Catalytic ring-opening polymerization of L-lactide by titanium biphenoxy-alkoxide initiators

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Abstract

Six different titanium biphenolate complexes were synthesized and investigated as initiators for the ring opening polymerization of L-lactide in the bulk phase but typically below the degradation temperature of the monomer. All the titanium complexes are effective in forming polylactide with good conversions. The nature and steric bulk of the phenolic ligands coordinated to the central titanium greatly influence polymer properties. In all cases the PLA obtained display low molecular weights and narrow disperisities. Both ^{1}H and ^{13}C NMR spectra indicate the polymers to be essentially isotactic in nature. High crystallinity and controlled morphology of polylactides are uniquely different compared to conventional high molecular weight PLA obtained with tin based initiator.
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1. Introduction

One of the most extensively studied biodegradable polymers over the past two decades has been polylactide (PLA), which can be commercially obtained from renewable materials, such as corn, beet, dairy products, etc. [1]. The biocompatibility of PLA has found increasing application in medical, packaging, film and as thermoplastics [2]. These degradable polyesters can be synthesized either by polycondensation of lactic acid or from ring-opening polymerization (ROP) of the cyclic dimer, namely lactide [3]. The polycondensation route has inherent drawbacks like poor kinetic control and removal of liberated byproduct water which induces reverse reaction resulting in the hydrolysis of the ester linkages of polymer. Moreover, commercially prepared L-lactic acid by fermentation contains about 10 wt.% water (w/w) necessitating the use of water-tolerant catalysts for dehydropolymerization. Consequently, there exists a need for developing other methods for preparation of these degradable polymers in a reproducible fashion. Thus, a large number of Lewis acidic catalysts have been shown to facil-

itate the ROP of lactide allowing for better control over the molecular weights and molecular weight distributions. A review of literature suggests that compounds of tin, such as stannous octoate (Sn(II)-2-ethylhexanoate) and its derivatives are the most extensively studied for this reaction [4]. Other catalysts, such as aliphatic alkoxides of Al [5], Zn [6], Mg [7], carboxylates of Fe(II) [8], aryl oxides of lanthanides [9,10] and more recently examples of actinide complexes containing cyclopentadienyl ligand [11] have all been shown to promote polymerization of lactide but are relatively less effective. A common conclusion from these studies is that different catalysts lead to different kinds of PLAs with significant differences in molecular weights and MWD. One of the reasons for this is the effect of ester interchange and racemization that occurs under the polymerization conditions employed. Though a large number of metal alkoxide based initiators are capable of polymerizing LA, the search for new-catalysts remains actively pursued to generate polylactide with well-defined stereochemistry and precise control over physical properties for end use.

In view of the above it is rather surprising to note that application of initiators based on titanium in ROP of lactide is rather scanty though they have been demonstrated as potential catalysts for α-olefin polymerization [12]. Homogeneous catalysts based on titanium, such as $TiCl_x(OPr^i)_{4-x}$ [13], chalcogen-bridged

bis-aryloxides of Ti [14], titanatranes [15] and amino-bisphenolate derivatives of titanium [16] have recently been investigated as catalysts for bulk and solution phase ring opening polymerization of *rac*, D,L- and L-lactide. Polymer properties varied widely depending on the ligating environment and method of polymerization. As part of our current interest in the application biphenolate compounds in ethylene polymerization it was found that Ti-BINOLates and analogues exhibited unique activity in producing polyethylene with controlled molecular weights and microstructure [17,18]. The versatility associated with these Ti-compounds and their ability to promote controlled olefin polymerization prompted us to explore them further as initiators for L-lactide polymerization. In the present work, we describe our results on the activity of alkoxy-biphenolate family of titanium catalysts and examine in detail the properties of polylactides obtained *via* ROP. The strategy employed is based on selecting catalysts of the form $L_nTi(OR)_{n-4}$, where OR is the alkoxide that is readily capable of propagating the polymerization and L_n is an end capped bulky biphenol.

2. Experimental

2.1. Materials

L-Lactide was synthesized from commercial L-(+)lactic acid (>99%, Fluka) and was purified by repeated crystallization and drying under vaccum at 70–75 °C for 2–3 h. The optical purity of the monomer was >98%.

2.2. Catalyst preparation

The catalysts **1–5** were prepared by an alcohol exchange method by reacting $Ti(OPr^i)_4$ and the corresponding biphenols. The synthetic protocol and details of characterization have been described in a previous publication [17,18]. The pre-dried complexes were then used in the melt and solution polymerization of lactide as described below.

2.3. Polymerization

LA bulk polymerization was carried out by charging 1 g of LA and then the appropriate amount of catalyst precursor to 50 ml Schlenk flask. The flask was then immersed in the oil bath at 130 °C for specified time. The reaction was terminated by the addition of 5 ml of methanol. The precipitated polymer were dissolved in a minimum amount of methylene chloride and then excess methanol was added The resulting reprecipitated polymer was collected, washed with 3× 50 ml of methanol and dried in vacuum at 50 °C for 12 h.

2.4. Polymerization of L-LA by Sn(II)-2-ethylhexanoate

Melt polymerization was carried out at 180 °C for 1 h. After cooling the melt was dissolved in chloroform and precipitated from methanol. The dried white coloured PLA was fibrous in nature.

Solution polymerizations of LA were carried out in a 50 ml Schlenk flask using toluene as a solvent.

2.5. Measurements

Elemental analyses was carried out on a Perkin-Elmer Model 2400 instrument. Titanium content in catalysts was determined gravimetrically as TiO_2. A Perkin-Elmer FT-IR spectrometer model Spectrum BX was used to obtain the IR spectra of samples pressed into KBr pellets over 4000–400 cm^{-1} range. The ^1H and ^{13}C NMR spectrum of polylactides was recorded in CDCl$_3$ and DMSO-d_6 solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference.

Molecular weights of polymers were determined using size exclusion chromatography (SEC). The GPC analysis of the polymers was carried out using Perkin-Elmer, Series-200 chromatograph. A set of PL Gel 5 μm 10^4 Å (300 mm × 7.5 mm) column was used. Tetrahydrofuran (THF) was used as the mobile phase at 30 °C. Differential scanning calorimetry was performed under a continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 50 to 220 °C at a scan rate of 10 °C/min. Indium was used to perform the calibration. TGA/DTA of catalysts were recorded in air (heating rate 10 °C/min) from ambient to 600 °C on a TA Instrument (Universal V2). X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled Cu Kα radiation (λ = 1.5406 Å, generator voltage = 45 kV and current = 40 μA) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately 400 μm thick and were scanned into 2θ ranges from 13° to 45° at a rate 1°/min. Measurements were recorded at steps of 0.02°. Scanning electron micrographs of powdered polymer samples were taken on a JEOL JFC 1100 instrument ion sputter water. They were observed in JEOL 5600 CV Scanning Electron Microscope in Hv mode with operating voltage of 20 kV.

3. Results and discussion

3.1. Synthesis of titanium catalysts

The catalysts chosen for the lactide polymerization contain isopropoxide groups along with bulky biphenols attached to titanium. Thus, the complexes were obtained by direct reaction of $Ti(OPr^i)_4$ or $Ti(OPr^i)_3Cl$ and the corresponding phenol as outlined in Scheme 1.

The liberated isopropanol was separated by repeated washing of catalyst and followed by azeotropic distillation. In order to have proper comparison of activity levels of all catalysts, the starting $Ti(OPr^i)_4$ complex was also evaluated along with catalysts **1–6**. Moreover, since it is known that polylactide properties depend to a great extent on the nature of initiator a known lactide polymerization catalyst Sn(II) octoate was also included as reference to ensure reliable comparison of data.

3.2. Bulk polymerization

The different (isopropoxy)-titanium biphenolates **1–6** were employed as catalysts to initiate ring opening polymerization of
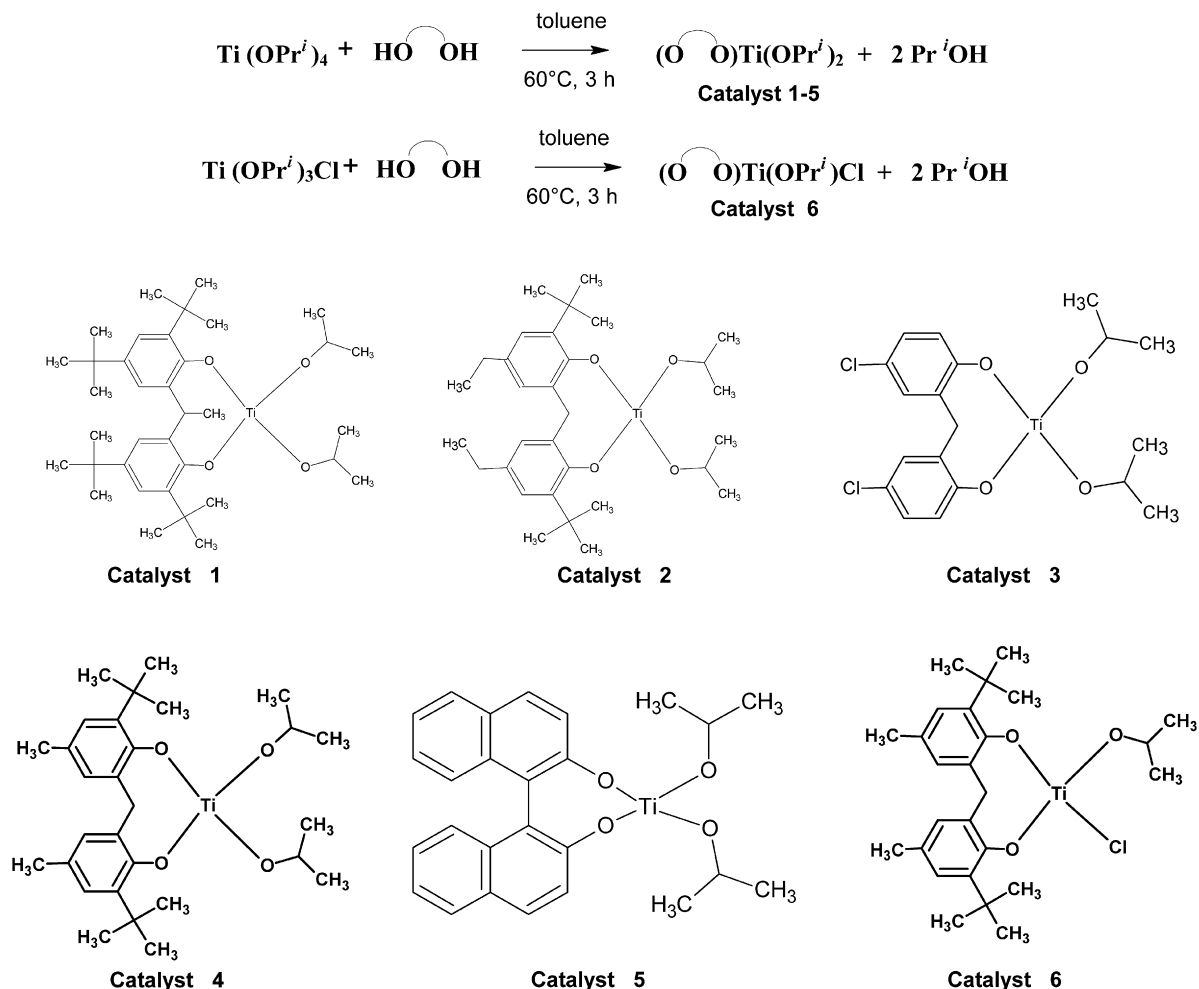
Scheme 1. Synthesis of Ti catalysts.

neat L-lactide by carefully heating the thoroughly mixed components under inert atmosphere at 130 °C. The initiation of lactide polymerization was visually indicated when the temperature of the mixture reached 110 °C accompanied by a distinct colour change of the melt to dark-brown viscous mass in case of titanium catalysts. For the Sn(II) catalyst the colour change was not apparent but a change of viscosity was clearly noticed.

For the titanium catalyst containing biphenols simple precipitation of the polylactide powder from methanolic solution lead to polymers having light brown to pale yellow colouration. Repeated reprecipitation was found essential to decolourize the polymers to acceptable levels for further characterization. We aimed at unraveling the effect of bulky biphenolate ligand and the nature of substituent on the ROP of L-lactides. All the Ti-catalysts gave polymers which were very fine powders. In Table 1 is compiled the results of polymerization of L-lactide with different catalysts.

The observed molecular weights based on GPC with catalysts **1–6** are below 1×10^4. This is in sharp contrast to very high molecular weights typically obtainable by tin compounds. An increase of polymerization temperature from 130 to 180 °C while maintaining other parameters same showed a marked increase of polymer molecular weight as is evident (Table 1,

entries 1 and 8) for catalyst **1**. Similarly the reaction time also showed a positive effect on overall conversion of lactide (Table 1, entry 7). On the other hand, the influence of biphenolate ligand or the linkage/substituent on the phenyl ring did not show any specific trend on molecular weights of polymer. However, the narrow molecular weight distribution in most cases suggest the presence of single site catalyst. Nevertheless the low molecular weights and higher crystallinity are rather unique to these mixed alkoxy-biphenolate catalysts [19]. Interestingly the reference polylactide based on Sn(II) octoate showed presence of higher contents of amorphous materials (Table 1, entry 12). The comparison of variation in PLA properties in presence of titanium isopropoxide initiator under different reaction conditions is shown in Table 2. The results indicate that the Ti(OPr^i)$_4$ acts as a living ring opening polymerization catalyst. Alkoxy titanium(IV) complexes containing chelating tetradentate dianionic phenolate ligands [Ti(ONNO)(OPr^i)$_2$] exhibited lower activity requiring extended reaction times, typically 20–50 h. Similarly alkoxy-titanatrane catalysts of the type Ti(OOON)(OPr^i)$_2$ displayed higher M_w/M_n values (1.8–2.2) than the present biphenolate based complexes [14,15]. These results lead us to infer that control of polymerization is much better with bidentate biphenolate type of ligands as revealed by PDI between 1.3 and 1.6.

Table 1
L-Lactide polymerization with titanium biphenoxy-alkoxide initiators[a]

Entry	Catalyst	Time (h)	Temperature (°C)	Yield (%)	M_w	M_n	PD	T_m (°C)	X_c (%) XRD	DSC
1	1	2	130	96	6,760	4,400	1.5	130	51	49
2[a]	5	2	130	95	9,170	5,500	1.5	130	47	43
3[a]	2	2	130	87	6,300	3,990	1.6	126	50	44
4[a]	4	2	130	81	6,220	3,930	1.5	130	53	50
5[a]	3	2	130	67	–	–	–	–	–	–
6[a]	6	2	130	33	4,670	3,170	1.5	–	–	–
7	1	8	130	96	8,560	5,035	1.7	–	–	–
8[a]	1	2	180	95	14,470	8,330	1.7	133	52	45
9[b]	1	12	80	00	–	–	–	–	–	–
10[b]	2	12	80	00	–	–	–	–	–	–
11[a]	Ti(OPr^i)$_4$	2	130	94	6,300	4,150	1.5	131	52	–
12[b]	Sn (octoate)	1	180	98	108,000	52,110	2.1	–	–	–
13[c]	Ti(OPr^i)$_4$	12	200	–	19,800	10,400	1.9	144	–	4.3

[a] [LA]/[Ti] = 300.
[b] [LA]/[Ti] = 1000.
[c] Ref. [26].

Table 2
Comparison of polymer properties derived from Ti(OPr^i)$_4$

Entry	Catalyst	Time (h)	Temp (°C)	Yield (%)	M_w	M_n	PD	T_m (°C)	X_c (%) XRD	DSC
1	Ti(OPr^i)$_4$	2	130	94	6,300	4,150	1.5	131	52	–
2[a]	Ti(OPr^i)$_4$	2	130	75	35,700	16,000	2.2	–	–	–
3[a]	Ti(OPr^i)$_4$	0.5	130	20	–	–	–	–	–	–
4[b]	Ti(OPr^i)$_4$	12	180	–	12,000	6,600	1.8	151	–	49

[a] Ref. [13].
[b] Ref. [26].

3.3. Solution polymerization

Our efforts to synthesize polylactide by reacting the monomer and the catalysts **1–6** in toluene solutions were unsuccessful (Table 1, entries 9–10) under the conditions employed (80–100 °C). In all cases the initial light-yellow/orange colour of the solution remained unchanged. It is possible that the formation of dimeric or higher agglomerates involving titanium isopropoxy bridges may preclude the insertion/interaction of the monomer and facilitate propagation. This aspect was not investigated further.

3.4. Polymer characterization

Polylactides obtained with titanium biphenoxy isoproxide catalysts at 130 °C generally showed lower molecular mass as revealed by GPC (Figs. 1 and 2). At the given temperature, regardless of the type of chelating biphenol attached to titanium
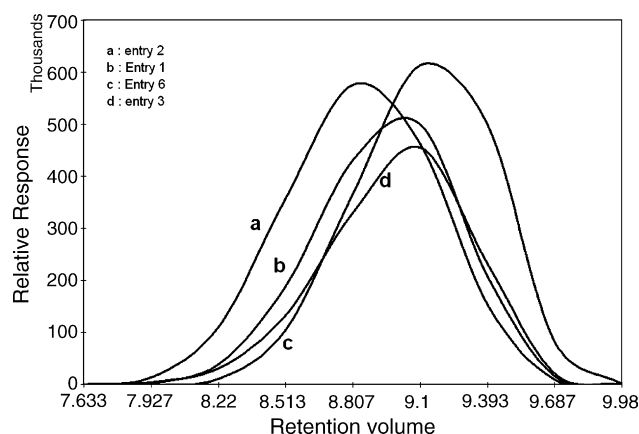

Fig. 1. GPC profiles of L-PLA: Table 1, (a) entry 2, (b) entry 1, (c) entry 6 and (d) entry 3.
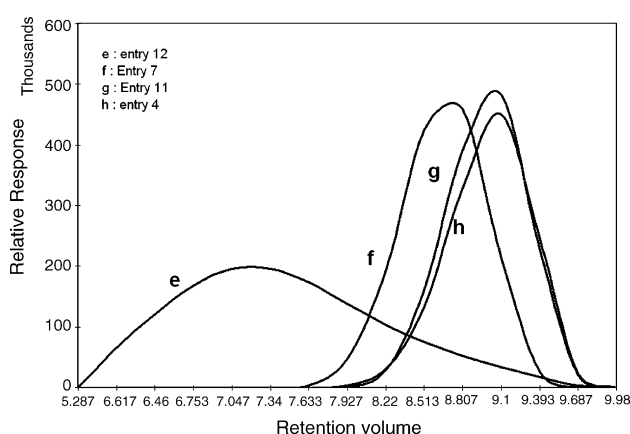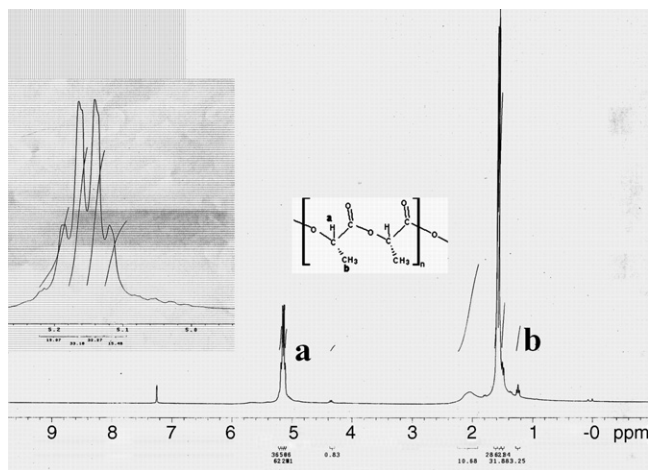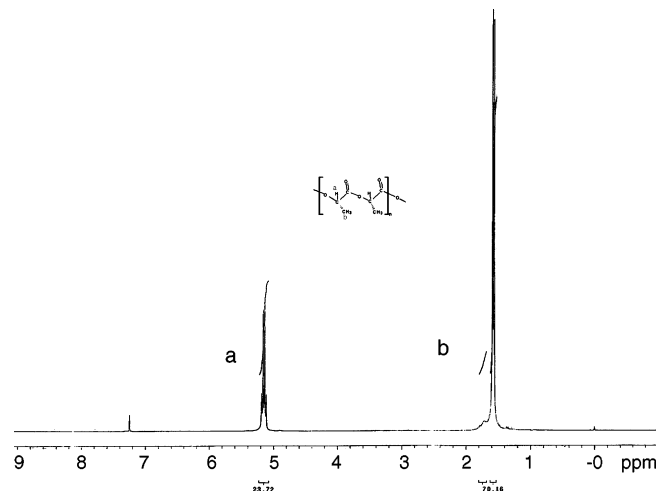

Fig. 2. GPC profiles of L-PLA: Table 1, (e) entry 12, (f) entry 7, (g) entry 11 and (h) entry 4.

Fig. 3. ^{1}H NMR of L-PLA: Table 1, entry 1.

Fig. 4. ^{1}H NMR of L-PLA: Table 1, entry 12.

the variations in MWD are only marginal and the peak M_w values centered around 0.6×10^4. Increase in reaction temperature for e.g., in case of **1** lead to an increase in M_w to about 1.4×10^4 though the MWD showed only a slight increase. The polylactide prepared by Sn(II) complex displays M_w in the range of 1.1×10^5, but PDI values are some what higher at 2.1.

Homonuclear decoupled ^{1}H NMR as well as ^{13}C NMR spectrum of the polylactides were recorded to elucidate the microstructure of both the low molecular and high molecular weight polymers synthesized using the Ti as well as the Sn catalyst. Depending on the stereochemical configuration three possible polymer types *viz.* isotactic, heterotactic or syndiotactic can be distinguished by the peak positions and nature of methine and methyl resonances in the spectra [4b]. The ^{1}H NMR spectrum of PLA in (Figs. 3 and 4) reveals only two major sets of signals, namely the well resolved quartet of CH protons cen-

tered at $\delta \sim 5.1$ ppm and doublet for CH$_3$ protons at $\delta \sim 1.2$ ppm [20]. Such an absorption pattern is indicative of isotactic nature (-SSSS or -SSRR-stereosequence) of PLA. In the ^{13}C NMR spectrum (Figs. 5 and 6), the peak appearing at ~ 169.7 ppm is due to the ester carbonyl group but there was no peak due to the free carboxylic end groups in the low field region. In the high field spectrum methine and methyl resonances appear at ~ 69.4 ppm and 17.3 ppm, respectively [21]. The pattern is nearly identical for both the Ti as well as Sn(II) initiators indicating that the same stereochemical sequence is present in the polymers derived from these catalysts, though the molecular weights differ widely. The absence of carboxylic resonance may indicate possibility of formation of macrocyclic oligomers. However, the proportion of this lactide may be minimum as the M_n values obtained by GPC are generally well above 0.5×10^4. Moreover, cyclization would require extensive intramolecular
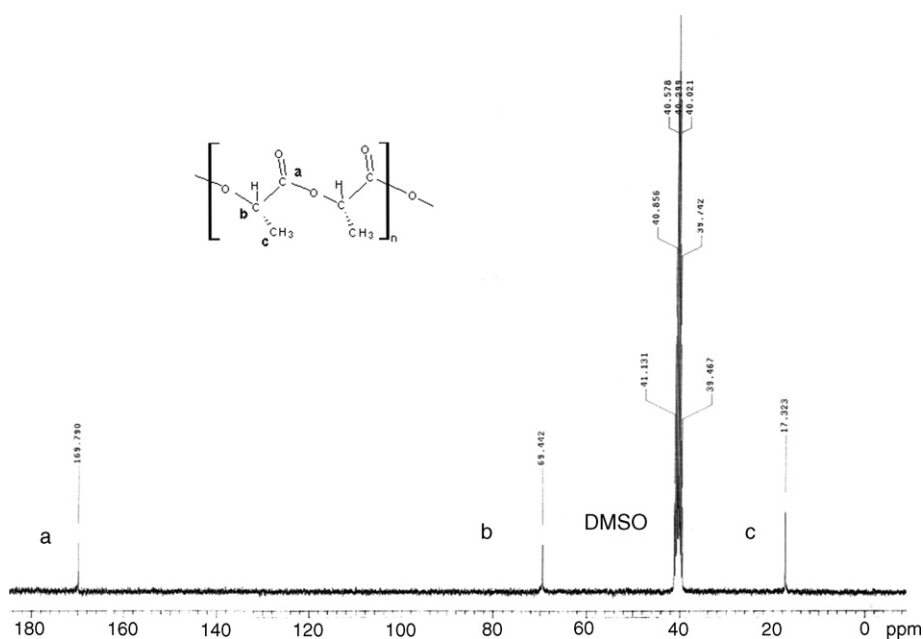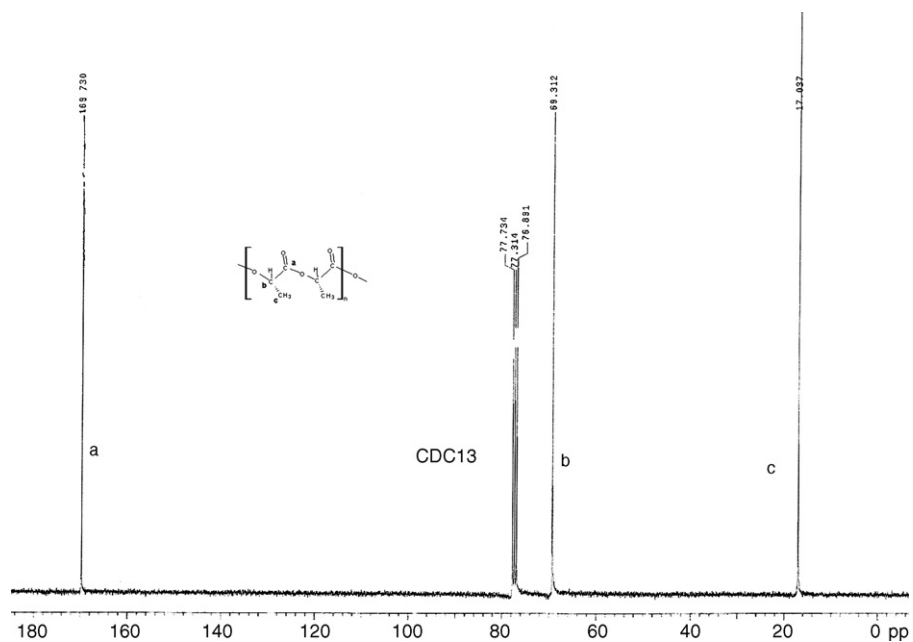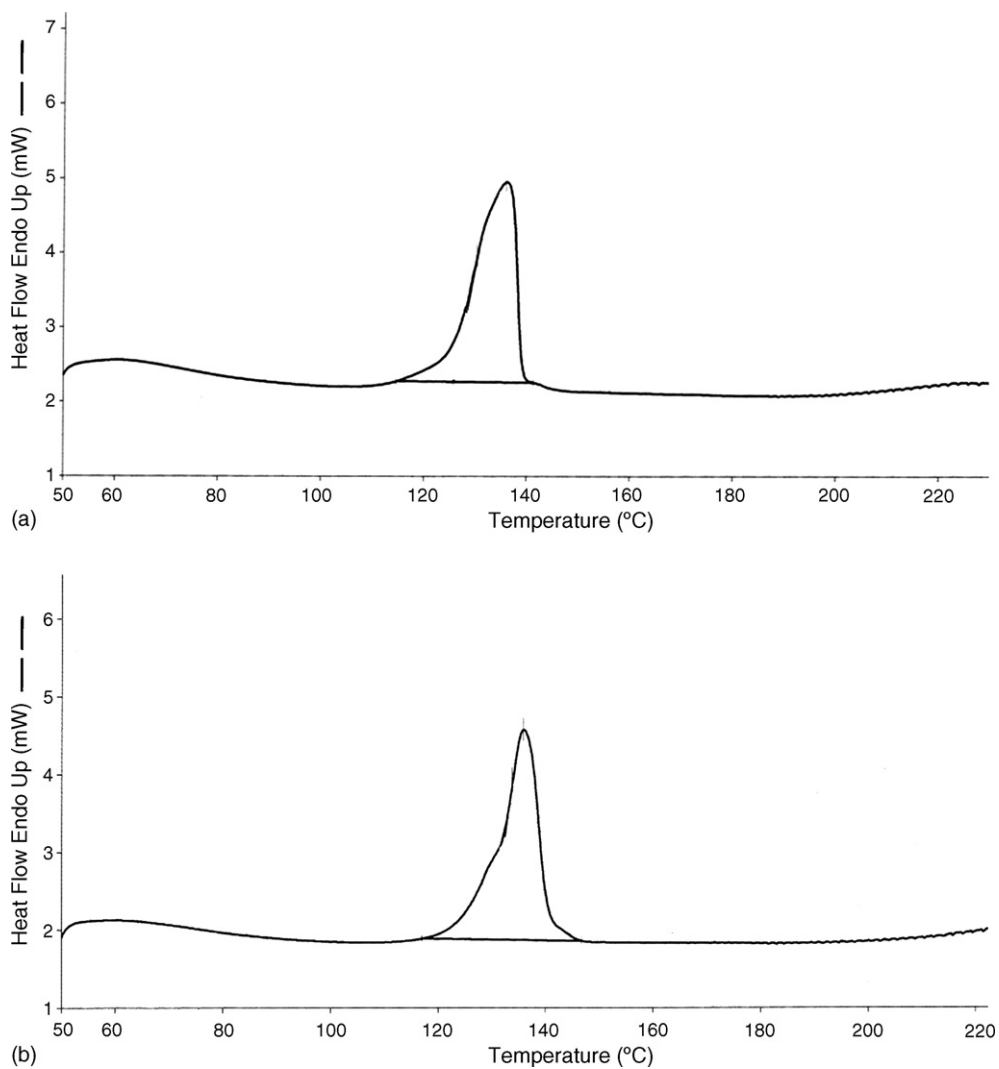

Fig. 5. ^{13}C NMR of L-PLA: Table 1, entry 1.

Fig. 6. ^{13}C NMR of L-PLA: Table 1, entry 12.

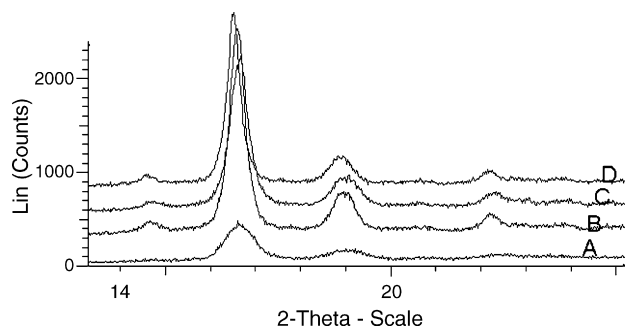Fig. 7. Representative DSC of L-PLA: Table 1, (a) 1 and (b) 3.

Fig. 8. XRD of L-PLA: Table 1, (A) entry 12, (B) entry 1, (C) entry 2 and (D) entry 3.

transesterification involving long post-polymerization periods. Similar phenomena have been noted earlier for ROP of cyclic esters by other initiators [22,23]. Since polymerization is likely to proceed *via* coordination—insertion mechanism it is necessary to check for possible end groups in the isolated polymer. Weak signals due to isopropoxy methyl groups were noticed at $\delta \sim 1$ ppm [20] consistent with the above polymerization process. However, resonance due to hydroxy protons were not easy to assign. We believe that one of the ester end groups of PLA may be strongly bound to Ti-catalyst residues. Absence of any other signals in ^{13}C NMR also suggests that effects of trans-esterification or racemization may be insignificant [4a,24,25].

The semi-crystalline nature of all the polylactides was confirmed by percentage crystallinity obtained by the endothermic peak in the DSC (Fig. 7). In all the PLAs prepared by the Ti-catalysts X_c values are around 50% which is by far the

highest than any of the previously achieved by titanium alkoxide based initiators [26]. The higher crystallinity (>40%) of PLAs in all cases resulted in no glass-transition temperature (T_g) to be observed while the T_m values were in the range of 125–138 °C indicating semi crystalline nature of the polymer [13,26].

The DSC values were also consistent with the crystallinity results obtained by X-ray powder diffractogram (Fig. 8). The XRD reveal strong signals centered at $2\theta = 19°$ due to (2 2 0 plane, Bragg distance $d = 4.7$ Å) and another at $2\theta = 16.6°$ (2 0 0 plane, Bragg distance $d = 5.3$ Å). All these peaks correspond to the α form while the β form was not observed suggesting that the L-PLA exists in a single phase. Low intensity crystalline peaks (α form) were also observed at 14.6° and 22.3° in case of PLA synthesized by Ti complexes (Fig. 8B–D) whereas they are less pronounced in case of Sn(II) initiator (Fig. 8A) [27]. X_c values obtained for PLA derived from Sn(II) octoate by DSC and XRD were around 35%. These variations are reflective of the subtle differences in Lewis acidic nature of Ti and Sn centers and their ligand environment. The scanning electron micrographs of PLAs (Fig. 9) reveal the polymer derived from Ti-catalysts to consist of loosely bound particles with smooth surface. In the case of the high molecular weight PLA obtained by Sn(II) catalyst the particles are less smooth but are seen as long strands attached to one another.

It is thus possible to tailor the catalyst in order to obtain PLAs with desired morphological features for end application. In the present PLAs prepared by Ti-biphenolate catalysts the average particle size was between 100 and 200 nm of 'as-synthesized' polymer.
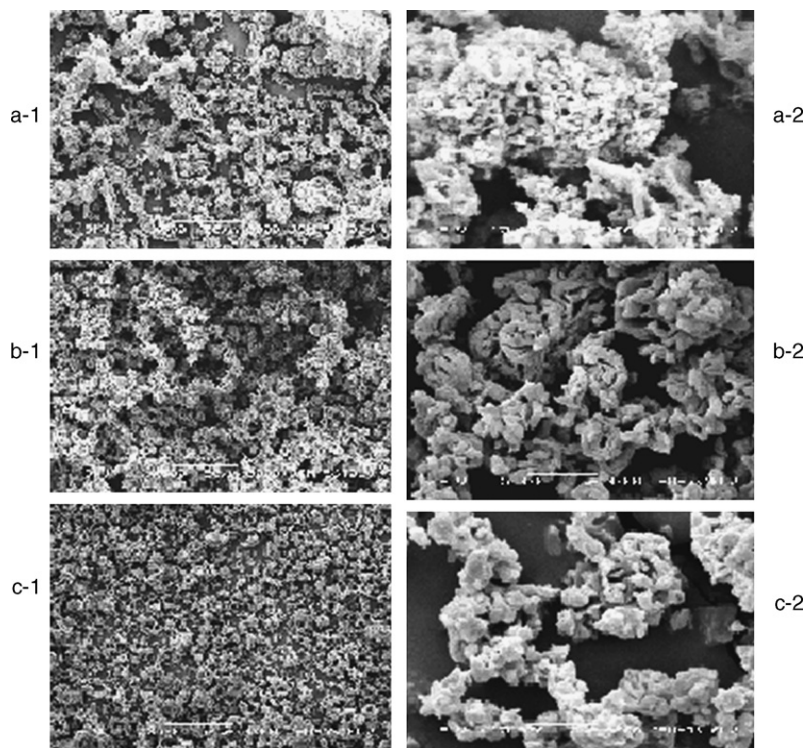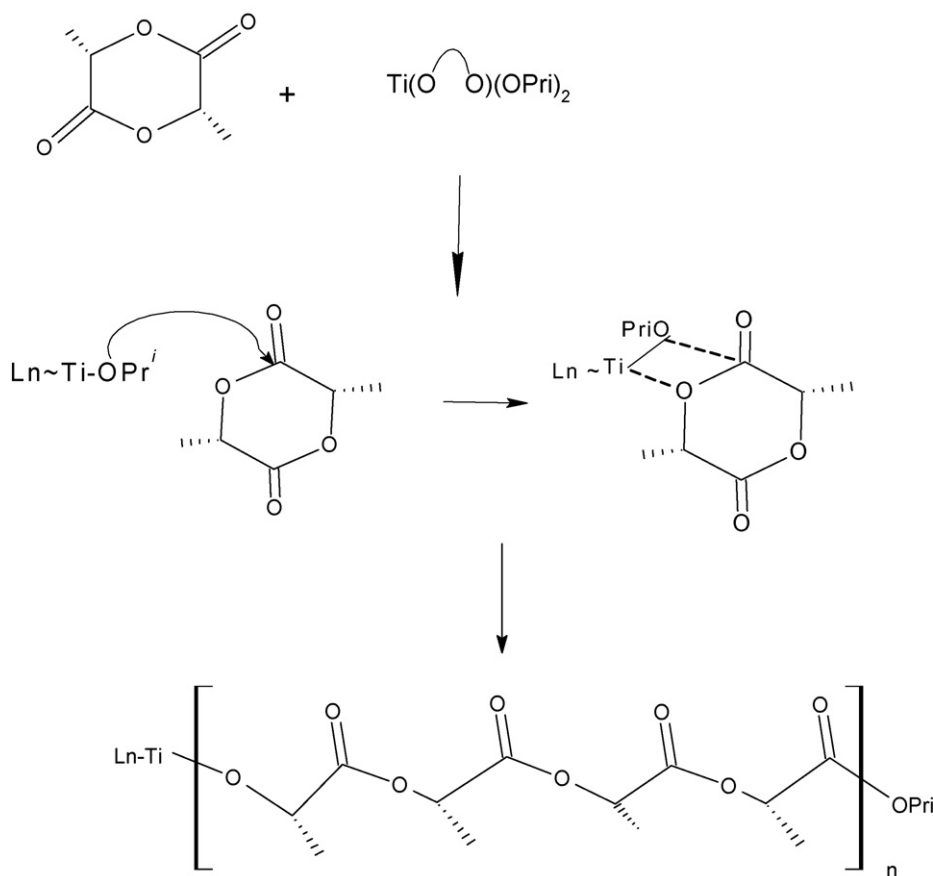

Fig. 9. SEM of L-PLA: Table 1, (a-1) entry 12 (500×), (a-2) entry 12 (5000×), (b-1) entry 7 (500×), (b-2) entry 7 (5000×), (c-1) entry 1 (500×) and (c-2) entry 1 (5000×).

Scheme 2. Proposed mechanism for ROP.

3.5. Mechanistic consideration

The NMR spectral profiles of PLAs lead us to speculate on the possible mechanistic pathway responsible for the polymerization of L-lactide. Initiation and propagation of isopropoxide catalyzed ROP was clearly evident but the termination may occur either by end capped Ti-biphenolate rests or by formation of cyclic oligomers [3,28]. Some of the key steps involved are outlined below (Scheme 2), which assumes an insertion–coordination pathway process as in the case of many other Lewis acidic metal alkoxide based initiators [29].

4. Conclusion

Well-defined biphenoxy-titanium alkoxide complexes were synthesized following a standard alcohol exchange protocol. All these metal complexes were found to be active in the melt polymerization of cyclic ester such as L-lactide while the catalytic activity was found to be strongly dependent on the reaction temperature and also on the duration of polymerization. Preliminary experiments show that higher reaction temperature favour the formation of high molar mass polymers and also improves the monomer conversion. The substituent effects on the biphenolate ligand was less pronounced in terms of overall productivity but the nature of Lewis acidic centre appears to contribute towards formation of highly crystalline polylactide albeit with very low

molecular weights. Absence of intermolecular transesterification during polymerization and the possibility of synthesizing PLAs having particle size close to the nano-region using novel titanium based initiators holds promise for specific end applications.

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