

Synthesis of Poly (L-Lactic Acid) by Dehydropolycondensation Using Various Pore Sizes of Zeolite

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ABSTRACT

This novel work is to remove by-product water efficiently and synthesize high-molecular-weight PLA by direct polycondensation, to obtain high-molecular-weight PLA by direct polycondensation because of equilibrium between free acids, water and polyesters causing difficulty in removing water as a by-product High molecular weight PLA by direct polycondensation. The polymerization conditions were optimized by screening various catalysts such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1, 3- dicloro-1, 1, 3, 3 -tetra (n-butyl) distannoxane and tetraphenyltin. These reactions were carried out in presence of various zeolites such as ZSM-5, ZSM-12 and β -zeolite as catalyst and desiccating agent.

INTRODUCTION

In recent years, poly (L-lactic acid) (PLA) has attracted tremendous attention among commonly used commodity plastic as an environmentally friendly biodegradable polymer suitable for large-scale application due to its good transparency, mechanical strength and safety.^{1,2} PLA is not only used in medical applications but also in packaging, consumer goods and many other article of short-term use.³ For fiber application, the molecular weight of poly (L-lactic acid) needs to be relatively high in order to the mechanical properties to be acceptable. Among all biodegradable polymers reported in the literature, poly (lactic acid) (PLA) has been acknowledged for the use of packaging material and commodity because of its excellent properties. The high molecular weight PLA is achieved through the ring opening polymerization of lactide. Several steps are included the production and isolation of intermediate lactide which results high process costs of synthesizing and purifying lactide. However lactide production is relatively complicated and expensive. PLA has been restricted to medical applications such as suture materials. Therefore, alternate polymerization routes for lactic acid are thus of considerable interest.

The main focus of the work is to remove by-product water efficiently and synthesize high-molecular-weight PLA by direct polycondensation to find its better applicability in packaging and commodity.

However, it was reported that it was very difficult to obtain high-molecular-weight PLA by direct polycondensation because of equilibrium between free acids, water and polyesters causing difficulty in removing water as a by-product.⁴ The breakthrough for direct process is attributed to overcome the three subjects, i.e. kinetic control, suppression of depolymerization and efficient removal of water.

Poly (hydroxyl carboxylic acid) has been prepared by ring opening polymerization of lactide in presence of aluminum silicate.⁵ Transesterification of aromatic diester forming derivatives with glycols in the presence of metal catalysts have been reported and synthetic zeolites have been used for removal of metal catalysts. Finally the product has been further polymerized in presence of Me_3PO_4 and Sb_2O_3 . There are few literature reports where molecular sieves of various pore sizes have been used in dehydropolycondensation reactions by raising temperature as well as vacuum.⁶ The polymer yield varied from 70 to 78 %. Woo et al⁷, have studied the effect of desiccating agents i.e. molecular sieves 3A^0 using various catalyst systems such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SnO , tin powder, trifluoro methanesulphonate and found that \bar{M}_v of PLA synthesized with molecular sieves is little bit higher than that of PLA synthesized in solution. The other catalysts such as SnO , Sn powder and trifluoro methanesulphonate did not show any increase in \bar{M}_v of PLA with 3A^0 molecular sieves because it is an irreversible process

where molecular sieve will get saturated as polymerization proceeds even though molecular sieves are the most effective drying agent to reduce the dissolved water contents in organic solvents. Therefore, solution polymerization of L-lactic acid to PLA is an inefficient route. Zeolites like ZSM-5, ZSM-12 and β -zeolite are generally used as a Lewis acid catalyst^{8,9} as well as better desiccating agents in presence of minimum amount of water. There is no literature report available so far regarding the use of zeolites as desiccating agents like ZSM-5, ZSM-12 and β -zeolite.

The proposed work was undertaken to synthesize high molecular weight PLA by direct polycondensation to find its better applicability in fiber application, packaging material and commodity. However, it was reported that it was very difficult to obtain high molecular weight PLA by direct polycondensation because of equilibrium between free acids, water and polyesters causing difficulty in removing water as a by-product. To overcome these problems, the polymerization conditions were optimized by screening various catalysts such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1, 3-dichloro-1, 1, 3, 3-tetra (n-butyl) distannoxane and tetraphenyltin. These reactions were carried out in presence of various zeolites such as ZSM-5, ZSM-12 and β -zeolite. Because the surface area of ZSM-5, ZSM-12 and β -zeolite are 300, 392 and 435 m^2/g respectively and the zeolite having high surface area absorb more water, well documented in the literature. The effect of various solvents (polar and non polar) and reaction temperatures were also investigated. In this contribution, the influence of process variables on the molecular weight of PLA synthesized by direct polycondensation will be highlighted.

EXPERIMENTAL

L-lactic acid was obtained from Purac (United States) as an 88 % aqueous solution and was used without further purification. 1, 3-dichloro-1, 1, 3, 3-tetra (n-butyl) distannoxane catalyst was prepared through the condensation of equimolecular amounts of di (n-butyl) tin dichloride and di (n-butyl) tin dioxide in toluene for 10 h. The crude product was obtained through the evaporation of toluene. It was purified by crystallization from minimum amount of hot n-hexane. The yield of pure product (dichloro distannoxane) was 88 %, mp 109-111 $^{\circ}\text{C}$ (reported 110-112 $^{\circ}\text{C}$) Analytical Calculation for $\text{C}_{16}\text{H}_{36}\text{Sn}_2\text{OCl}_2$ (552.42): C, 34.75; H, 6.52; Sn, 42.98, found. C, 33.62; H, 6.93; Sn, 43.47. Tin chloride dehydrates ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and tetraphenyltin (Ph_4Sn) from Aldrich (United States) were used as such without any further purification. The structures of catalyst were shown in Figure 1.

Synthesis of distannoxane catalysts

Catalyst C was prepared by condensing 1.5192 g (0.5 mmol) n-butyltin dichloride and 1.2446 g (0.5 mmol) di-n-butyltin dioxide in toluene for 10 h. Crude product was obtained by evaporating toluene and purified by crystallization from a minimum amount of hot n-hexane. Pure catalysts were identified by melting points and gravimetric analysis.

Passivation of glass surface

Inner surface of glass reactors whenever required were passivated by treating with trimethyl silyl chloride (30 % w/v acetone solution), washed with methanol, dried at 150 $^{\circ}\text{C}$ in an oven and cooled immediately before polymerization reaction.

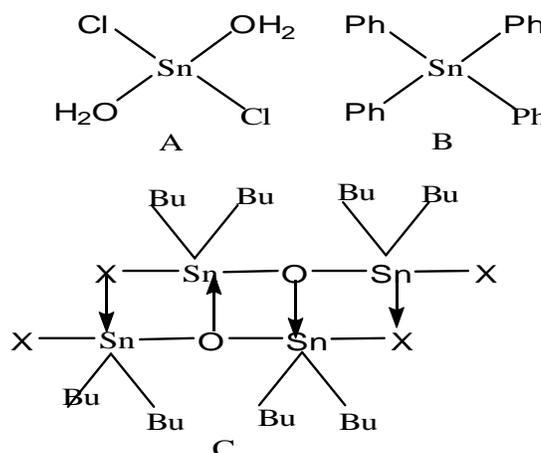


Fig. 1: Structure of catalysts (A) tin chloridedihydrate, (B) tetraphenyl tin and (C) dichloro distannoxane

With a quartz reactor vessel equipped with a Dean-Stark-type condenser, the solution polymerization was carried out by varying the polymerization time, the amount of catalyst and kind of catalyst including stannous compounds, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, Ph_4Sn and dichloro distannoxane catalyst in argon atmosphere. An aqueous solution of L-Lactic acid (88 %) was azeotropically dehydrated with xylene for 5 h at reflux temperature without any catalyst. After the removal of water in the trap of the Dean-Stark condenser, the reaction vessel was cooled to 50 °C, the required amount of catalyst was added and this was followed by slow heating of the reaction mixture to the refluxing temperature of the solvent under mild stirring with the help of magnetic stirring bar. The reaction time was 5h. The reaction mixture was cooled to room temperature, and 50 mL of chloroform was added to dissolve the resultant mixture. The resultant solution was poured into 200 mL of n-hexane for the precipitation of the polymer. The polymer was collected by filtration and further purified repeated dissolution and precipitation. PLA oligomer was prepared, fully characterized and was used as a starting material for post polymerization. The post polymerization was carried out using prepolymer, catalyst and desiccating agents (ZSM-5, ZSM-12 and β -zeolite) to remove traces amount of by-product water. A tube packed with activated zeolite was mounted on the reaction flask in the place of the Dean-Stark trap so as to recycle the distilled azeotropic mixture through desiccating agents. The resultant mixture containing prepolymer, catalyst and solvent was polymerized at different temperature 145, 155, 165 and 190 °C for different time 1-5, 15, 30, 45 h using the Dean-Stark trap and a tube packed zeolite under inert atmosphere. After the required polymerization time, the following steps were the same as for the above-mentioned method.

Characterization

Molecular weights: Molecular weights (relative, \bar{M}_n and \bar{M}_w) and polydispersity (\bar{M}_w/\bar{M}_n) were determined with respect to polystyrene standards by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25 °C by eluting PLA solutions of 10 mg/ mL concentration in CHCl_3 , with toluene as internal standard, through a series of five μ -Styragel columns of pore sizes 10^5 , 10^4 , 10^3 , 500, and 100 Å⁰ respectively, and length 30 cm each. CHCl_3 was used as the mobile phase (flow rate 1 mL/ min) and a refractive index detector (Spectra Series RI-150) was used for detection of different molecular weight fractions. Molecular weights were calculated with respect to polystyrene calibration.

Nuclear Magnetic Resonance; For NMR measurements, the samples were dissolved in Chloroform-d in 5 mm dia. NMR tubes at room temperature. The sample concentration for ¹³C NMR measurements was 10 % by weight. Proton decoupled ¹³C NMR spectra with NOE were recorded on a Bruker DRX 500 MHz NMR spectrometer working at 125.577 MHz for carbon-13. CDCl_3 served as solvent and TMS as internal standard for all ¹³C-NMR measurements. Relative peak areas were proportional to the number of carbon atoms. Peak areas were calculated by deconvolution method using WIN-NMR software.

Thermal Analysis

Differential scanning calorimetric (DSC) measurements were made on a Perkin-Elmer thermal analyzer model DSC-7 in a nitrogen atmosphere. The measurements were run from -40 to 200 °C at a heating rate of 10 °C/ min and a cooling rate of 100 °C/ min. The glass transition temperature (T_g) and the crystallinity data were recorded from the second and first heating curves, respectively. Crystallinity values for different polymers were calculated from the heat of fusion. By integrating the normalized area of the melting endotherm, determining the heat involved, and rating it to the reference 100 % crystalline polymer (93.6 J/ g)¹⁰, the relative crystallinity of the polymer was assessed. In the present work, the relative degree of crystallinity is referred to as crystallinity, and T_m is the melting temperature.

X-ray Analysis

Wide-angle X-ray scattering (WAXS) pattern of the samples was obtained in reflection mode using a Rigaku Dmax 2500 diffractometer and Ni filtered copper radiation. The sample was scanned in the range $2\theta = 10 - 35^\circ$ and the generator was operated at 40 kV and 150 mA. The FWHM of the 110 peak was determined by peak fitting software available with the Rigaku diffractometer.

MALDI-ToF MS Analysis

MALDI-ToF MS analysis was performed on a Kratos Kompact MALDI IV spectrometer equipped with 0.7-m linear and 1.4 m reflection flight tubes as well as a 337 nm nitrogen laser with pulse width of 3 ns. All experiments were carried out at an accelerating potential of 20 kV. In general mass spectra from 200 shots were accumulated to produce a final spectrum. The obtained data were smoothed to reduce the spikiness by the average method; the smoothing filter moved along the collected data channels, adding together a number of channels and dividing by that number to give an average signal. This

smoothing, however, did not eliminate or hide minor signals distinct from the baseline noise. The samples were dissolved in CHCl_3 (1 mg/ mL) and mixed with matrix (15 mg/mL of tetrahydrofuran) before being dried on the sample plate. 4-hydroxy cinnamic acid (CHCA) was used as the matrix. The sample plate was inserted in to the apparatus under a high vacuum (10^{-5} Pa).

RESULT AND DISCUSSION

The prepolymer was prepared by dehydropolycondensation using xylene as a diluent and tin chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) as a catalyst. With a quartz reactor vessel equipped Dean-Stark-type condenser, 20 gm of 88 % L-LA was azeotropically dehydrated with 40 mL of xylene for 5h at the reflux temperature. Thereafter, the polymerization was carried out at 145°C for another 5h, where the concentration of monomer 20gm/40mL and the amount of catalyst was 0.2%. The weight average molecular weight (\bar{M}_w) was found to be 3500 and used as starting material for post polymerization.

Solution post polymerization with zeolites

Table 1 shows the effect of reaction time with different zeolites keeping all other parameters are constant. It was observed that there is an increase of

molecular weight trend up to 30 h in presence of ZSM-5, ZSM-12 and β -zeolites. The molecular weight remains constant even after further increase in reaction time except β -zeolite. β -zeolite is a high-silica large-pore zeolite consisting of unidimensional channels with 12-membered ring pore-openings. The polycondensation system of PLA oligomer involves two thermodynamic equilibria, the dedhydration/hydration equilibrium of ester formation and ring/chain equilibrium of lactide. The absorbed water may be leached out because of large-pore of zeolites and cause degradation of the polymer chain.

Molecular weight determination

Table 2 shows the effect of catalyst concentration ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) on conversion and molecular weight of PLA. The polymerization was carried out at 145°C for 30 h where the concentration of PLA oligomers was 4g/10mL and length to diameter ratio of each bed is fixed irrespective zeolites such as ZSM-5, ZSM-12 and β -zeolites in all reactions. The catalyst concentration of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was varied keeping all other parameters constant. The maximum values of \bar{M}_n and \bar{M}_w are obtained as 20,500 and 30,200 respectively and PDI=1.4. Thereafter the trend leveled off after 0.2 wt %. Similar kind of trend was observed in presence of ZSM-12 and β -zeolites

Table 1: Effect of L-lactic acid polymerization time on various type zeolites

Polymer samples	Time (h)	ZSM-12 (II) (\bar{M}_w) (GPC)	ZSM-5 (I) (\bar{M}_w) (GPC)	β -Zeolites (III) (\bar{M}_w) (GPC)
PLA-0	0	3,500	3,500	3,500
PLA-1	15	17,000	29,000	29,000
PLA-2	30	30,000	30,000	34,000
PLA-3	45	22,000	30,500	34,500

Xylene as solvent and temperature of the polymerization reaction was 145°C

The maximum \bar{M}_n and \bar{M}_w was observed 21,000 and 34,000 in case of β -zeolites using 0.2 wt % of catalyst concentration. The catalyst $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ had a better activity than any other catalysts and the molecular weight of PLA was about 30,000.

Table 3 shows the effect of various the nature of catalysts, the catalyst tetraphenyltin showed about 29,000 Da, whereas dichloro distannoxane was

11,000 Da. Similarly the catalyst $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ had better activity than other two catalyst in presence of ZSM-12 system. The weight average molecular weight (\bar{M}_w) were 30,000, 27,000 and 24,000 Da respectively due to the corresponding catalyst such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, tetraphenyltin and dichlorodistannoxanes. Tin chloride dihydrate undergoes self-condensation reaction to form an activated hydrate and hydrochloric acid.

Table 2: Dehydropolycondensation of L- lactic acid prepolymer using various catalyst concentrations

Polymer samples	Zeolites	Catalyst Conc ^{an} (wt %)	Conv. (%)	\bar{M}_n (NMR)	\bar{M}_n (GPC)	\bar{M}_w (GPC)	% cryst powder (XRD)	T _m (°C)	T _g (°C)
PLA-4	Blank	A (0.2)	99.1	3,570	5300	11,000	nd	160.6	38.9
PLA-5	I	A (0.05)	99.2	nd	17,900	27,000	nd	162.3	39.2
PLA-6	I	A (0.1)	99.0	nd	19,400	29,000	nd	165.4	38.1
PLA-7	I	A (0.2)	99.2	5,200	20,500	30,200	82.5	167.7	38.2
PLA-8	I	A (0.3)	99.3	nd	19,400	29,000	nd	165.2	37.9
PLA-9	II	A (0.05)	98.9	nd	16,400	25,000	nd	161.6	35.6
PLA-10	II	A (0.1)	99.0	nd	17,400	28000	nd	164.5	37.8
PLA-11	II	A (0.2)	98.7	9,500	18,200	30,000	83.0	163.7	49.6
PLA-12	II	A (0.3)	98.6	nd	17,500	26,000	nd	161.8	43.0
PLA-13	III	A (0.05)	99.3	nd	16,000	24,000	nd	164.8	41.9
PLA-14	III	A (0.1)	99.4	nd	18,500	28,000	nd	163.3	41.0
PLA-15	III	A (0.2)	99.6	18,200	21,000	34,000	84.0	167.7	52.7
PLA-16	III	A (0.3)	98.5	nd	19,000	29,000	nd	169.5	40.5

I: ZSM-5, II: ZSM-12, III: β -zeolite and A: SnCl₂.2H₂O. Xylene as solvent and temperature of the polymerization was 145 °C.

The terminal carboxylic group of the L-lactic acid oligomers reacts with hydroxyl group of activated hydrate to produce water and the product. The hydroxyl terminal group of L-lactic acid oligomers should be coordinated towards the reaction center to show that condensation may be induced around the metal such as tin to form polymer having ester-linkage and activated hydrate form. It can be thought that the dehydropolycondensation proceeds via such a cycle.

The dehydropolycondensation reaction was carried out in presence of ZSM-5 with variation of SnCl₂.2H₂O catalyst. The remarkable increase in the molecular weight was observed in comparison with PLA synthesized in solution polymerization without using zeolite. The \bar{M}_w value of PLA increased from 27,000 to 30,200 with increase in SnCl₂.2H₂O concentration, from 0.05 to 0.2 wt % and thereafter decreases. Two diffraction maxima, characteristic of the α -crystal cell of PLA, were observed at 2 θ angles of 16.8 and 19.2°. The degree of crystallinity calculated from XRD was 80 %. Similarly in the presence of ZSM-12, the \bar{M}_w of PLA increased from 25,000 to 30,000 with increase in SnCl₂.2H₂O concentration from 0.05 to 0.2 wt % and decreases further increase of catalyst concentration. The degree of crystallinity calculated from XRD was 79 %. PLA

obtained using β -zeolite showed an increase of \bar{M}_w from 24,000 to 34,000 with increase in catalyst concentration and decreases further increment of catalyst. ZSM-5, ZSM-12 and β -zeolite have pore size as ZSM-5 (5.6 x 5.3 Å⁰) \leftrightarrow (5.5 x 5.1 Å⁰), ZSM-12 (5.6 x 6.0 Å⁰) and β -zeolite (7.6 X 6.4 Å⁰ \leftrightarrow 5.5 X 5.5 Å⁰), ZSM-5 (Si/Al = 100), ZSM-12 (Si/Al = 60) and β -zeolite (Si/Al=25). The amount of acid site is greater in β -zeolite in comparison with ZSM-5 and ZSM-12. ZSM-5 is considered that 10-oxygen-member-ring medium pore channels get saturated as polymerization proceeds even though zeolites is the most effective drying agent to reduce the by product water. On the other hand, in case of ZSM-12 having 12-oxygen member-ring large-pore structures showed the similar kind of trend as ZSM-5. The highest molecular weight obtained using β -zeolite must be ascribed to its three dimensional large-pore (12-oxygen-member-ring) channels without super cages. It is obvious that the pore structure like β -zeolite and the amount of acid site is necessary effective polymerization of PLA oligomers to high molecular weight PLA.

Table 4 showed the effect of solvents i.e. polar and nonpolar solvents. The solvent decaline at 190 °C showed the high molecular weight \bar{M}_n 18,000 and \bar{M}_w 35,000 (PLA-15). In presence of diphenyl ether (polar solvent) in 2 h the molecular weight was obtained \bar{M}_n 4000 and \bar{M}_w 14,000. After 2 h polymerization in diphenyl ether gives colored

polymer. The solvent mesitylene at 165 °C, showed the molecular weight \bar{M}_n 11,000 and \bar{M}_w 35000 and the PDI was 3.0 and anisole shows the number

average molecular weight 4,500 and weight average molecular weight 8,000 at 155 °C.

Table 3: Effect of catalyst concentration on the dehydropolycondensation of L-lactic acid

Polymer samples	Zeolites	Catalyst concentration and variation (wt %)	Conv. (%)	\bar{M}_n (NMR)	\bar{M}_n (GPC)	\bar{M}_w (GPC)	cryst powder (XRD)	T_m (°C)	T_g (°C)
PLA-5	I	A (0.2)	99.2	nd	20,500	30,200	83.0	167.7	nd
PLA-17	I	B (0.2)	98.3	9,330	19,700	29,000	nd	165.5	53.9
PLA-18	I	C (0.2)	98.3	nd	9,700	11,000	nd	163.8	53.2
PLA-11	II	A (0.2)	98.7	nd	18,200	30,000	83.0	163.7	49.6
PLA-19	II	B (0.2)	98.2	6,300	16,700	27,000	nd	161.2	51.6
PLA-20	II	C (0.2)	98.5	19,500	16,700	24,000	nd	163.2	51.3
PLA-15	III	A (0.2)	99.6	nd	21,000	35,000	83.0	167.7	52.7
PLA-21	III	B (0.2)	98.5	6,100	20,000	30,000	nd	165.7	54.3
PLA-22	III	C (0.2)	99.4	5,000	19,500	28,000	nd	165.3	55.0

I: ZSM-5, II: ZSM-12, III: β -zeolite, A: $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, B: dichloro distannoxane and C: tetraphenyltin. Xylene as solvent and temperature of the polymerization was 145 °C.

The reaction time for PLA-23 to PLA-26 was 15 h. Table 5 shows the effect of time in a solvent (decaline) at very high temperature 190 °C. The high molecular

weight i.e. $\bar{M}_n=24,000$ and $\bar{M}_w=42,000$ were obtained in case of PLA-33. The molecular weight increased from PLA-29 to PLA-33 and decreased thereafter in PLA-34 due to backbiting reaction. The GPC curve of PLA-29 to PLA30 and PLA-31, PLA-32, PLA-33 and PLA-34 was shown in Figure 2.

Table 4: Effect of solvent (polar and nonpolar) on the dehydropolycondensation of L- lactic acid

Polymer samples	Solvent	Temperature (°C)	Time (h)	Conv. (%)	\bar{M}_n (NMR)	\bar{M}_n (GPC)	\bar{M}_w (GPC)	T_m (°C)	T_g (°C)
PAL-23	E	145	15	98.5	Nd	17,000	29,000	144.5	48.4
PAL-24	F	154	15	99.0	3,800	4,500	8,000	164.2	51.0
PAL-25	G	165	15	99.4	25,000	11,000	34,000	151.7	43.3
PAL-26	H	190	15	99.2	Nd	18,000	35,000	nd	45.3
PAL-27	I	190	2	99.4	9,600	4,000	14,000	115.2	37.7
PAL-28	I	190	1	99.1	Nd	2,400	8,200	137.5	33.0

E-xylene, F- anisole, G- mesitylene, H-decaline, I-diphenyl ether and nd- not detected.

Thermal characterization

Result of thermal characterizations are shown in Table 2 to Table 5. The values of T_g and T_m followed the similar trend like molecular weight. The maximum values of T_g and T_m are 55.5 and 169.7 °C respectively (Table 2). Table 3 showed the maximum values of T_g and T_m are 55.0 and 167.7 °C respectively. Table 4.4 shows the maximum T_g and T_m values are 51.0 and 164.2 °C (PLA-24). The glass transition temperature (T_g) of the polymers varied from 54.3 to 42.2 °C (Table 4.5). The melting

temperature (T_m) of the polymers varied from 139.7 to 159.8 °C, and thermograms are all shown in Figure 3 and 4.

The degree of crystallinity was calculated from powder XRD patterns and are shown in Figures 5 to 7 and the values are tabulated in Table 2, Table 3 and Table 5. Typically, the degree of crystallinity was found between 83% to 78 % except in case of PLA-33 and PLA-34, which were abnormally low. These could be due to racemization of L-LA to D-LA and its copolymerization.¹¹

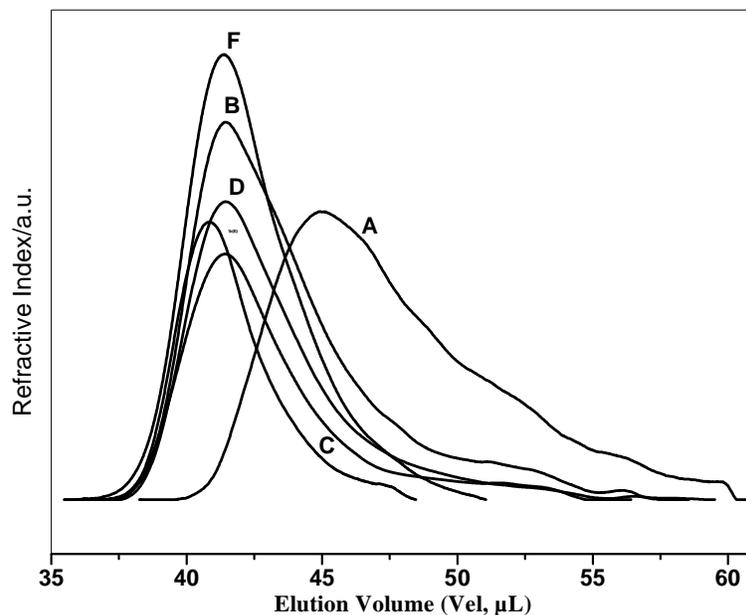


Fig. 2: SEC elograms of PLA oligomers (a) PLA-29, (b) PLA-30, (c) PLA-31, (d) PLA-32, (e) PLA-33 and (f) PLA-34

End group analysis by ^{13}C NMR: ^{13}C NMR has been utilized as a useful tool for determining the number average molecular weight, \bar{M}_n quantitatively. Besides end group determination, this technique has also been used for the determination of residual L, L-lactic acid, lactide formed due to unzipping of chain ends^{12,13}, and the optical purity of the polymer. In

the present study, NMR was used to determine end groups, residual lactic acid, lactide and stereosequence of poly (lactic acid) in PLA samples. For this purpose the PLAs were prepared by using various parameters such as catalyst concentration, reaction time, reaction temperature variation are shown in Table 2, Table 3, Table 4 and Table 5.

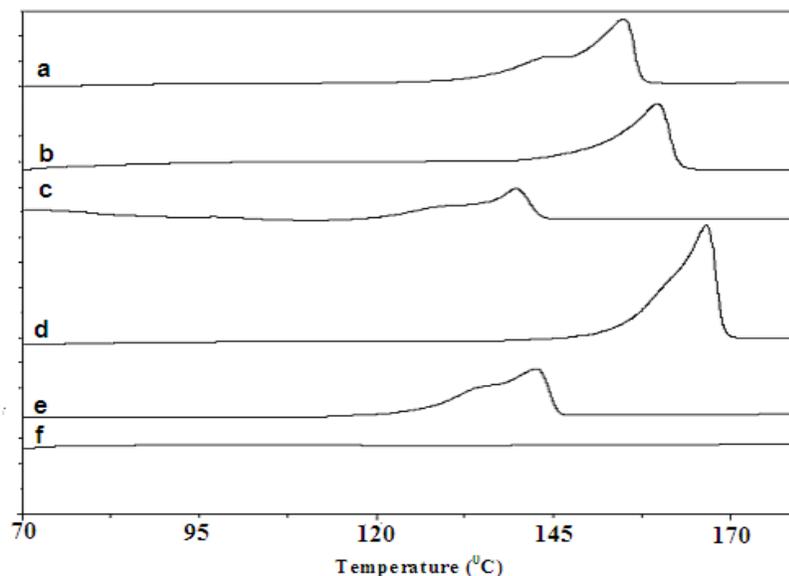


Fig. 3: DSC thermograph showing melting temperature of PLA oligomers (a) PLA-29, (b) PLA-30, (c) PLA-31, (d) PLA-32, (e) PLA-33 and (f) PLA-34

The spectra of oligomers, PLA-4, PLA-1 and PLA-15 are shown in Figure 8. The peaks appearing from 169.23 to 169.70 ppm are due to ester carbonyl groups and peaks arising from 172.9 to 173.4 ppm are due to carboxylic acid end functional groups. The accuracy of degree of polymerization (DP_n) estimate, which was same in two consecutive NMR measurements. There are no peaks due to lactide in these polymers. In the spectrum of PLA-29, PLA-30, PLA-31, PLA-32, PLA-33 and PLA-34 (Figure 9), the peaks for ester carbonyl groups and the carboxylic acid end groups were assigned 169.13

to 169.72 ppm and 172.9 to 173.5 ppm respectively. The DP_n and \bar{M}_n were calculated in same way by taking the ratio of these two signals and the values were depicted in Table 5. In the Figure 10, ¹³C NMR spectra of PLA-24 and PLA-25 showed the effect of solvents (polar and nonpolar solvent) presented in Table 4. PLA-24 was prepared in anisole at 15 h and the polymerization temperature was 154 °C. The spectrum showed the NMR assignments ranges from 169.07 to 169.55 ppm for ester carbonyl groups.

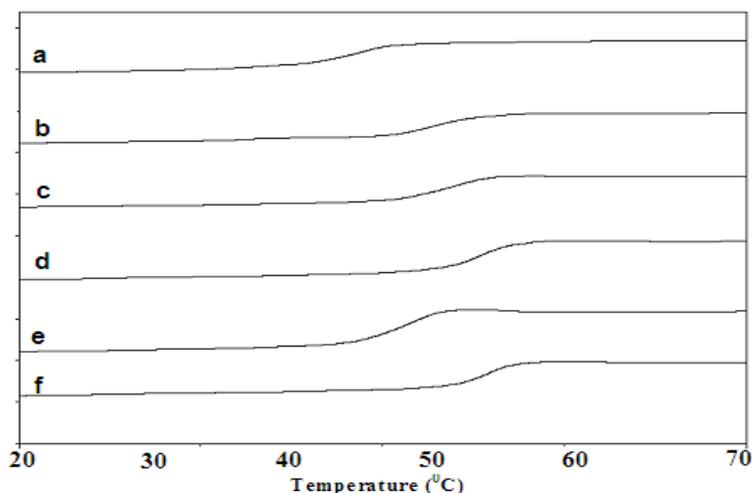


Fig. 4: DSC thermogram showing glass temperature of PLA oligomers (a) PLA-29, (b) PLA-30, (c) PLA-31, (d) PLA-32, (e) PLA-33 and (f) PLA-34

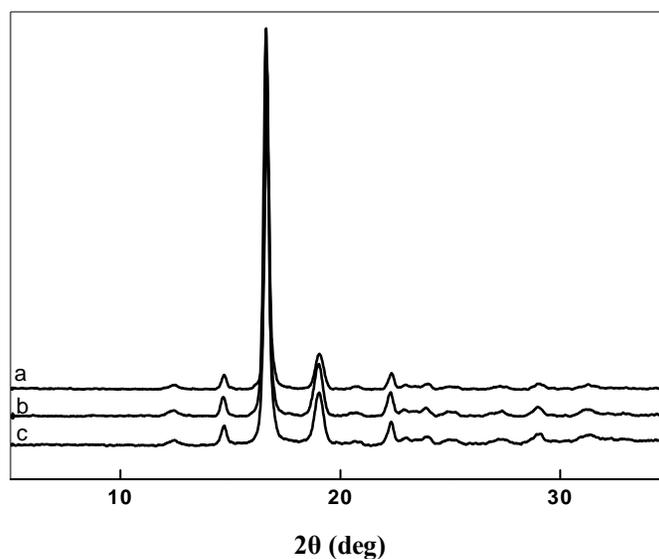


Fig. 5: XRD pattern of PLA oligomers (a) PLA-15, (b) PLA-19 and (c) PLA-20

Table 5: Effect of reaction time on the dehydropolycondensation of L-lactic acid in decaline

Polymer samples	Time (h)	Conv. (%)	\bar{M}_n (NMR)	\bar{M}_n (GPC)	\bar{M}_w (GPC)	% cryst powder (XRD)	T_m (°C)	T_c (°C)
PAL-29	1	98.8	3,900	1,700	2,900	83.0	155.0	42.2
PAL-30	2	99.0	4,770	4,500	8,000	78.0	159.8	48.5
PAL-31	3	99.1	nd	11,000	34,000	nd	139.7	49.1
PAL-32	4	99.3	4,900	18,000	35,000	76.5	152.2	54.3
PAL-33	5	99.2	nd	24,000	42,000	48.2	143.2	46.3
PAL-34	15	98.3	14,000	18,000	35,000	5.0	nd	45.3

nd- not detected and polymerization reaction temperature 190 °C.

The peak value for carboxylic acid was appeared at 172.8 ppm. The number average molecular weight (\bar{M}_n) of the polymer sample was 3,800. The PLA-25 was synthesized in mesitylene, polymerization temperature was 165 °C and reaction time was same as PLA-24. The peaks for ester carbonyl group and carboxylic end group were assigned at 169.24 to 169.57 ppm and 172.9 ppm respectively, the calculated \bar{M}_n was 10,500. The proportion of formed lactide in PLA-24 was determined by

calculating the integral ratio of peaks for lactone carbonyl and ester carbonyl, and the value was found 0.5 mol %. In the spectrum (Figure 11), PLA-27 and PLA-28 were synthesized in diphenyl ether and reaction temperature was 190 °C. The polymerization time was 1 h and 2 h respectively. Assignments for ester carbonyl ranges from 169.12 to 169.67 ppm were depicted in Table 4 and carboxylic end groups were appeared at 173.1 ppm. The calculated \bar{M}_n was 2,200 and 9,600 respectively.

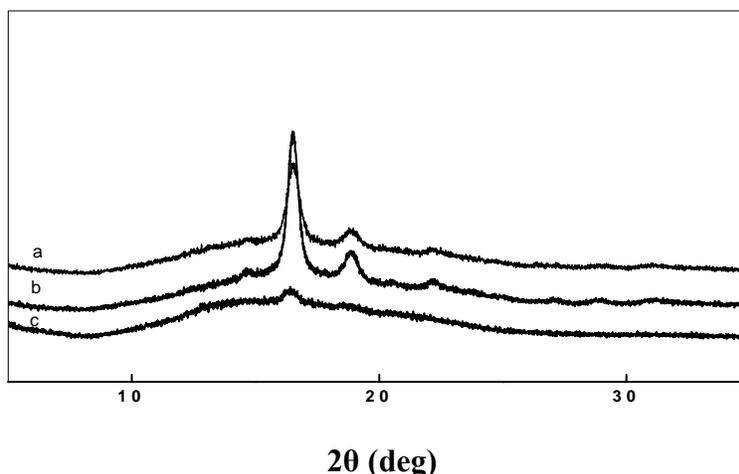


Fig. 6: XRD pattern of PLA oligomers (a) PLA-30, (b) PLA-33 and (c) PLA-34

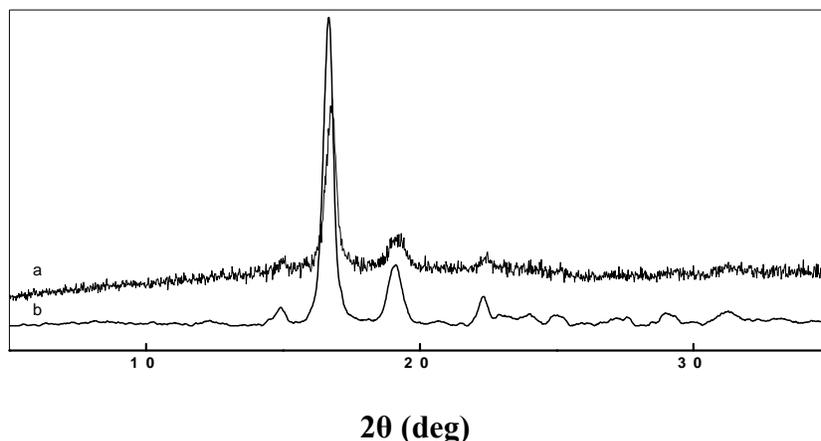


Fig. 7: XRD pattern of PLA oligomers (a) PLA-27 and (b) PLA-28

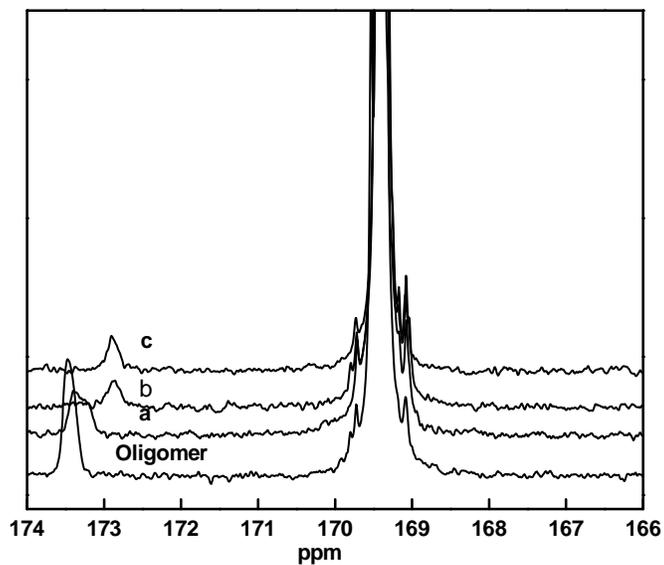


Fig. 8: ^{13}C NMR spectra (500 MHz) around carbonyl (ester), carbonyl (acid) and carbonyl (lactide) areas of PLA oligomers (a) PLA-4, (b) PLA-1 and (c) PLA-15

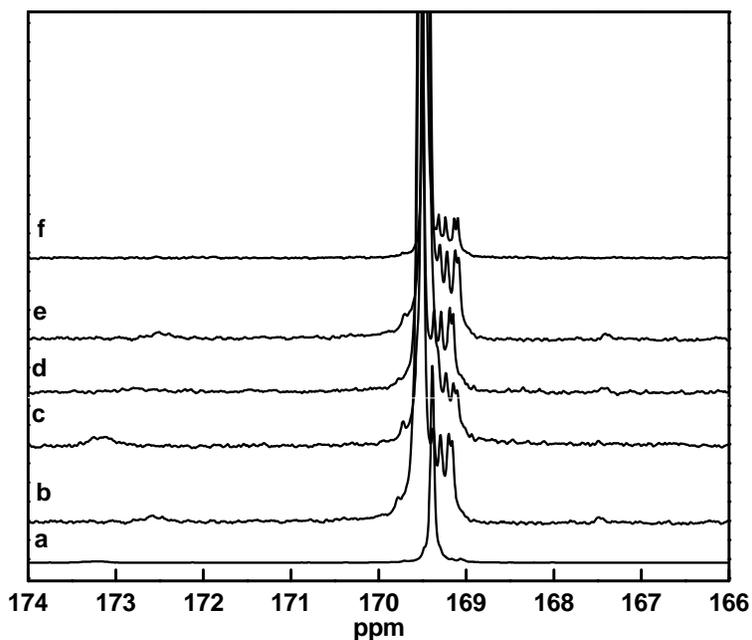


Fig. 9: ^{13}C NMR spectra (500 MHz) around carbonyl (ester), carbonyl (acid) and carbonyl (lactide) areas of PLA oligomers (a) PLA-29, (b) PLA-30, (c) PLA-31, (d) PLA-32 (e) PLA-33 and (f) PLA-34

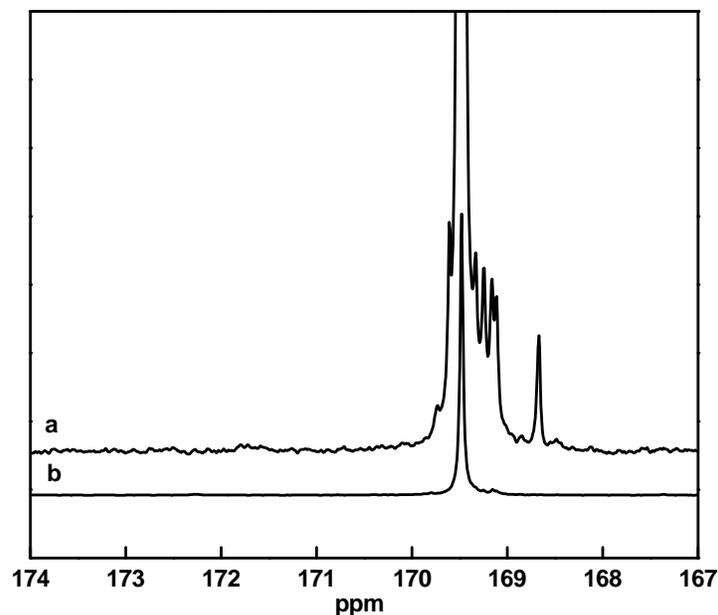


Fig. 10: ^{13}C NMR spectra (500 MHz) around carbonyl (ester), carbonyl (acid) and carbonyl (lactide) areas of PLA oligomers (a) PLA-24 and (b) PLA- 25

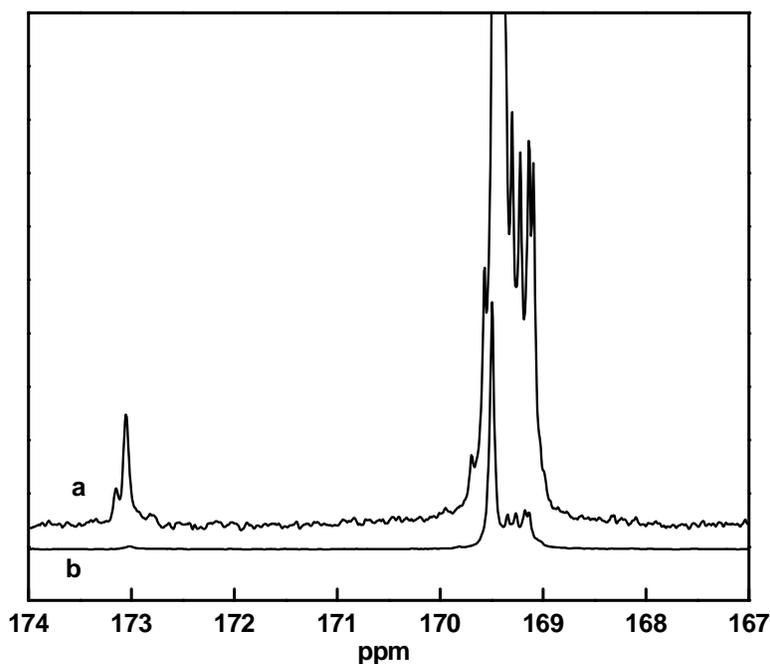


Fig. 11: ^{13}C NMR spectra (500 MHz) around carbonyl (ester), carbonyl (acid) and carbonyl (lactide) areas of PLA oligomers (a) PLA-27 and (b) PLA- 28

MALDI-TOF MS Analysis

MALDI-ToF MS technique has employed for the determination of molecular weight of synthetic polymer chains as well as determination of their end groups.¹⁴

Low molecular weight polymers (oligomers) are amenable to analysis by MALDI-ToF. The identification and quantification of end groups becomes very important if the polymer have very high molecular weight. There are several analytical

tools for end group determination techniques such as NMR, titration method etc. NMR is an accurate as well as quantitative technique.

However, it has detector sensitivity limitation. Titration (for carboxylic acid end groups) is not feasible for aliphatic polyester, which undergoes main chain hydrolysis under this condition. MALDI-ToF MS can detect all end groups and impurities with a high level of sensitivity. However, quantification is difficult by using this technique.

The result of the analysis is shown in Figure 12 reports the MALDI-ToF mass spectrum of PLA.13 The oligomer was found to contain chain terminated by $-OH$ on one side and $-COOH$ on the other. The MALDI-ToF spectrum is dominated by series of intense peaks ranging from mass 617.23 to 1769.62 Da, corresponding to sodiated adduct molecular ion of type $H-[-O-CH(CH_3)CO]_n-OH-----Na^+$, (mass. $72.0n+18+23$), where n is found to be ranging from 7 to 24 being the mass number of sodium (Na)

ion that formed the adduct molecular ion. The spectrum shows other peaks of lower intensities, which described as potassiated ions (K^+ adduct molecular ions, mass = $72.0n+18+39$, see peaks at 849, 921 and 1137 Da respectively.

Figure 13 shows the MALDI ToF spectrum of PLA-4. The most intense peak belonging to this series corresponding to oligomers with $n = 11$ to 20 in the spectrum. The spectrum also shows the potassiated ions (mass = $72.0n + 39+18$). see peaks from 1064 to 1279 Da). Figure 14 shows MALDI ToF spectrum of PLA-24 as expected and the spectrum shows a series of intense peak ranging from 832 to 1479 Da corresponds to sodiated adduct molecular ions (mass = $72.0n+18+23$), where n is found to ranging from 11 to 20. The spectrum also shows the potassiated ions (mass= $72.0n+39+18$, see peaks from 832.40 to 1493.0). The spectrum shows some other mass series of lower intensity.

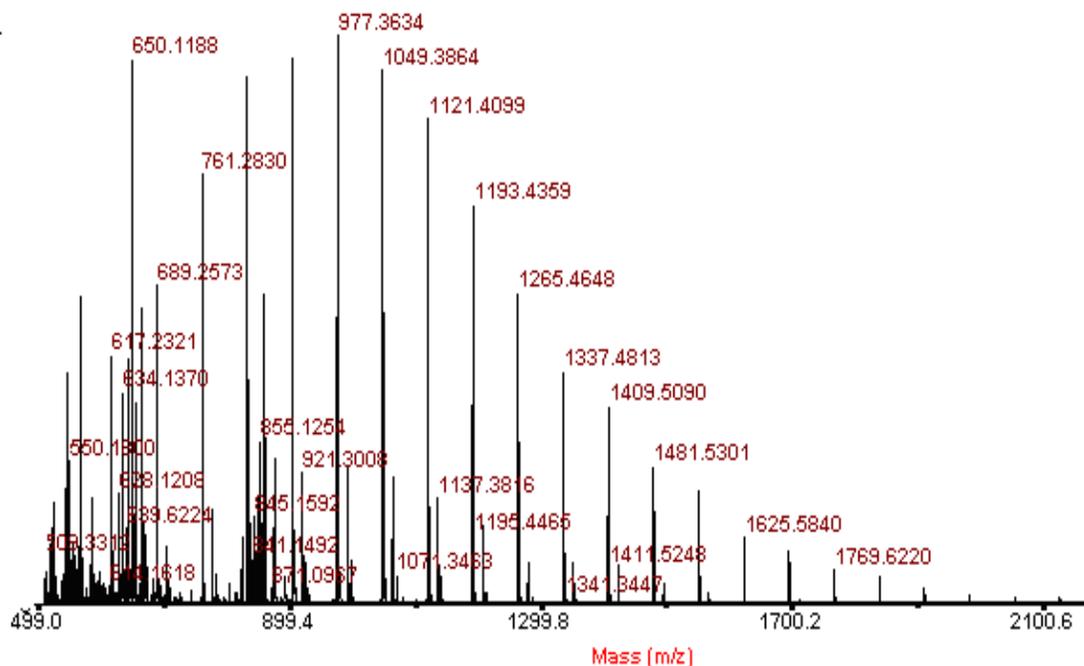


Fig. 12: MALDI ToF spectrum of PLA prepolymer

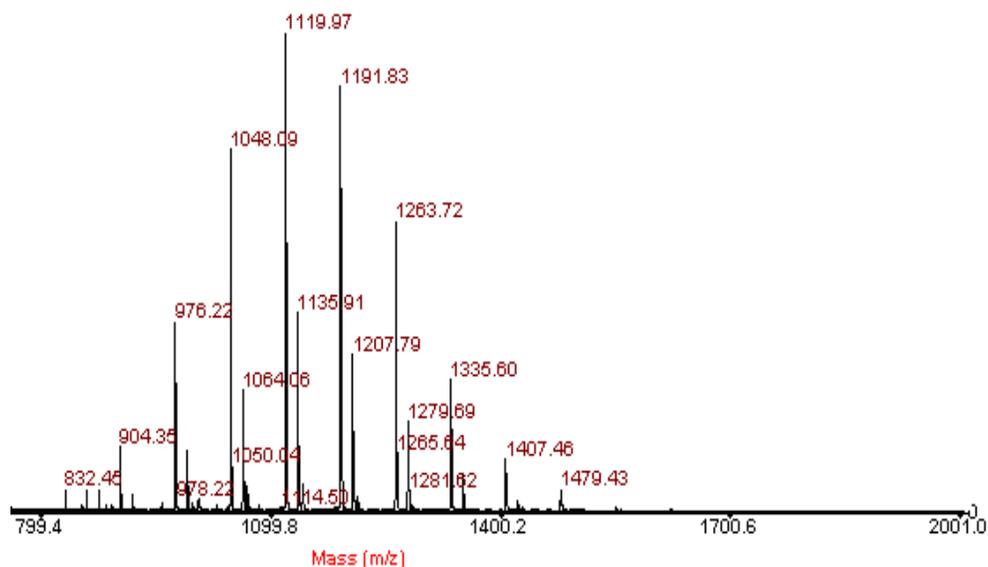


Fig. 13: MALDI ToF spectrum of PLA-4

Figure 15 shows MALDI ToF spectrum of PLA-25. The most intense peaks ranging from 526 to 1102 Da correspond to sodiated cyclic oligomer molecular ions where n range 7 to 15. The potassium ions that appear in the region from 687 to 1263 Da are also of the cyclic oligomers present in this sample. MALDI ToF mass spectrum shows a series of peaks ranging from 687 to 1335 Da correspond to sodiated

adductmolecular ions ($72n+18+23$), where n is found to ranging from 9 to 18. Some other peaks of lower intensity shows the impurity profile of lactic acid present in end groups. The MALDI ToF spectrum of PLA-26 (Figure 16) shows the intense inset ranging from 527 to 1246 Da corresponds to macrocyclic end group with sodiated molecular ions having masses ($72.0n+23$) and ($72.0n+39$), respectively.

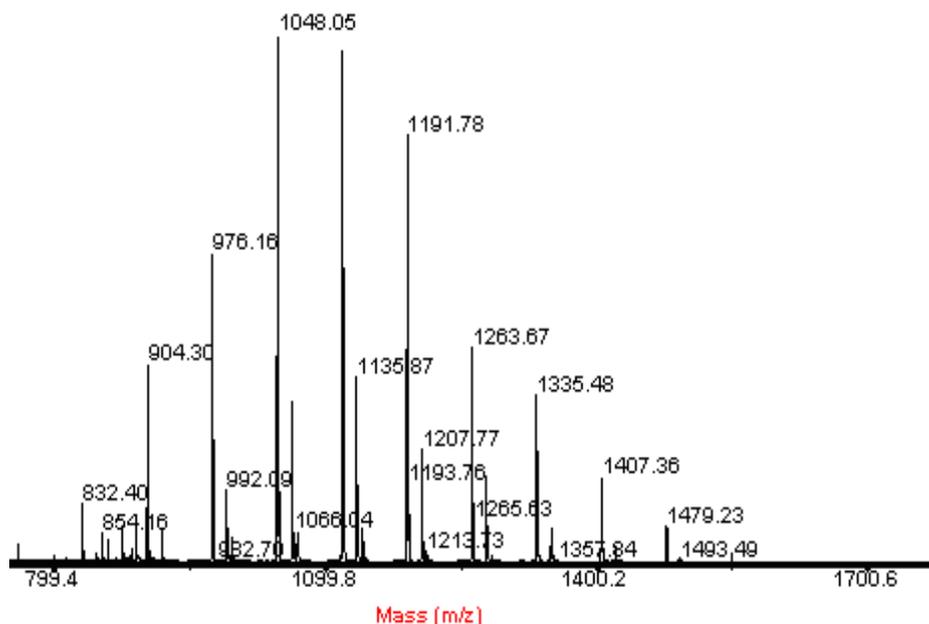


Fig. 14: MALDI ToF spectrum of PLA-24

The intensity of peaks due to cyclic compound fall sharply at higher molecular masses. The peaks ranging from 545 to 1121 is arising from sodiated molecular ions of linear polymer chains. The sample expected to be formed by oligomers bearing $-\text{COCH}_3$ and $-\text{OH}$ as terminal groups, corresponding to a general formula $\text{CH}_3\text{-CO-}[\text{-O-CH}(\text{CH}_3)\text{-CO}]_n\text{-OH---Na}^+$, shows peak in this region have molecular mass $(72.0n+60+23)$.

MALDI-TOF spectrum of PLLA oligomer (PLA-27) is shown in Figure 17. The mass spectrum of PLA-

27 have both cyclic and linear polymer molecular ions with Na^+ adduct and K^+ adduct.

MALDI-TOF spectrum of PLLA oligomer (PLA-33) is shown in Figure 18. The spectrum shows both linear and cyclic polymer chains with sodiated and potassium molecular ions having masses $(72.0n+23)$ and $(72.0n+39)$. The sample expected to be formed by oligomers bearing $-\text{COCH}_3$ and $-\text{OH}$ as terminal groups, corresponding to a general formula $\text{CH}_3\text{-CO-}[\text{-O-CH}(\text{CH}_3)\text{-CO}]_n\text{-OH---Na}^+$, shows peak in this region have molecular mass $(72.0n+60+23)$.

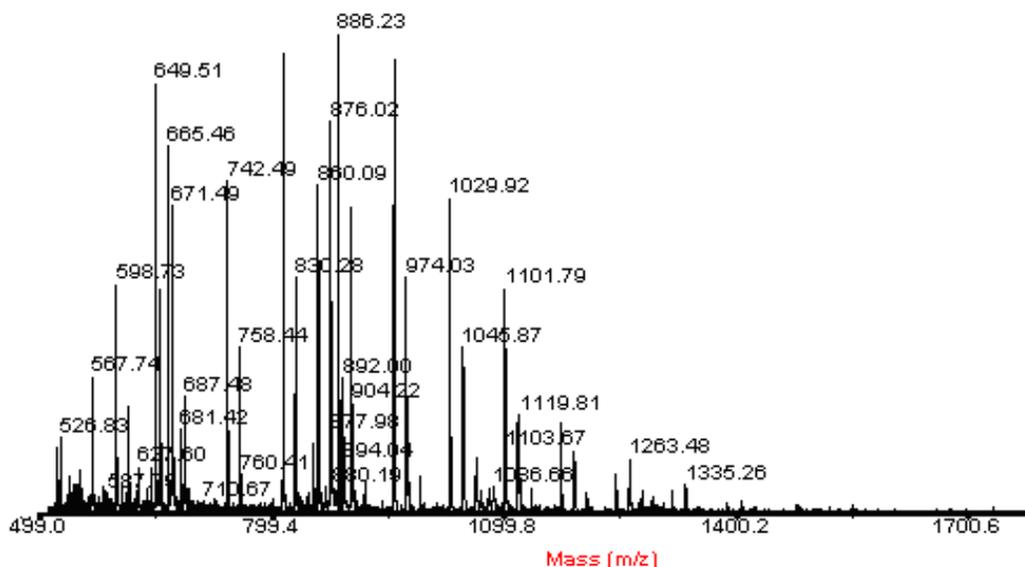


Fig. 15: MALDI ToF spectrum of PLA-25

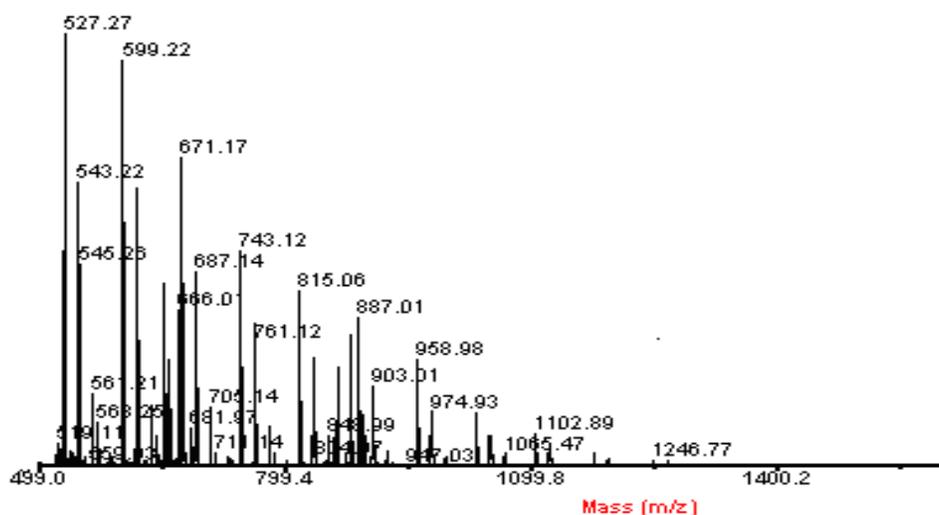


Fig. 16: MALDI ToF spectrum of PLA-34

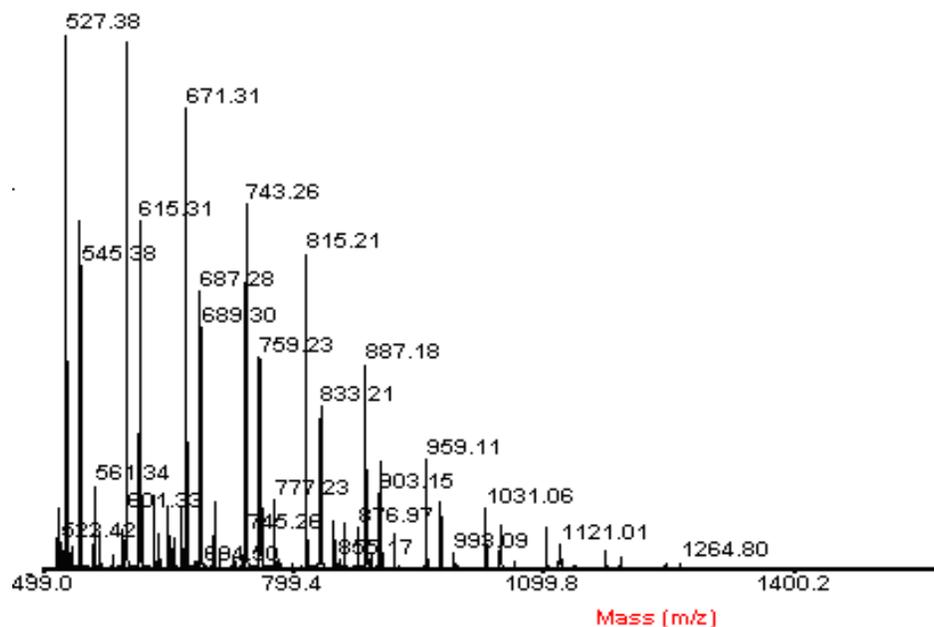


Fig. 17: MALDI ToF spectrum of PLA-27

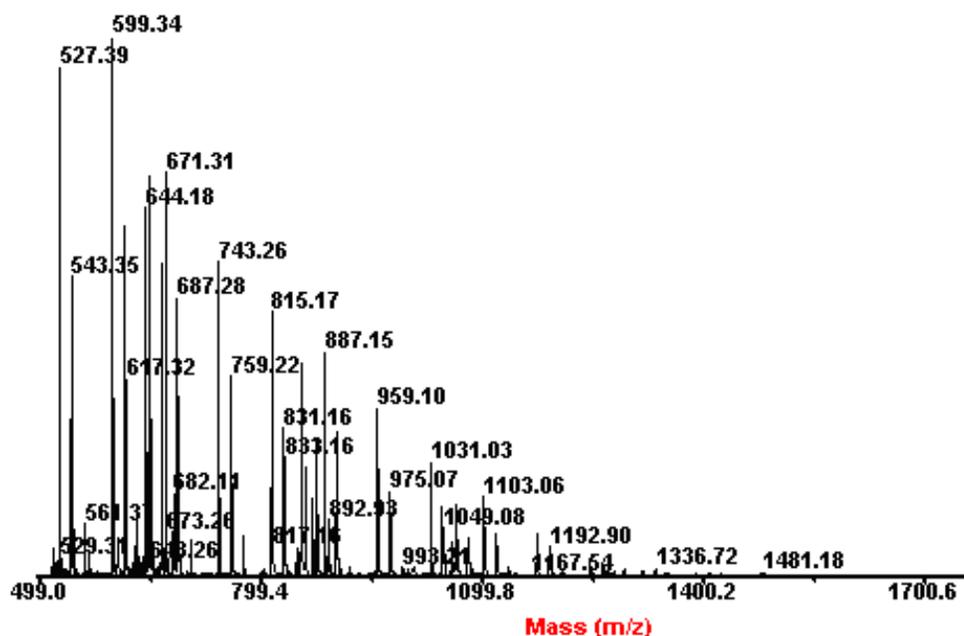


Fig. 18: MALDI ToF spectrum of PLA-33

CONCLUSION

PLA prepolymers were synthesized by direct dehydrative polycondensation using quartz reactor with Dean-Stark trap. Various types of zeolites such as ZSM-5, ZSM-12 and β -zeolite were used to reduce the small amount of water in ppm level from the reaction system (organic solvent). The longer the polymerization time (30 h), the higher the molecular weight of PLA became, because of the higher

activation energy of the polycondensation. However, the highest molecular weight was about 42,000 (\bar{M}_w) was obtained when $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was used as catalyst, β -zeolite as desiccating agent, reaction time (5 h) and reaction temperature (190°C). NMR has confirmed the absence of L-lactic acid and lactide except PLA prepared by using anisole as solvent. MALDI-TOF also confirmed the presence of linear oligomer at 143°C , mixture of linear and cyclic

oligomer at 165 °C and predominantly cyclic oligomer at 190 °C. The carbonyl carbon atoms of L-lactic acid stereo polymers are sensitive to hexads at 125 MHz, when the resolution enhancement techniques were used. It was confirmed that the mechanism of dehydropolycondensation polymerization of L-lactic acid consists primarily addition of repeating units. PLA prepared at various conditions such as using β -zeolite as a desiccant, did not change the stereosequence.

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