry with dsp^2 hybridization.

2.4 Nickel complexes in the ring opening polymerization of L-lactide

A representative polymerization process was demonstrated by the synthesis of PLA-150 ([LA]/[Ni] = 150) at room temperature. To a rapidly stirred solution of *L*-lactide (2.88 g, 20 mmol), Ni-HMBED (0.051 g, 0.133 mmol) in toluene (30 mL) was added along with the requisite amount of benzyl alcohol. An increase in viscosity was observed and finally stirring was ceased after 25 h. Volatile materials were removed under vacuum, and the residue was extracted with THF (30 mL). The extraction was dried again and the white precipitate was washed with n-hexane three times and dried under vacuum overnight, giving a crystalline white solid. Yield: 2.1 g (72.9%)

The molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) were determined by using gel permeation chromatography (GPC) manufactured by Waters. The GPC instrument was equipped with a Waters 1525 Binary HPLC pump. Two columns, namely Waters Styragel HR4 7.8×300 mm WAT10573 and Waters Styragel HR3 7.8×300 mm WAT044223, were used in series. THF was used as the mobile phase. The flow rate of THF was 1.0 ml/min. An ELS detector, Waters 2420, was used for the detection of different molecular weight fractions.

Polystyrene standards with a low dispersity were used to generate a calibration curve. The GPC chromatograms were analyzed through Breeze version 3.3 software.

3. RESULTS AND DISCUSSION

3.1 Nickel complexes in the ring opening polymerization of L-lactide

On the basis of the "immortal" property of lactide polymerization [51] and the evidence of the in situ formation of metal alkoxides in the presence of alcohol [11-33], the complexes Ni-HMBED, Ni-HMBPD and Ni-HMBBD were expected to behave as catalysts toward the ROP of lactide in the presence of benzyl alcohol. The nickel complexes Ni-HMBED, Ni-HMBPD and Ni-HMBBD in the presence of benzyl alcohol initiate the ring-opening polymerization of *L*-lactide (LA) in dichloromethane at 30 °C (Scheme 2). The polymerization results are listed in Tables 1, 2 and 3. All the runs displayed good activities for the polymerization of *L*-lactide and showed great control of molecular weight, and the presence of benzyl alcohol has a significant influence on the polymerization behavior of the corresponding complexes.

The ring-opening polymerization of *L*-lactide using nickel complexes, with a monomer to benzyl alcohol ratio 150/1, has been systematically studied at 30 °C (Table 1). It is worth noting that the nickel complexes are more active in CH_2Cl_2 than in toluene or THF. The difference in activity is probably due to higher solubility of the complexes in CH_2Cl_2 in comparison to toluene. The slowest polymerization rate is found with THF, which may be attributed to the coordination ability of THF with the nickel metal, which retards the reaction rate [22-23].

By comparing the polymerization results listed in Tables 2 and 3, several structure-activity trends may be drawn. The experimental results indicate that the nickel complexes are efficient catalysts for the ROP of *L*-lactide in the presence of BnOH when the $[M]_0/[I]_0$ ratio ranges from 50 to 200. The polymerization is well controlled and the “living” character is demonstrated by the low polydispersity index (PDI), ranging from 1.07 to 1.16 for the polymers, and by the linear relationship between M_n and the $[Ni]_0/[BnOH]_0$ ratio (Figure 2). It is interesting to note that the ROP of *L*-lactide catalyzed by the Ni complexes in the presence of benzyl alcohol (BnOH) shows immortality. The ‘immortal’ character was examined using two or four equivalent ratios of benzyl alcohol as the chain transfer agent (Table 4). It was found that for polymerization without the use of BnOH, there is almost negligible conversion (<5%), (Tables 2 and 3), but the use of BnOH changes the activities of the catalyst drastically. The reaction time decreases from 24 to 15 h with the use of a greater amount of BnOH (Table 3). This may be due to active participation of the initiator in the polymerization reaction. The molecular weight of the polymers was also affected by the ratio of BnOH used. By the addition of two or four equivalents of benzyl alcohol in the polymerization reactions, the molecular weights became half or one fourth, respectively (Table 3). It was also observed that for polymerization using only the ligand or nickel chloride, there is almost zero conversion (Table 2). To observe the influence of the substituents towards the ROP of lactide, a series of nickel complexes have been prepared. Among all the nickel complexes, Ni-HMBED showed better activity based on percentage of conversion in 24 hours (Tables 1, 2 and 3) [30]. This may be due to the creation of more electrophilicity at the nickel center in comparison to the other nickel complexes, Ni-HMBPD and Ni-HMBBD, and is favorable for the coordination and insertion of LA monomers. The catalytic activity was also found to decrease with the increased steric hindrance offered by the diamine substituent (Tables 1, 2 and 3).

^{1}H NMR (Figure 3 and Figure S7-S8) studies on PLA catalyzed by the nickel complexes in the presence of BnOH was carried out to determine the process of initiation. The ^{1}H NMR spectrum of PLA-200, prepared from a $[LA]_0/[BnOH]$ ratio of 200, indicates that the polymer chain is capped with a benzyl ester group on one end and a hydroxyl group on the other end, suggesting that the initiation occurred through the insertion of the benzyl alkoxy group into *L*-lactide giving an intermediate, which further reacts with an excess of *L*-lactide yielding polyesters. The polymerization procedures agree well with the processes found in other metal alkoxides [11-33]. A literature report [36] for the polymerization of *L*-lactide using a nickel complex at 130 °C shows PLA with M_n = 1200 g mol^{-1} has been achieved, which suggests that the results obtained in the present investigations are superior in terms of M_n (Tables 2 and 3). Further, considerably higher molecular weight PLA has been obtained in all entries (Tables 2 and 3) which indicates that the propagation is faster than the initiation or partial hydrolysis of the initiating functionality.

3.2 Kinetics of the ROP of lactide

Kinetic studies for the polymerization of *L*-lactide using the nickel complexes (Figures S9-S11) as catalysts in the presence of the initiator BnOH with a [LA]o/[Ni]/[BnOH] ratio of 100/1/1 has been performed. The $\ln[M]_o/[M]_t$ vs time plots were found to be linear, where $[M]_o$ is the initial lactide monomer concentration and $[M]_t$ is the lactide concentration at a given reaction time [52-53]. It has been concluded from these plots that the polymerization reactions obey first order kinetics. The values of the apparent rate constant (k_{app}) may be calculated from the slope of these plots. The value of k_{app} and the standard deviation (SD) for *L*-lactide polymerization in the presence of the initiator were found to be 00.08003 h^{-1} and 0.06316, 0.01056 h^{-1} and 0.01466 and 0.06317 h^{-1} and 0.02638 for Ni-HMBED, Ni-HMBPD and Ni-HMBBD respectively [22-23].

3.3 Mechanism of the ROP of lactide using the nickel complexes

The mechanism for the polymerization of L-lactide proceeds as outlined in Scheme 3. Coordination of *L*-lactide with the nickel complexes yields a monomeric penta-coordinated intermediate **I**, which by the insertion of a benzyl alkoxy group into the L-lactide produces a new initiator **II**. Increasing the steric hindrance and including an electron-donating group on the imine carbon atom tends to stabilize the monomeric intermediate and hence increases the reaction rate. Finally, subsequent addition of lactide produce PLA.

4. CONCLUSIONS

Nickel complexes supported on Salen type ligands were shown to be efficient catalysts for the ring opening polymerization of lactide when benzyl alcohol is taken as an initiator. Use of benzyl alcohol plays a vital role towards the ROP. Without benzyl alcohol, the nickel complexes show much lower activity. However, the presence of a two or four fold excess of benzyl alcohol has produced PLA with half or one fourth of the molecular weight, respectively. The PLA thus produced by the ROP of *L*-lactide shows a moderate molecular weight with a narrow PDI, ranging from 1.07 to 1.16. Among the diamine groups, the polymerization rate follows the order: ethylene group > propylene group > benzene group, based on the percentage conversion.

Supporting Information

This includes FTIR spectra of the Schiff bases, ^{1}H NMR spectrum of PLA, Semi-logarithmic plots of *L*-lactide conversion catalyzed by the nickel complexes, FTIR frequencies and electronic transitions of the Schiff bases and their nickel complexes (Table S1).

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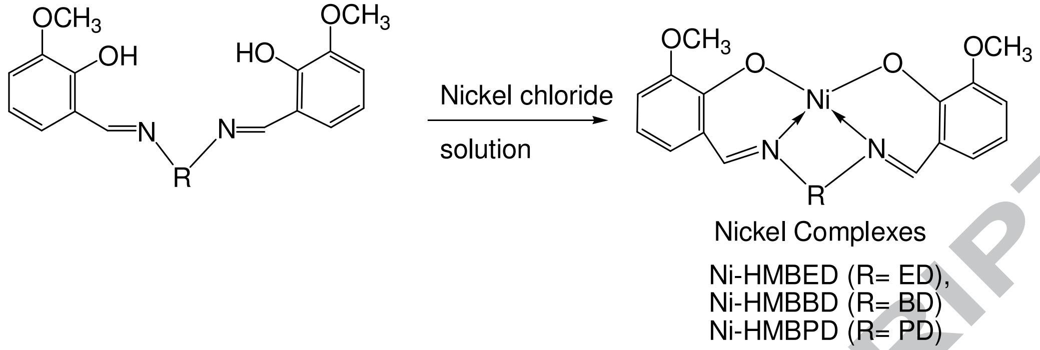
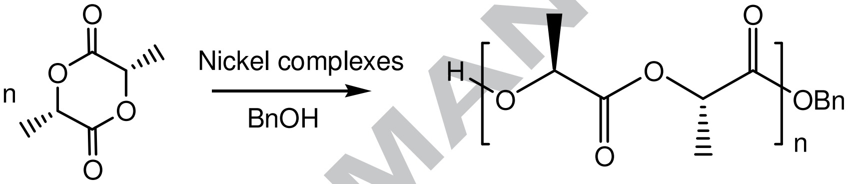
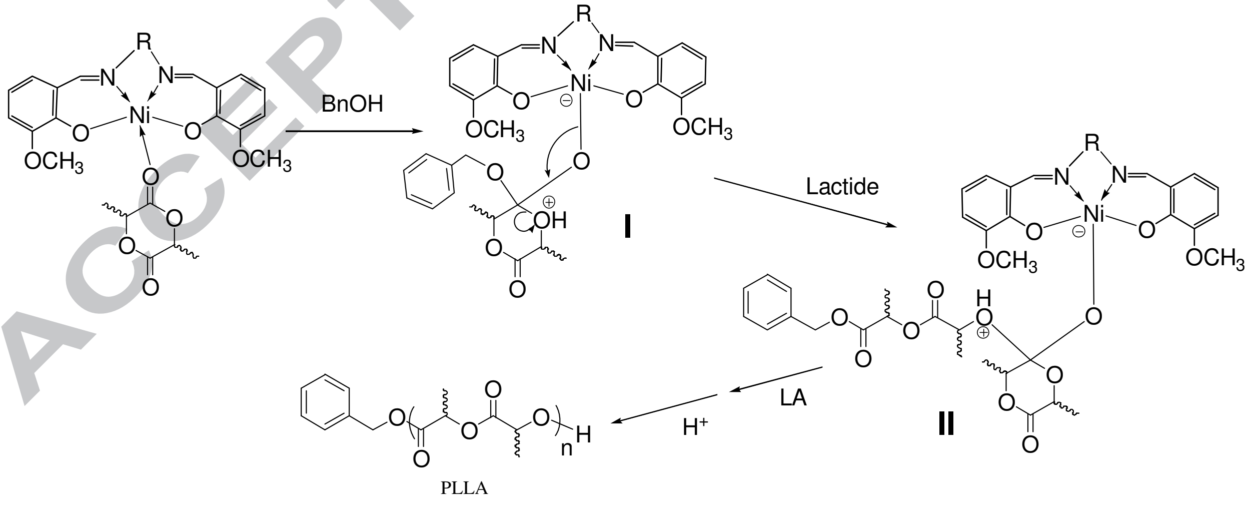


Scheme 1. Nickel complexes



Scheme 2. ROP of lactide using the nickel complexes.



Scheme 3. Proposed mechanism for the ring opening polymerization of *L*-lactide

Table 1. ROP of *L*-lactide using the nickel complexes at 30 °C.

Entry	Complex	Parameter	Solvents		
			CH_2Cl_2	Toluene	THF
1	Ni-HMBED	Conversion(%)[a]	91.3	80.4	64.2
		M_n (Theory)[b] (g mol^{-1})	19800	17400	13900
		M_n (VPO)[c] (g mol^{-1})	22300	12200	8000
		Mn(GPC)[d]	27600	18000	14200
		PDI	1.16	1.09	1.14
2	Ni-HMBPD	Conversion(%)[a]	88.3	80.0	62.0
		M_n (Theory)[b] (g mol^{-1})	19200	17500	13500
		M_n (VPO)[c] (g mol^{-1})	21700	19500	16500
		Mn(GPC)[d]	24200	21300	18100
		PDI	1.10	1.07	1.12
3	Ni-HMBBD	Conversion(%)[a]	86.1	80.0	61.3
		M_n (Theory)[b] (g mol^{-1})	18700	17400	13400
		M_n (VPO)[c] (g mol^{-1})	21300	19200	16100
		Mn(GPC)[d]	23000	21100	17400
		PDI	1.11	1.17	1.08

Conditions: [*L*-LA] $_0$ = 20 mmol, room temperature, reaction time 24 h, $[M]_0/[Ni]/[BnOH]$ = 150/1/1

[a] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100].

[b] Calculated by $[([LA]_0/[BnOH]) \times 144.13 \times \text{conversion\%} + 108.14]$

[c] Determined by VPO.[54]

[d] Obtained from GPC analysis and calibrated by a polystyrene standard. Values are obtained from GPC times 0.58.

Table 2. ROP of *L*-lactide by the nickel complexes.

Entry	Complex	[*L*-LA]$_0$ / [Ni or Schiff base] /[BnOH]	Time (h)	Conversion^a (%)	M_n (Theory)^b (g mol^{-1})	M_n (VPO)^c (g mol^{-1})	M_n (GPC)^e (g mol^{-1})	PDI^e
1	HMBED	100:1:0	24	-	-	-	-	-
2	HMBPD	100:1:0	24	-	-	-	-	-
3	HMBBD	100:1:0	24	-	-	-	-	-
4	$NiCl_2$	100:1:0	24	-	-	-	-	-
5	Ni-HMBED	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}
		50:1:1	24	78.2	5700	8100	8600	1.12
		100:1:1	24	87.3	12700	15900	22100	1.12
		150:1:1	24	91.3	19800	22300	27600	1.16
		200:1:1	24	92.7	26800	30600	32800	1.10
6	Ni-HMBPD	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}
		50:1:1	24	75.1	5500	7600	8600	1.09
		100:1:1	24	85.1	12400	15300	18300	1.07
		150:1:1	24	88.3	19200	21700	24200	1.10
		200:1:1	24	91.5	26500	27600	30600	1.09
7	Ni-HMBBD	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}
		50:1:1	24	73.9	5400	7100	8000	1.12
		100:1:1	24	82.4	11900	15400	18000	1.11
		150:1:1	24	86.1	18700	21300	23000	1.11
		200:1:1	24	89.3	25800	27100	28200	1.13

Conditions: [*L*-LA]$_0$ = 20 mmol, room temperature, solvent 30 mL of CH_2Cl_2

[a] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100].

[b] Calculated by [([LA]$_0$/[BnOH]) × 144.13 × conversion% + 108.14]

[c] Determined by VPO.[54]

[d] Data not available

[e] Obtained from GPC analysis and calibrated by a polystyrene standard.

Table 3. ROP of *L*-lactide by the nickel complexes with variation of the BnOH equivalents.

Entry	Complex	[*L*-LA]$_0$ / [M]/[BnOH]	Time (h)	Conversion^a(%)	M_n (Theory)^b (g mol^{-1})	M_n (VPO)^c (g mol^{-1})	M_n (GPC)^e	M_n (NMR)^f	PDI^e
1	Ni-HMBED	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}	-^{d}
		100:1:1	24	87.3	12700	15900	22100	11200	1.12
		100:1:2	20	90.1	6600	8200	10200	8200	1.10
		100:1:4	15	92.0	3400	4600	6300	4050	1.09
2	Ni-HMBPD	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}	-^{d}
		100:1:1	24	85.1	12400	15300	18300	10000	1.07
		100:1:2	20	88.4	6500	8100	10300	7200	1.07
		100:1:4	15	90.3	3400	4000	5200	3600	1.10
3	Ni-HMBBD	100:1:0	24	<5	-^{d}	-^{d}	-^{d}	-^{d}	-^{d}
		100:1:1	24	82.4	11900	15400	18000	8800	1.11
		100:1:2	20	85.2	6200	8000	9600	6400	1.09
		100:1:4	15	89.4	3300	3800	4300	3000	1.10

Conditions: [*L*-LA]$_0$ = 20 mmol, room temperature, solvent 30 mL of CH_2Cl_2

[a] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100].

[b] Calculated by [([LA]$_0$/[BnOH]) × 144.13 × conversion% + 108.14]

[c] Determined by VPO [54]

[d] Data not available

[e] Obtained from GPC analysis and calibrated by a polystyrene standard.

[f] Obtained from ^{1}H NMR analysis

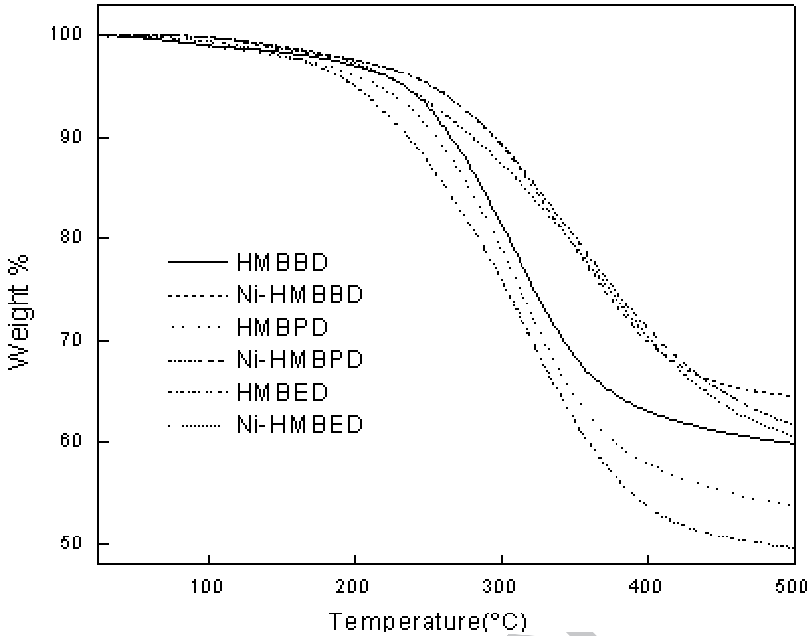


Figure 1. TGA curve of Schiff bases and their nickel complexes

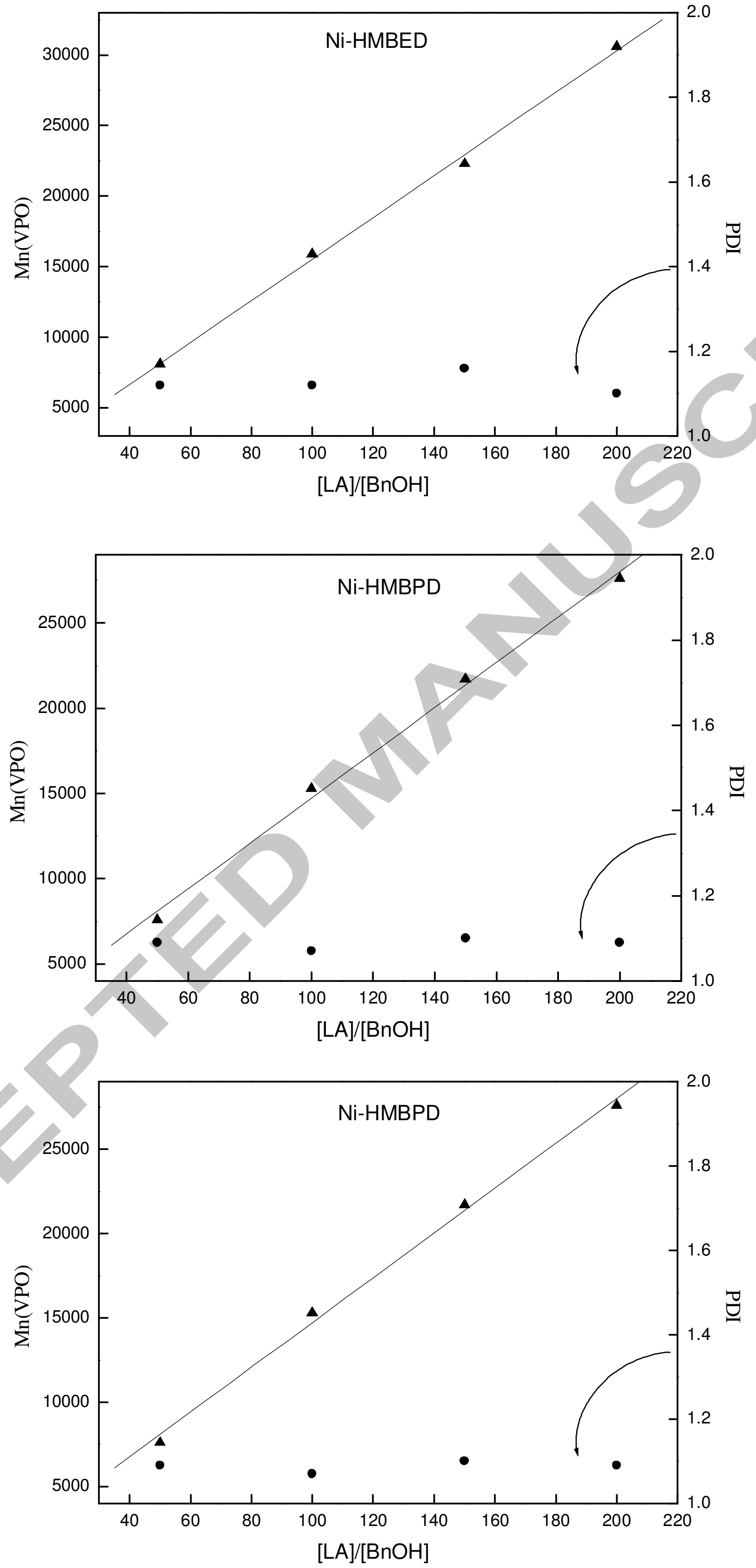


Figure 2. ROP of *L*-lactide catalyzed by the nickel complexes in CH_2Cl_2 at room temperature.

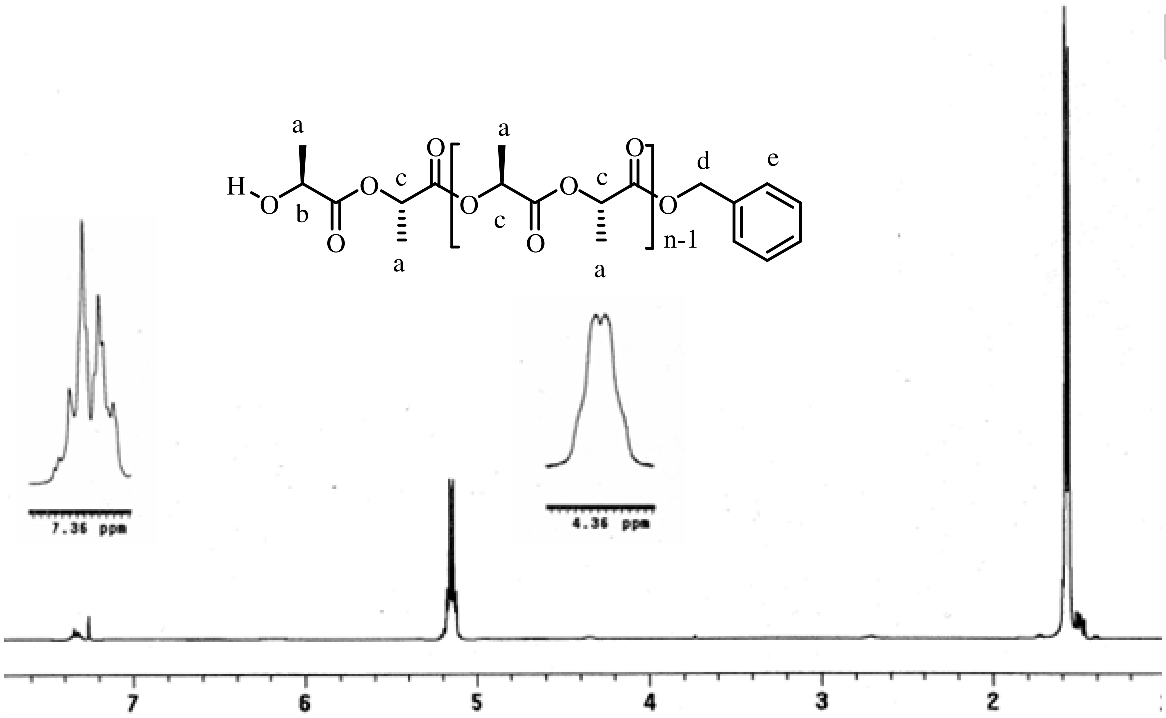
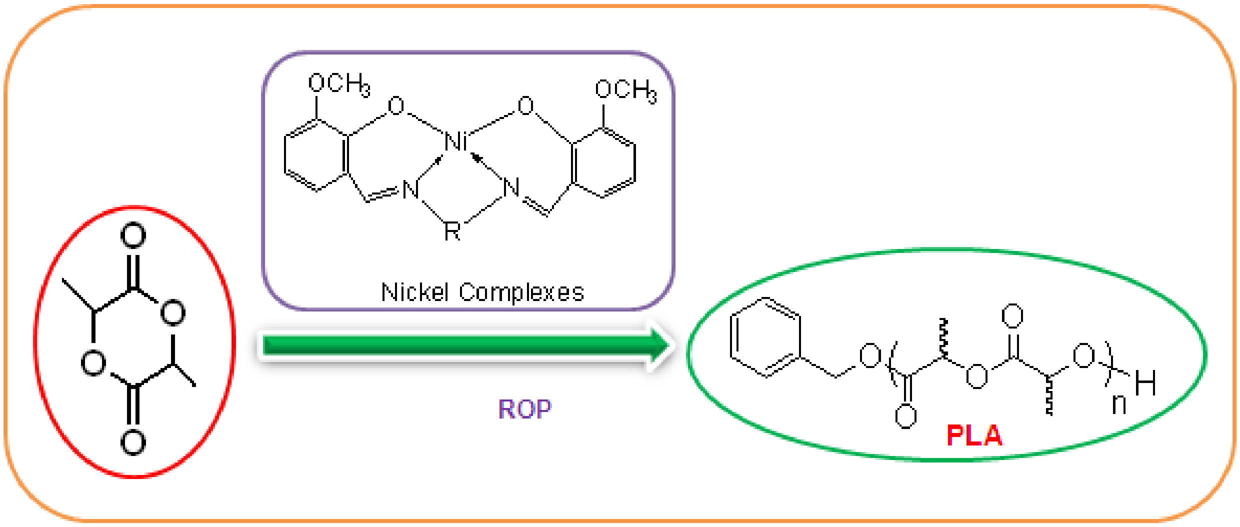


Figure 3. ^{1}H NMR spectrum of PLLA-200 (200 indicates $[LA]_0/[BnOH] = 200$) catalyzed by Ni-HMBED

Graphical Abstract Image



Short Abstract

Salen-type Schiff-base ligands and their nickel complexes have been synthesized and fully characterized. All of the nickel complexes were tested for the ring-opening polymerization of lactide. The PLA produced by the ROP of *L*-lactide shows a moderate molecular weight with a narrow PDI range.