Chapter 5

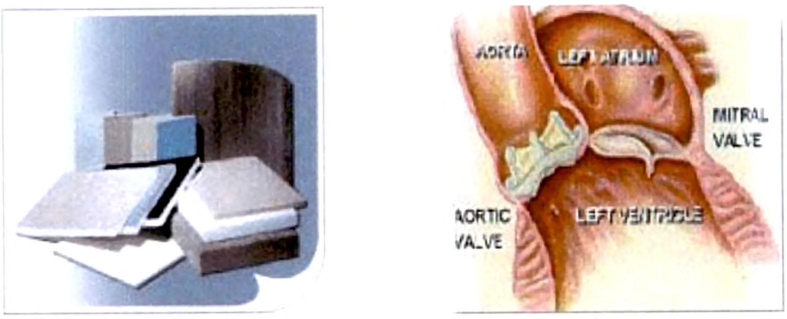
Ring Opening Polymerization of Lactide

In this chapter few of the titanium biphenolate catalysts that were studied for ethylene polymerization in earlier chapters have been examined as Lewis acidic initiators for Ring Opening Polymerization (ROP) of *l*-lactide.

5.1 Introduction

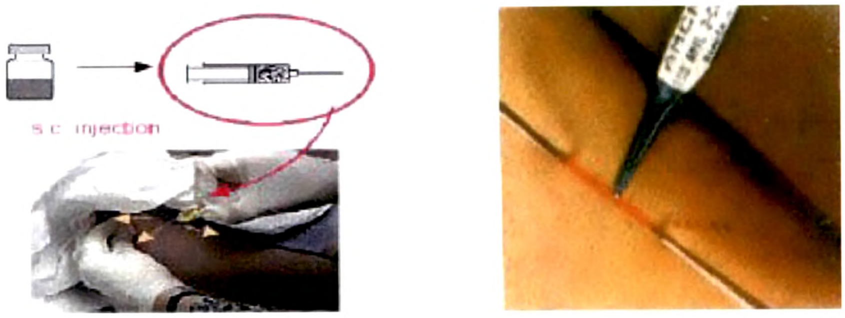
Synthetic petrochemical-based polymers have had a tremendous industrial impact since the 1940s. Convenience and safety, low price and good aesthetic qualities are the most important factors determining rapid growth in the use of plastics for manufacturing of packing materials. Recently, out of total plastic production, 41% is used in packaging industries, and 47% of them is used for the packaging of foodstuffs [1]. These are generally made from polyolefins e.g. polypropylene (PP), polyethylene (PE)), polystyrene (PS), poly(vinyl chloride) (PVC) mostly produced from fossil fuels, consumed and discarded into the environment, ending up as spontaneously nondegradable wastes. Despite the numerous advantages of these materials, two major drawbacks remain to be solved, namely, the use of non-renewable resources in their production and the ultimate fate of these large-scale commodity polymers. There are two approaches that can be used for keeping the environment free from these plastic wastes : First one is the storage of wastes at land fill sites. But because of very fast development of society, satisfactory landfill sites are also limited. On the other hand, burial of plastic wastes in landfill is a time bomb, with today's problems being shifted onto the shoulders of future generations. Another approach is the utilization, rather benign approach and can be divided into two steps : incineration and recycling. Incineration of the plastic wastes always produces a large quantity of carbon dioxide and creates global warming, and some times produces toxic gases, which again contribute to global pollution. On the other hand, recycling somehow solves the problem, even though it requires considerable expenditure of labour and energy: removal of plastics wastes, separation according to the types of plastics, washing, drying, grinding and, only then, reprocessing to final product. So this process makes packaging more expensive and the quality of the recycled plastic is also lower than that of the material produced directly by the primary manufacturer. On these backgrounds, there is an urgent need for the development of green polymeric materials that would not involve the use of toxic or noxious component in their manufacture and could be degraded in the natural environment. For these reasons, throughout the world today, the development of biodegradable materials with controlled properties has been a subject of great research challenge to the community of material scientists and engineers.

Due to their unique properties, biodegradable polymers have been considered as environmentally friendly polymers, and the spectacular advances achieved over the last 30 years in the synthesis, manufacture, and processing of these materials have given rise to a broad range of practical applications from packaging to more sophisticated biomedical devices [2].



Environmentally Friendly Insulating Material

Biomedical Polymers



Drug Delivery System (DDS)

Bioadhesive

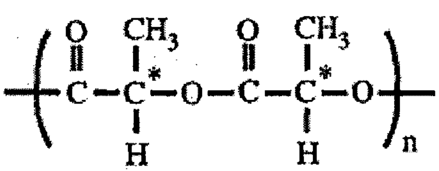
Fig. 5.1. Various application of biodegradable material

Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization. Biodegradable polymers may be made from bio-sources like corn, wood cellulose etc. or can also be synthesized by bacteria from small molecules like butyric acid or valeric acid that give polyhydroxybutyrate (PHB) and polyhydroxyvalerate (PHV)

Of the variety of biodegradable polymers known, linear aliphatic polyesters are particularly attractive and most used especially those derived from lactic acid , Glycolic acid and their copolymers [3].

Biodegradable polymers made from renewable resources like polylactides (PLA) are attracting much more attention because of more eco-friendliness from their origin as contrast to the fully petroleum-based biodegradable polymers and control of carbon dioxide (CO_2) balance after their composting. Even when burned it produces no nitrogen oxide gases and only one third of combustible heat generated by polyolefins and does not damage the incinerator and provides significant energy saving [4]. PLA has good thermal properties and biodgradibility and is readily fabricated and is thus as promosing polymer for various end use application [5] Its thermal and mechanical properties are superior to those of the other biopdegradable aliphatic polyesters such as poly(butylenes succinate), poly(3-hydroxybutyrate) and poly(ε-caprolactone) [6].

The combination of well-suited physical properties and degradable characteristics makes PLA a promising substitute for petrochemical based plastics in a wide range of single use packaging as commodity application [7]. PLA is a linear aliphatic thermoplastic polyester. Molecular structure of PLA is presented in Fig. 5.2.



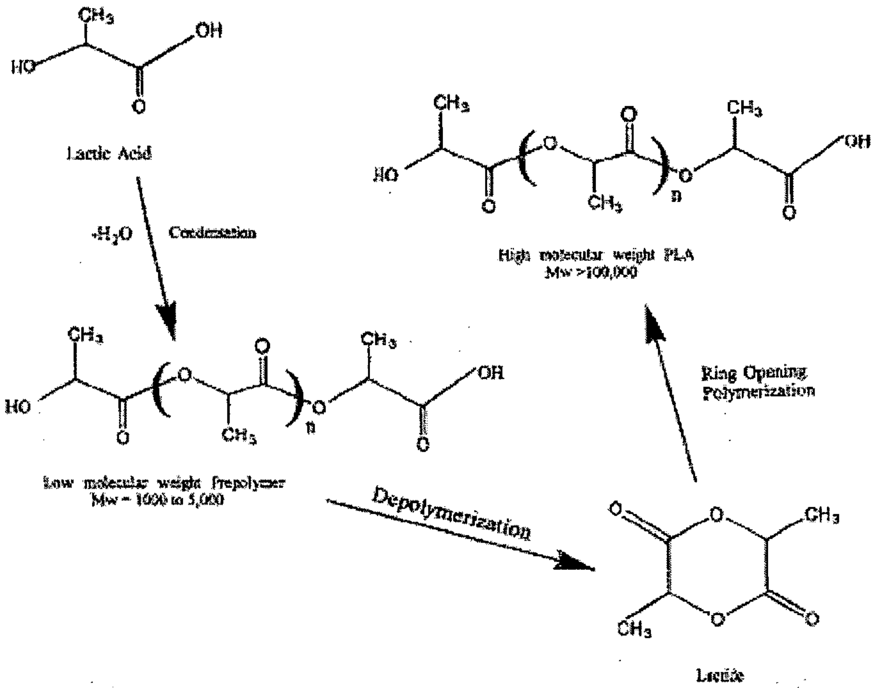
$$\left(-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C^*}}-O-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C^*}}-O- \right)_n$$

Poly(lactide)

Fig. 5.2. Molecular structure of PLA

From lactic acid there are two routes to produce PLA

1) Aqueous lactic acid solution is purified and concentrated. Then, direct condensation and cyclization reactions are performed at elevated temperature in presence of a catalyst. The condensate is removed by distillation.
2) Lactide is produced from two lactic acid molecules by cyclization and dimerization. Lactide oligomer can then be polymerized *via* ring opening to polylactide as shown in the scheme below (Scheme 5.1).



Scheme 5.1 ROP of lactide.

Since lactide is prepared from lactic acid it can be in the form of two diastereomeric forms *meso* lactide and *D, L* lactide also called *rac* lactide (Fig. 5.3)

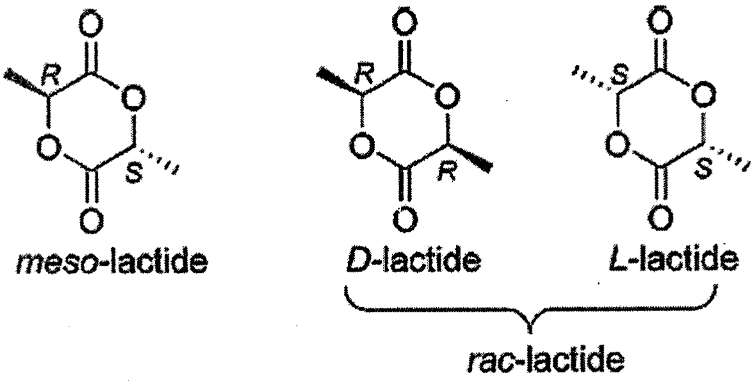


Figure 5.3. Different forms of Lactide

Enantiometrically pure monomer is also available. Polylactide can exihibit different microstructure depending on both the monomer involved and the course of polymerization reaction (Fig. 5.4)

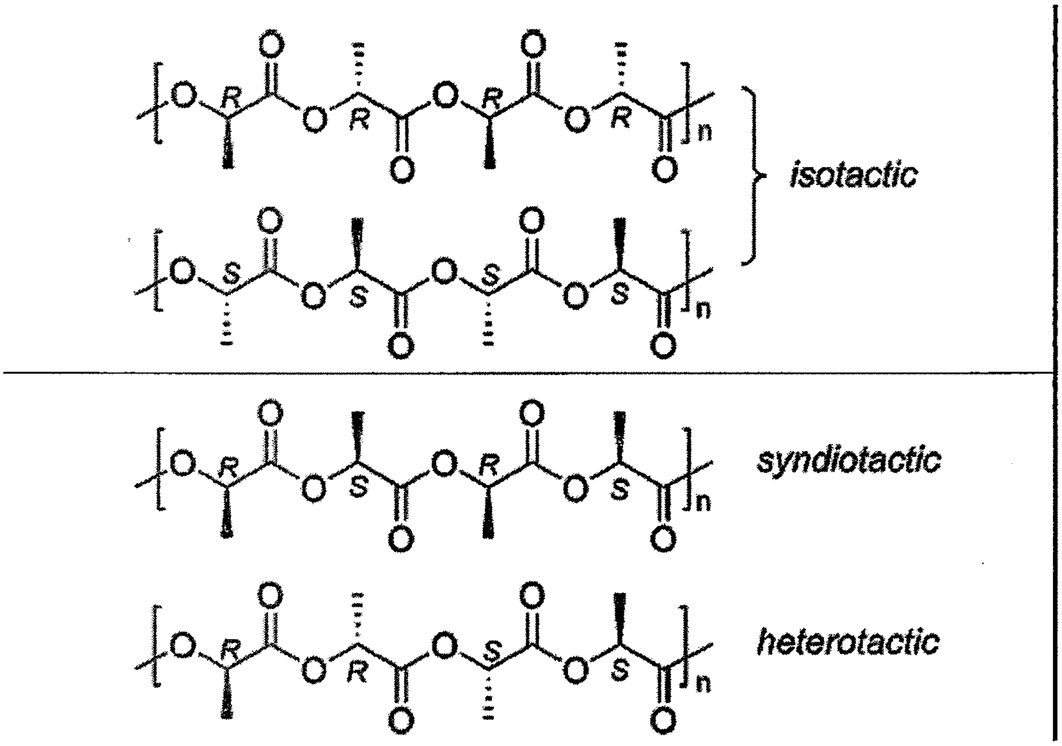
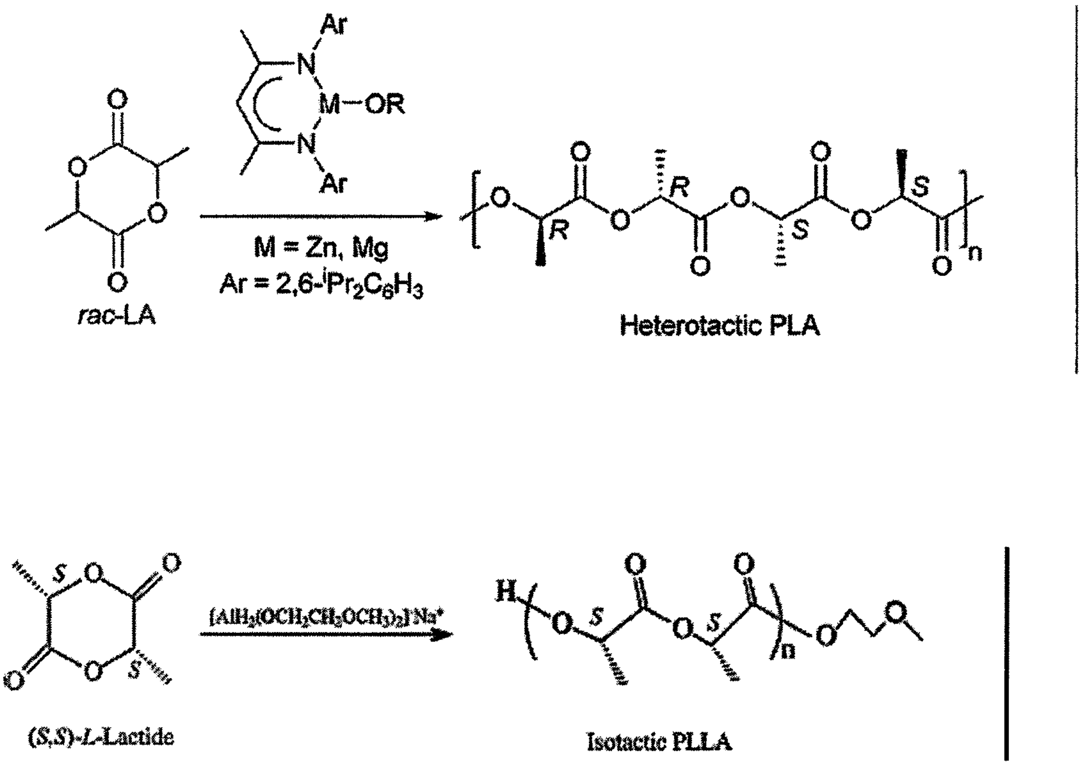


Fig. 5.4. Microstructure of polylactide

There are three types of PLAs because there are two stereoisomeric forms of lactic acid , poly (*l*-lactic acid) and poly (*d*-lactic acid) which are both semicrystalline and have identical chemical and physical properties. Poly(*d,l*-lactic acid) as racemic polymer obtained from an equimolar mixture of *d* and *l*-lactic acid is amorphous with weak mechanical properties [8] .

The polycondenastion route as shown in Scheme 5.1 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% water 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 facilitate the ROP of lactide allowing for better control over the molecular weights and molecular weight distributions (Scheme 5.2). Single site catalysts are those where enchainment of monomers occurs at metal center (M the active site) which is bound by an organic ligand (L). This ancillary ligand remain bound throughout the catalytic reaction, modifying the reactivity of the metal center. Typical single site catalyst for lactone polymerization are of the form LnMOR where the alkoxide group (OR) is capable of propagation. These complexes are of different class than typical lactone polymerization of the form $M(OR)_n$ where all the ligands are capable of forming polymer chain and no permanent ligand is present.[9].

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 [10], Zn [11], Mg [12], carboxylates of Fe(II) [13], aryloxides of lanthanides [14,15] and more recently complexes of actinide containing cyclopentadienyl ligand [16] have all been shown to promote polymerization of lactide but are relatively less effective.



Scheme 5.2. : Some typical Lewis acid catalysts for PLA synthesis.

A common conclusion from these studies is that different catalysts lead to different kinds of PLA's 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 [17]. Homogeneous catalysts based on titanium such as $TiCl_x(OPr^i)_{4-x}$ [18], chalcogen-bridged bis-aryloxides of Ti [19], titanatranes [20] and amino-bisphenolate derivatives of titanium [21] have recently been investigated as catalysts for bulk and solution phase ring opening polymerization of *rac*, *d,l* & *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 [22, 23]. 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.

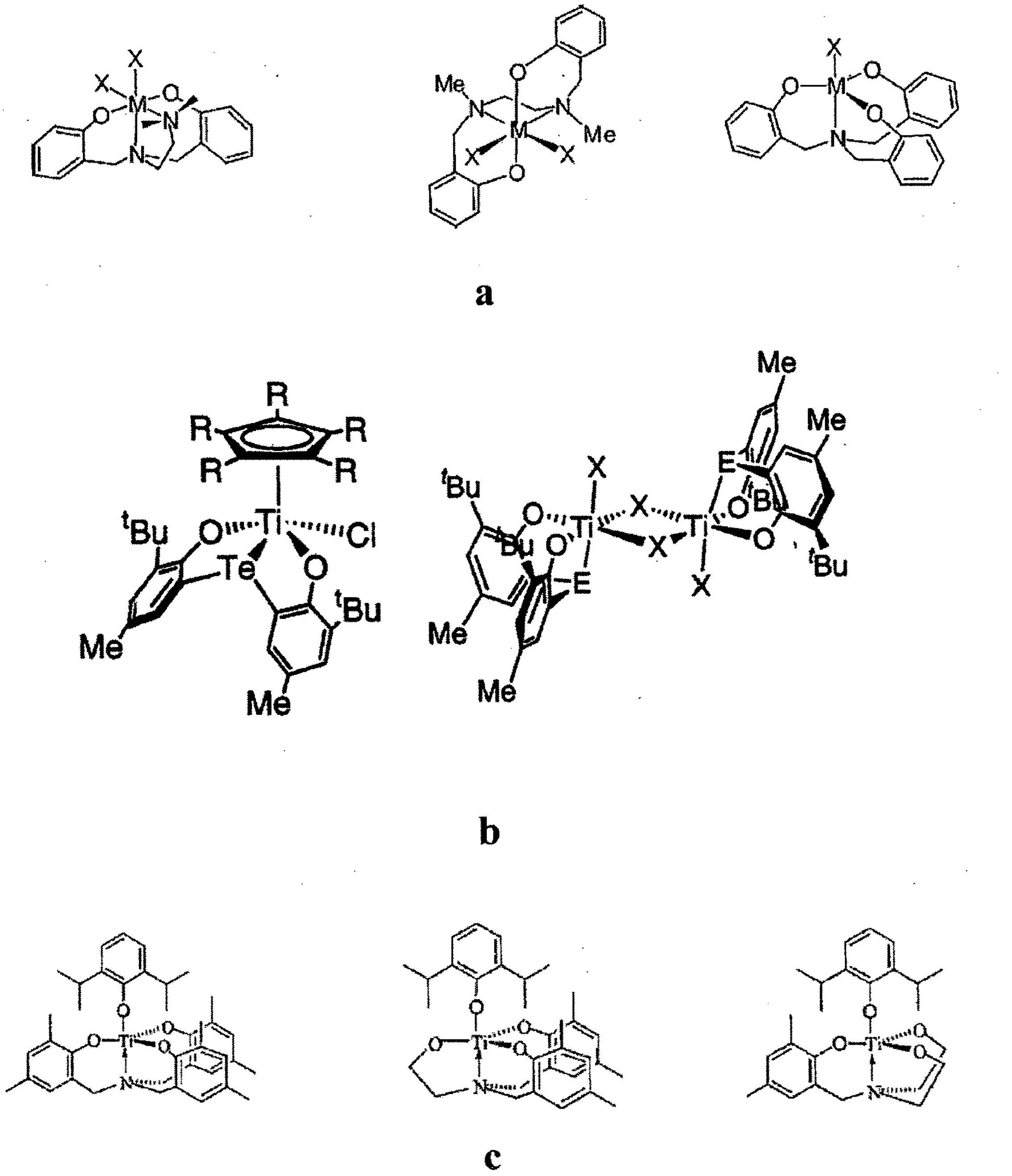


Fig. 5.5. Some recent examples of Ti based catalyst for ROP of lactides.(a) amino bis phenolate derivatives of Ti (b) Chalcogen – bridged bis-aryloxides of Ti (c) titanatranes

5.2 Experimental

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%.

Catalyst preparation.

All six catalysts **(2, 10-14)** were prepared by an alcohol exchange method by reacting $Ti(OPr^i)_4$ / $Ti(OPr^i)_3Cl$ and the corresponding biphenols. The synthetic protocol and details of characterization have been described in Chapter 3. The pre dried complexes were then used in the melt and solution polymerization of lactide as described below.

Polymerization

LA bulk polymerization was carried out by charging 1 g of LA and then the appropriate amount of catalyst precursor to a 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 x 50 ml of methanol and dried in vacuum at 50 °C for 12 h.

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.

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 to 400 cm^{-1} range.

The ^1H and ^{13}C NMR spectrum of polylactides was recorded in $CDCl_3$ and DMSOd_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 10^4A° (300 x 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 diffraction experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled CuKα radiation (λ =1.5406 A°, generator voltage = 45kV, current = 40 µA) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately 400µ thick and were scanned into 2θ ranges from 13°- 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.

5.3 Results and Discussion

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 **(2, 10-14)**. 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.

Bulk Polymerization:

The different (isopropoxy) – titanium biphenolates **(2, 10-14)** were employed as catalysts to initiate ring opening polymerization of 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 5.1 is compiled the results of polymerization of *l*-lactide with different catalysts.

The observed molecular weights based on GPC with catalysts **2, 10-14** are below $1x10^4$. This is in sharp contrast to very high molecular weights typically obtainable by tin compounds. An increase of polymerization temperature form 130°C to 180°C while maintaining other parameters same showed a marked increase of polymer molecular weight as is evident for catalyst **12** (Table 5.1, entry 1, 8). Similarly the reaction time also showed a positive effect on overall conversion of lactide (Table 5.1, 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 [24]. Interestingly the reference polylactide based on Sn(II)octoate showed presence of higher contents of amorphous materials (Table 5.1, entry 12). The comparison of variation in PLA properties in presence of titanium iso propoxide initiator under different reaction conditions is shown in Table 5.2. 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 hrs. Similarly alkoxytitanatrane 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 of 1.3-1.6.

Solution Polymerization

Our efforts to synthesize polylactide by reacting the monomer and the catalysts (**2, 10-14**) in toluene solutions were unsuccessful (Table 5.1, entry 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.

Polymer characterization

Polylactides obtained with titanium biphenoxy isoproxide catalysts at 130°C generally showed lower molecular mass as revealed by GPC (Fig. 5.11, 5.12). At the given temperature, regardless of the type of chelating biphenol attached to titanium the variations in MWD are only marginal and the peak M_w values centered around 0.6×10^4. Increase in reaction temperature for eg, in case of **12** 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 (Fig. 5.6, 5.8) reveals only two major sets of signals namely the well resolved quartet of CH protons centered at $\delta \sim 5.1$ ppm and doublet for CH_3 protons at $\delta \sim 1.2$ ppm [25]. Such an absorption pattern is indicative of isotactic nature (-SSSS or – SSRR- stereosequence) of PLA. In the ^{13}C NMR spectrum (Fig. 5.4, 5.7), 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 [26]. 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 macrocylic 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 transesterification involving long post-polymerization periods. Similar phenomena have been noted earlier for ROP of cyclic esters by other initiators [27, 28]. 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 [25] 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, 29, 30]

The semi-crystalline nature of all the polylactides was confirmed by percentage crystallinity obtained by the endothermic peak in the DSC (Fig. 5.10). In all the PLA's 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 [31]. The higher crystallinity (>40%) of PLA's 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 [18, 31].

The DSC values were also consistent with the crystallinity results obtained by X-ray powder diffractogram (Fig. 5.13). The XRD reveal strong peaks signals centered at $2\theta = 19°$ due to 220 plane, (Bragg dist. d = 4.7 A°) and another at $2\theta = 16.6°$ (200 plane, Bragg dist. d = 5.3 A°). 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.5.13, B-D) whereas they are less pronounced in case of Sn (II) initiator (Fig. 5.13, A)[32]. X_c values obtained for PLA derived from Sn(II) octoate by DSC & 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 PLA's (Fig. 5.14) 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 PLA's with desired morphological features for end application. In the present PLA's prepared by Ti-biphenolate catalysts the average particle size was between 100–200nm of 'as synthesized' polymer.

Mechanistic Consideration

The NMR spectral profiles of PLA's 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, 33]. Some of the key steps involved are outlined below (Scheme 5.4), which assumes an insertion-coordination pathway process as in the case of many other lewis acidic metal alkoxide based initiators [34].

5.4 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 PLA's having particle size close to the nano region using novel titanium based initiators holds promise for specific end applications.

5.5 References

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Table 5.1 *l* - Lactide Polymerization with Titanium biphenoxy-alkoxide initiators [a]

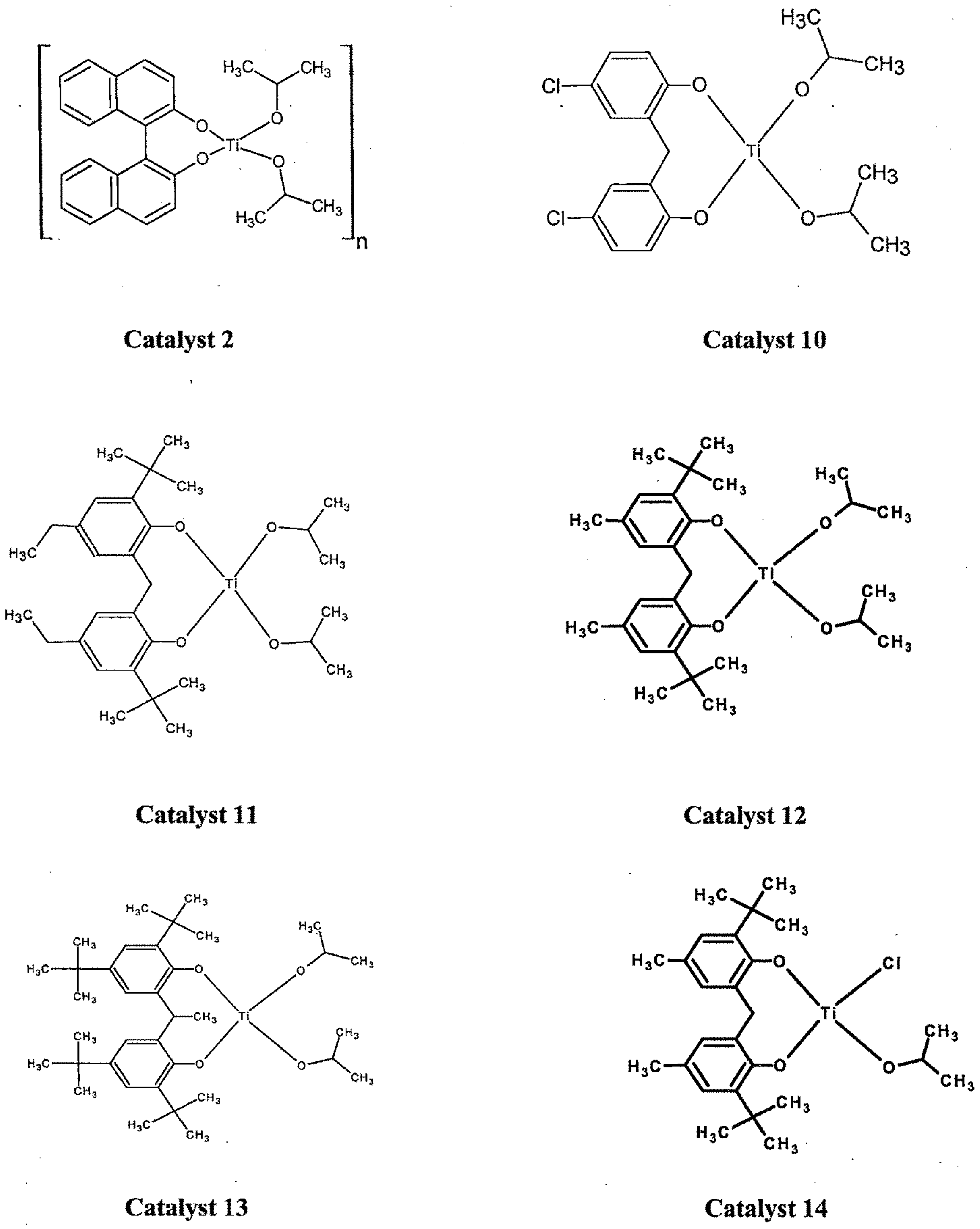
Entry	Catalyst	Time Hrs.	Temp °C	Yield %	M_w	M_n	PD	T_m °C	X_c (%)	
									XRD	DSC
1	**12**	2	130	96	6760	4400	1.5	130	51	49
2 [a]	**2**	2	130	95	9170	5500	1.5	130	47	43
3 [a]	**11**	2	130	87	6300	3990	1.6	126	50	44
4 [a]	**13**	2	130	81	6220	3930	1.5	130	53	50
5 [a]	**10**	2	130	67	--	--	--	--	--	--
6 [a]	**14**	2	130	33	4670	3170	1.5	--	--	--
7	**12**	8	130	96	8560	5035	1.7	--	--	--
8 [a]	**12**	2	180	95	14470	8330	1.7	133	52	45
9 [b]	**12**	12	80	00	--	--	--	--	--	--
10 [b]	**11**	12	80	00	--	--	--	--	--	--
11 [a]	$Ti(OPr^i)_4$	2	130	94	6300	4150	1.5	131	52	--
12 [b]	Sn (Octoate)	1	180	98	108000	52110	2.1	--	--	--
13*	$Ti(OPr^i)_4$	12	200	--	19800	10400	1.9	144	--	4.3

[a] [LA]/[Ti] = 300, [b] [LA]/[Ti] = 1000, * Ref. 31

Table 5.2. Comparision of polylactide properties derived from $Ti(OPr^i)_4$ under different conditions

Entry	Catalyst	Time Hrs.	Temp °C	Yield %	M_w	M_n	PD	T_m °C	X_c (%) XRD	X_c (%) DSC
1	$Ti(OPr^i)_4$	2	130	94	6300	4150	1.5	131	52	--
2[#]	$Ti(OPr^i)_4$	2	130	75	35700	16000	2.2	--	--	--
3[#]	$Ti(OPr^i)_4$	0.5	130	20	--	--	--	--	--	--
4*	$Ti(OPr^i)_4$	12	180	--	12000	6600	1.8	151	--	49

[#] Ref. 18, [*] Ref. 31



Catalyst 2

Catalyst 10

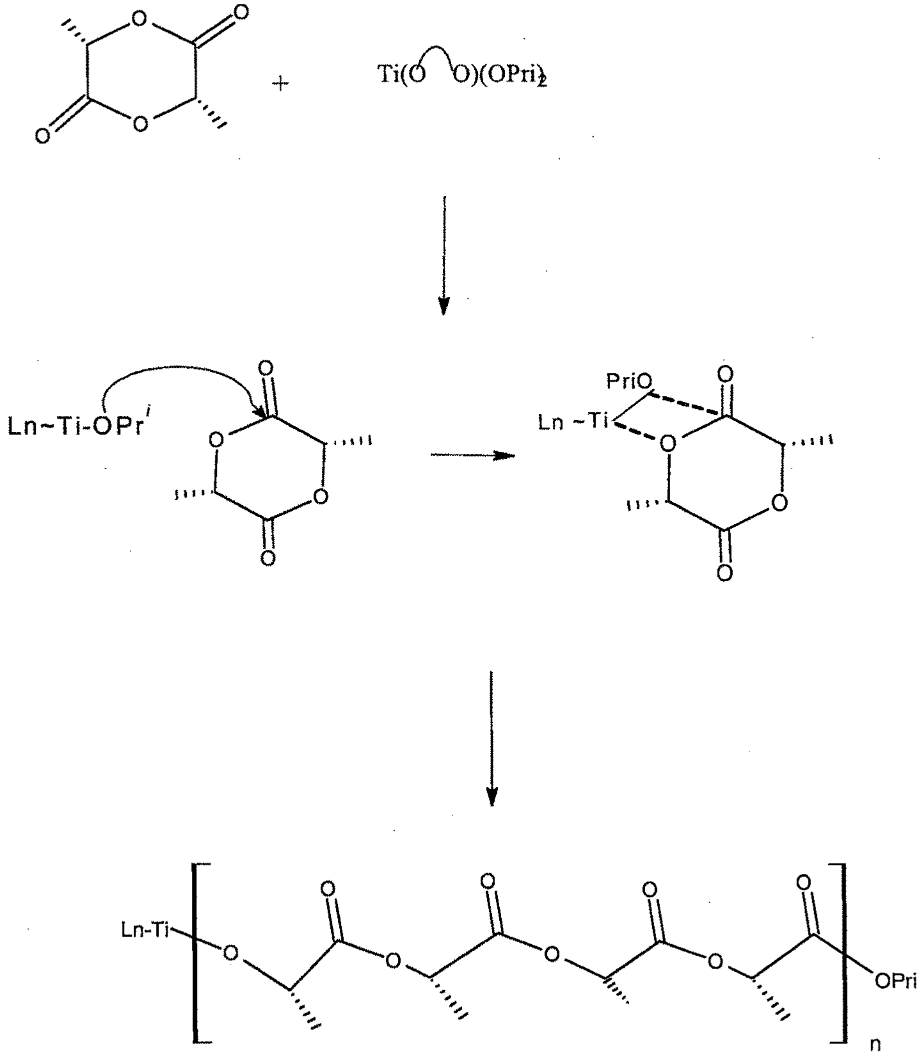
Catalyst 11

Catalyst 12

Catalyst 13

Catalyst 14

Scheme 5.3 Structure of Catalyst



Scheme 5.4. Proposed mechanism for ROP.

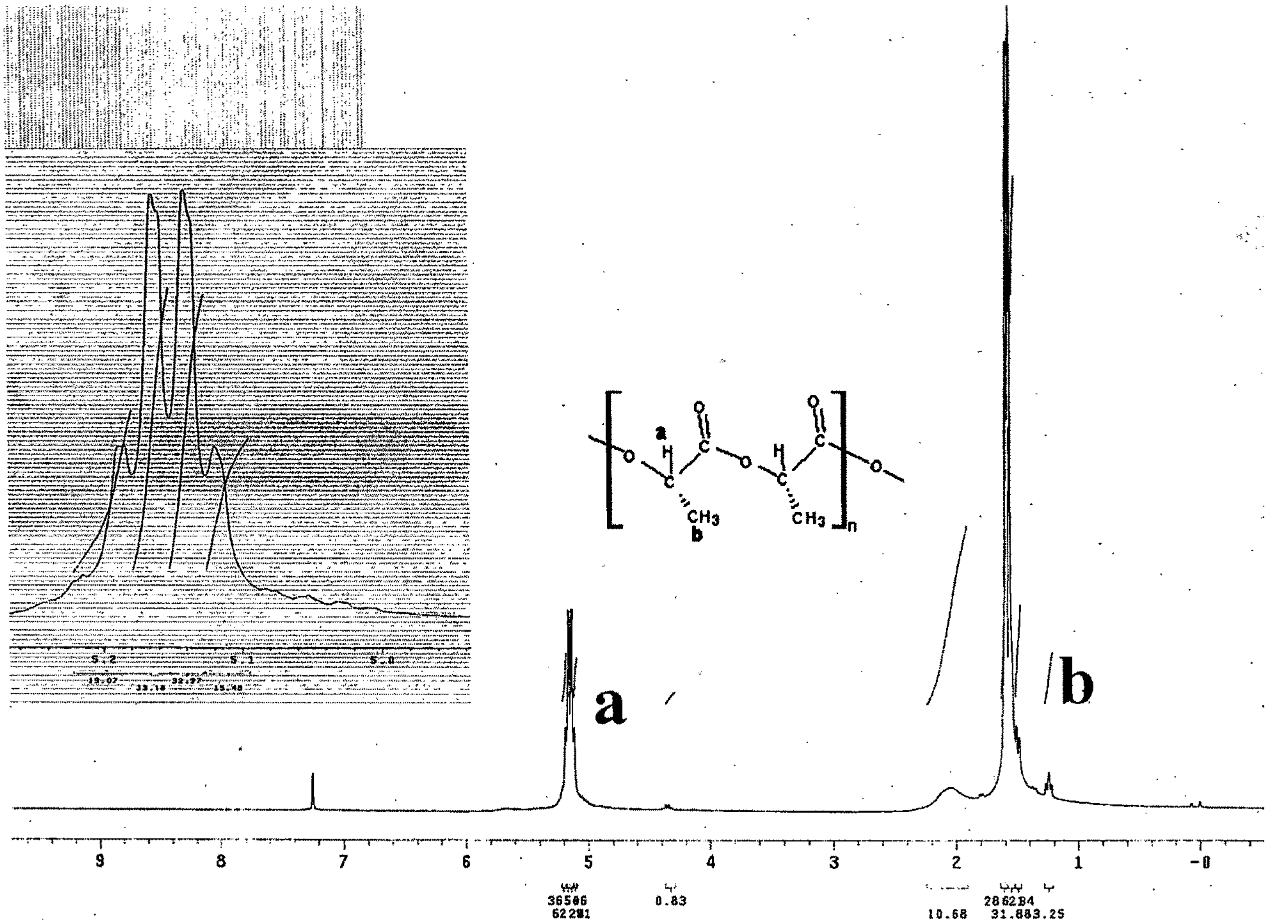


Fig.5.6. ^{1}H NMR of *l*-PLA produced using catalyst **12** (Table 5.1, entry 1).

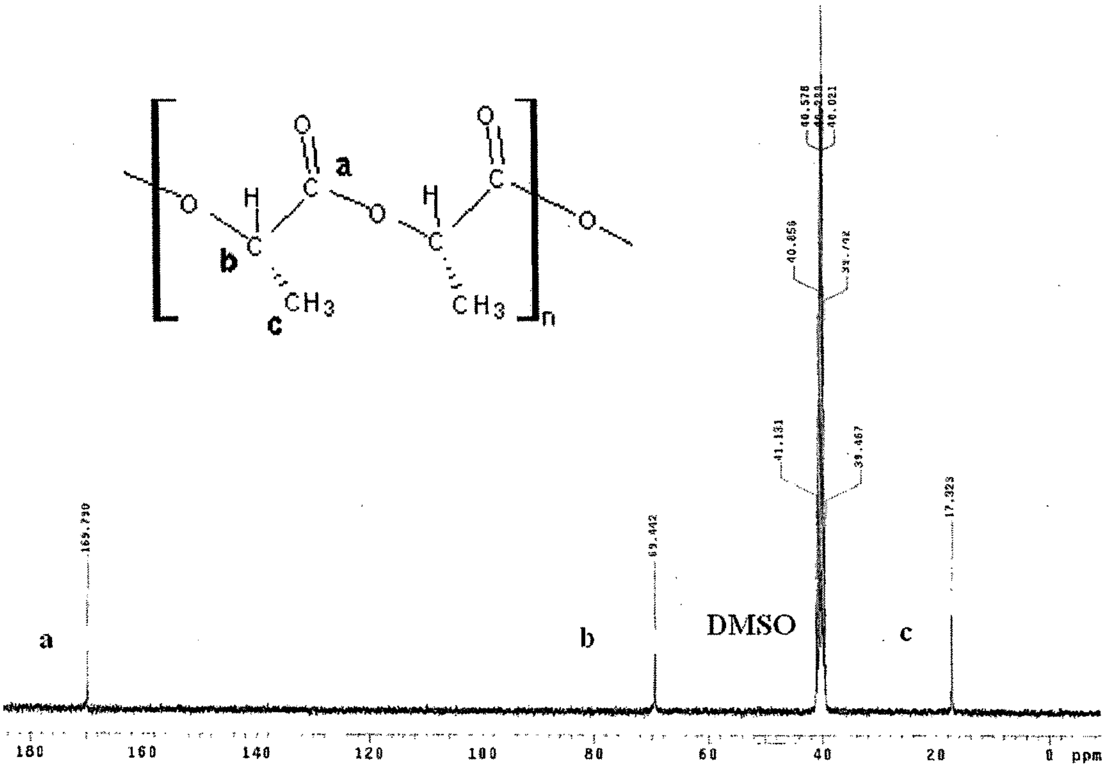


Fig.5.7. ^{13}C NMR of *l*-PLA produced using catalyst 12 (Table 5.1, entry 1)

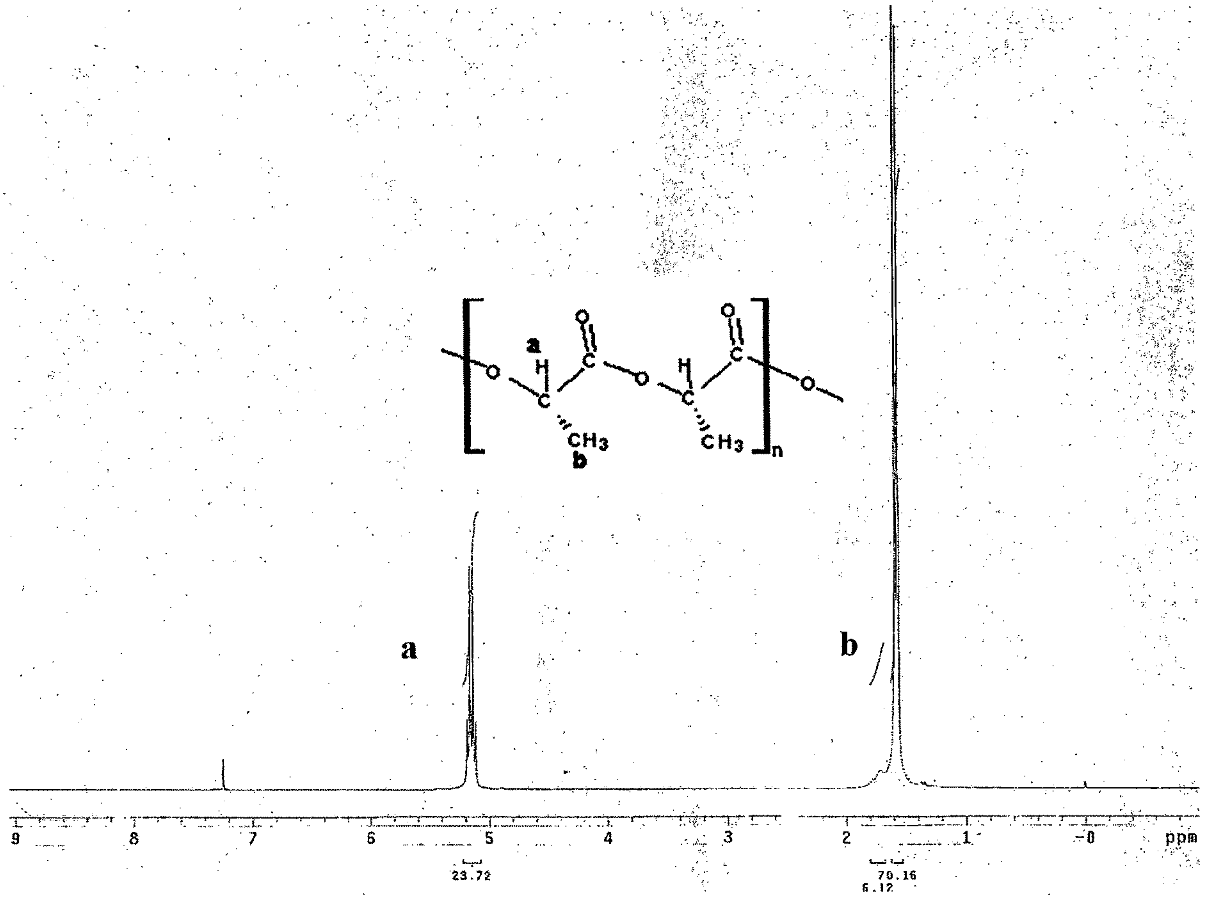


Fig.5.8. ^{1}H NMR of *l*-PLA produced using Sn(Octoate) (Table 5.1, entry 12)

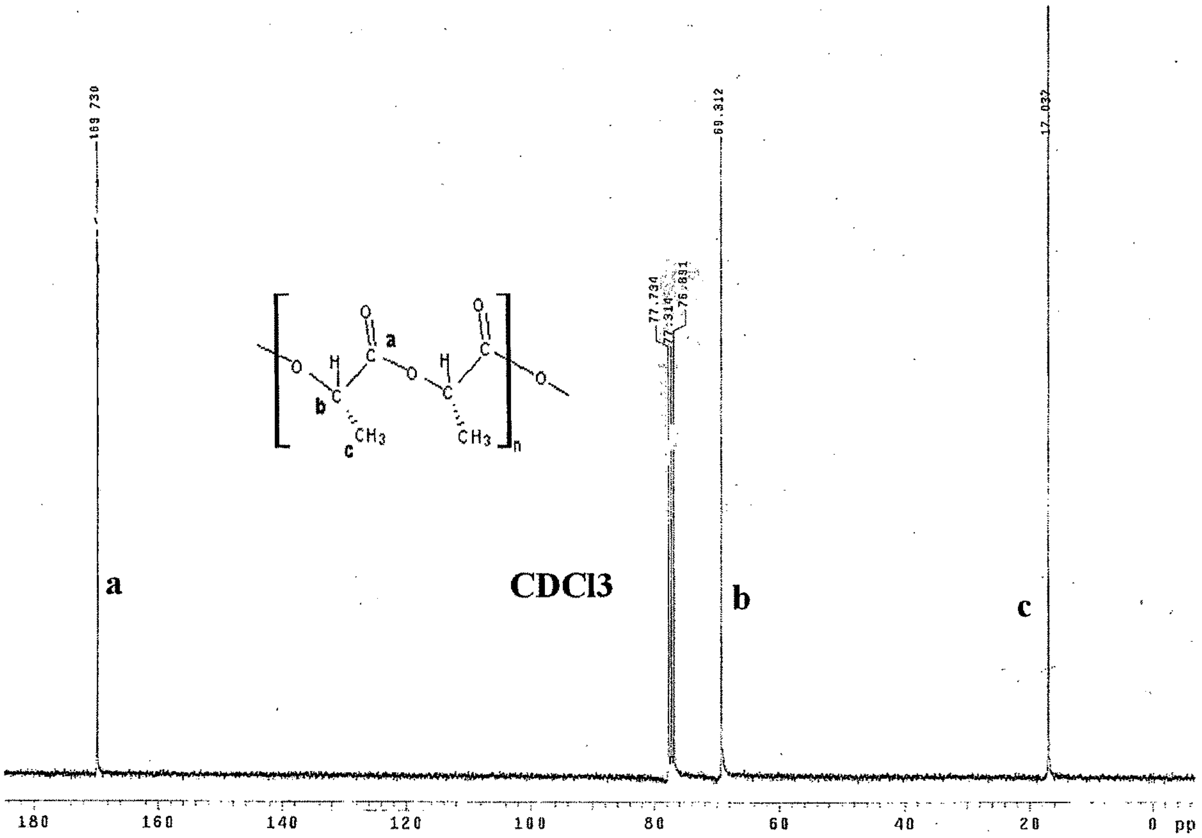


Fig. 5.9. ^{13}C NMR of *l*-PLA produced using Sn(Octoate) (Table 5.1, entry 12)

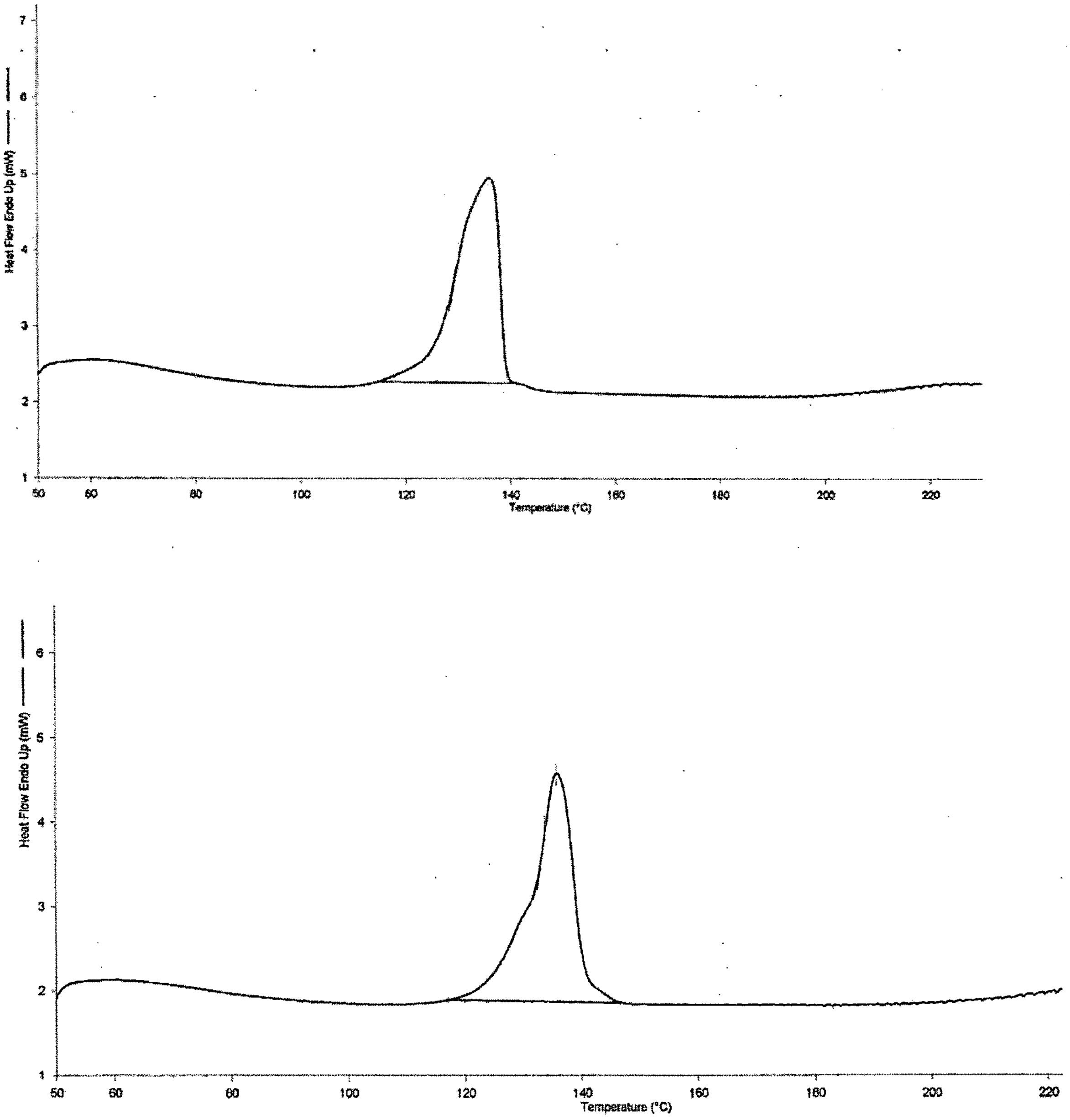


Fig.5.10. Representative DSC of *l* PLA Table 5.1 (a) 1 (b) 3.

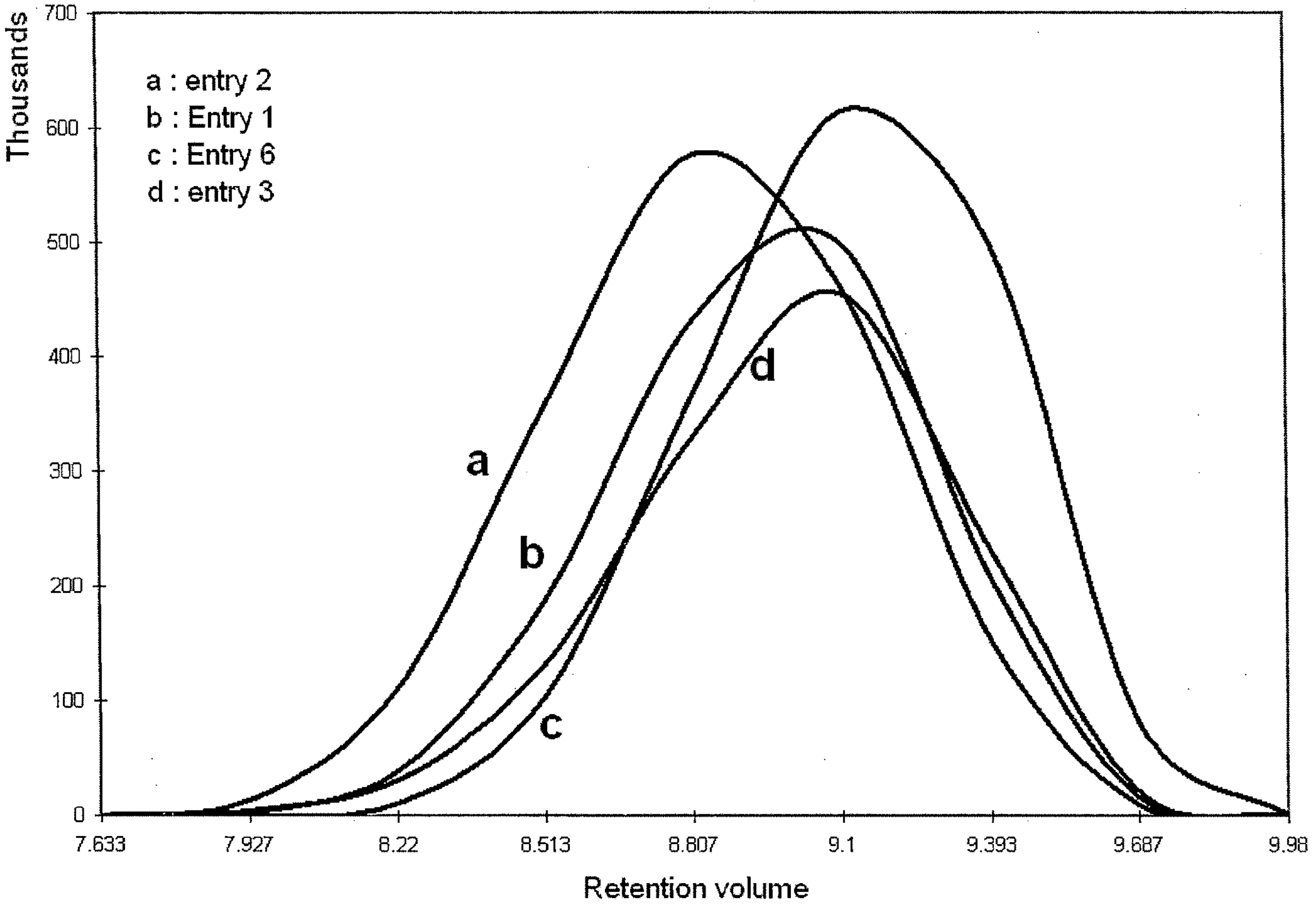


Fig.5.11. GPC profiles of *l*-PLA Table 5.1 a) entry 2, b) entry 1, c) entry 6, d) entry 3.

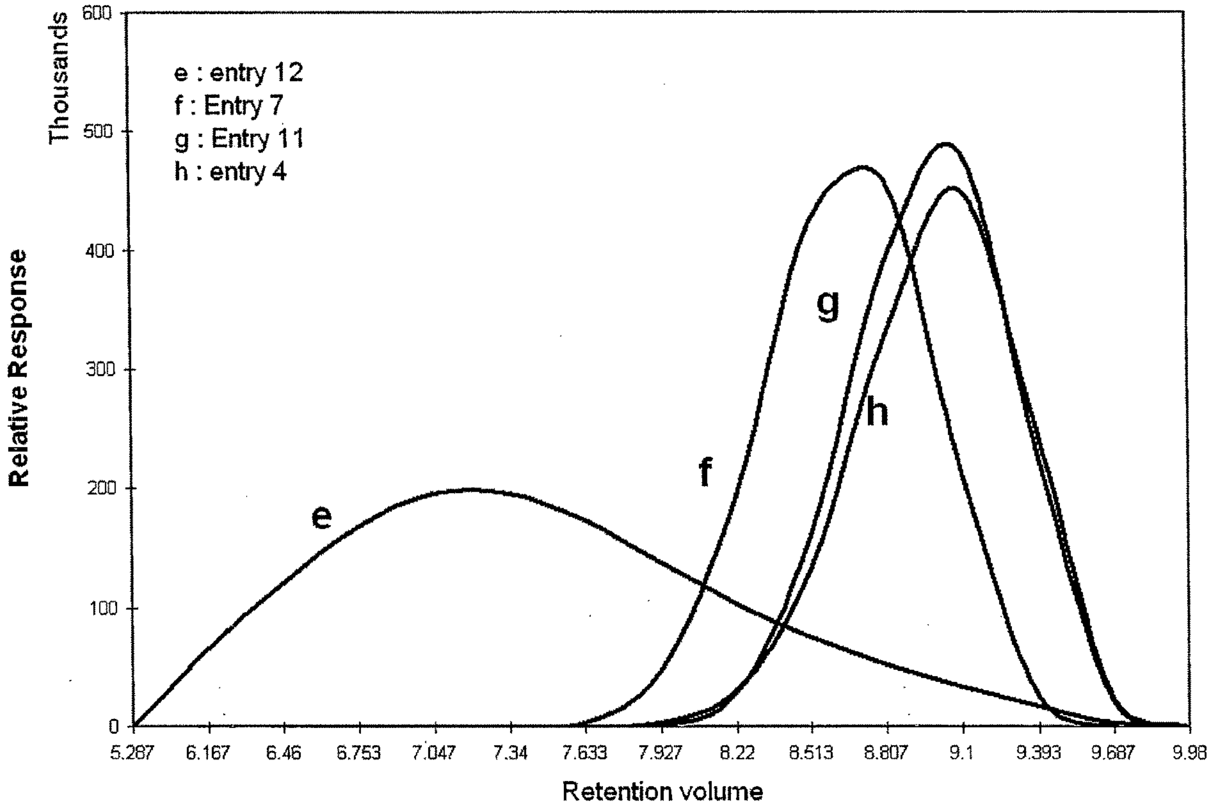


Fig.5.12. GPC profiles of *l*-PLA Table 5.1 e) entry 12 f) entry 7, g) entry 11, h) entry 4.

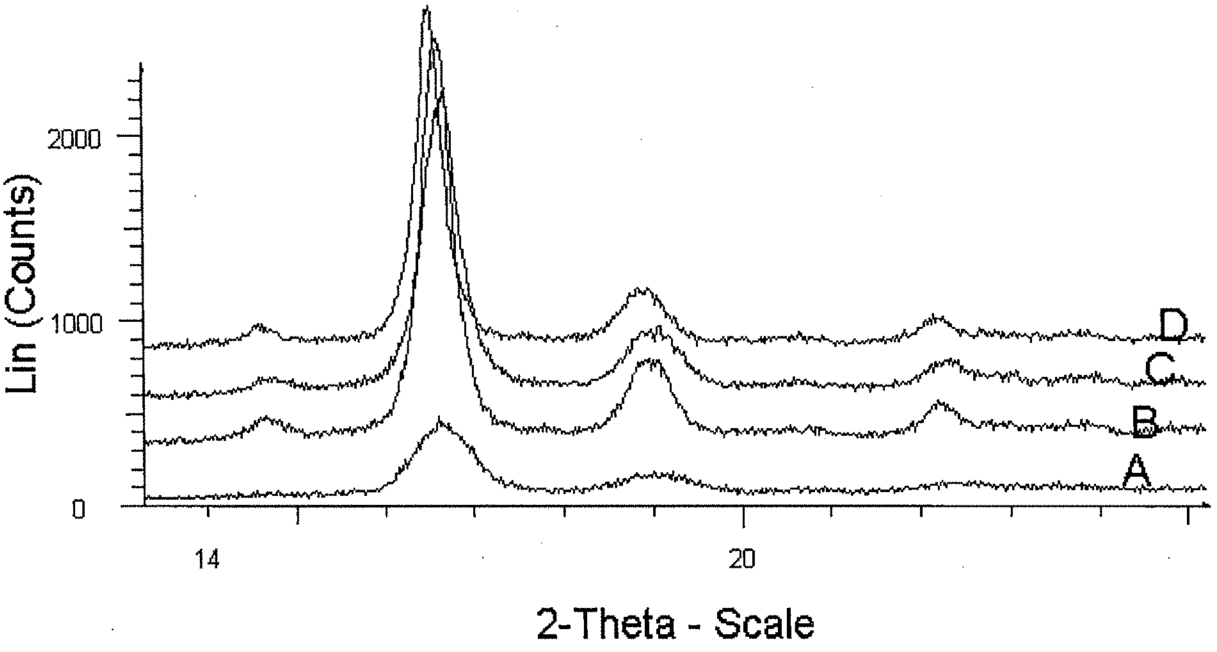


Fig.5.13. XRD of *l*-PLA Table 5.1, A) entry 12, B) entry 1, C) entry 2, D) entry 3.

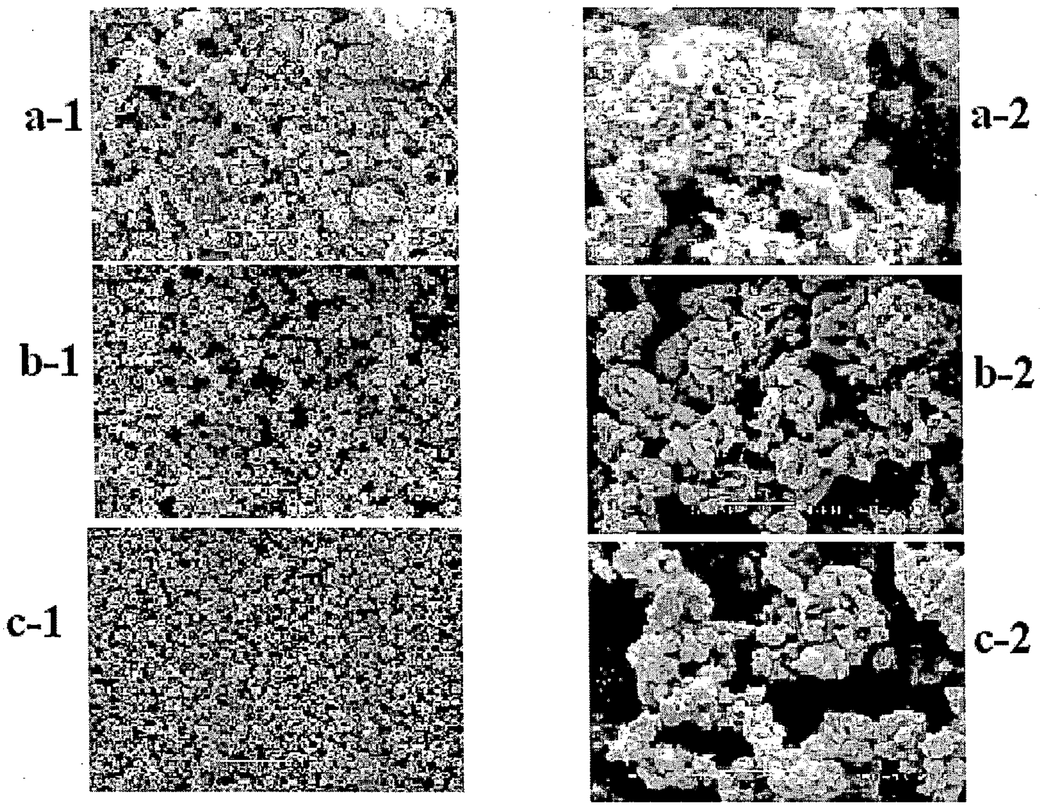


Fig.5.14. SEM of *l*-PLA Table 5.1,

a-1) entry 12 (x 500), a-2) entry 12(x 5000),

b-1) entry 7 (x 500), b-2) entry 7 (x 5000),

c-1) entry 1(x 500), c-2) entry 1 (x5000).