



CHARACTERIZATION OF POLY (LACTIC ACID) SYNTHESIZED VIA DIRECT POLYCONDENSATION WITH DIFFERENT TREATMENTS OF SnCl₂ AS A CATALYST

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ABSTRACT

Different treatments of SnCl₂ were utilized as a catalyst to synthesize poly (lactic acid) through direct polycondensation in solution. These treatments were in (i) a hydrous form (SnCl₂·2H₂O), (ii) an anhydrous form (SnCl₂) and (iii) an impregnated form (SnCl₂/γ-Al₂O₃). The polycondensation was done at 138 °C and in nitrogen atmospheric with flow rate of 100 ml/min. L-lactic acid and a catalyst (1 wt. % of l-lactic acid) were mixed in solution of m-xylene and reacted in 500 ml flask. The maximum molecular weight (Mw) of obtained poly (lactic acid) was 104,392 Da after 72 hours with catalyst SnCl₂/γ-Al₂O₃. Grafting of obtained poly (lactic acid) chains into glycerol supported by hexamethyl diisocyanate (HMDI) was successfully done. The grafted poly (lactic acid) had an average molecular weight three times higher than that of obtained poly (lactic acid). Infra-red spectra showed that the poly (lactic acid) can be produced using this synthesis technique and has molecular structure arranged mainly in amorphous phases. The maximum degree of crystallinity was found at 12.91% (DSC) or 14.56% (XRD) for obtained poly (lactic acid) with catalyst of SnCl₂/γ-Al₂O₃. These results showed that impregnation SnCl₂ on γ-Al₂O₃ enhanced its performance to polymerize l-lactic acid and able to graft it into glycerol.

Keywords: characterization, synthesis, poly (lactic acid), polycondensation, catalyst.

INTRODUCTION

Recently, much attention was devoted by researchers to accomplish the increasing bio-plastic demand, especially poly (lactic acid). Their investigation covered the three steps to produce desired properties of poly (lactic acid), namely: fermentation or hydrothermal reaction of biomass and separation, polymerization and modification. Poly (lactic acid), an aliphatic polyester, has been widely used in many applications due to its mechanical properties, transparency and UV light barrier can be compared to conventional polymer [1].

Lactic acid as monomer poly (lactic acid) exists in two stereo isomers: l-lactic acid and d-lactic acid [2]. Both of them affected in poly (lactic acid) properties significantly [3]. Poly (lactic acid) can be synthesized through direct polycondensation of lactic acid and ring opening polymerization (ROP) of lactides. Direct polycondensation is a one-step process and more economical method than ROP. The optimization condition process of this method was reported by researchers, such as: catalyst, temperature, time and pressure [4, 5]. The main factor affected in polycondensation is the equilibrium between free acids, water and obtained polyesters. The presence of water is preventing the reaction to produce high molecular weight of poly (lactic acid). To optimize the obtained poly (lactic acid), removing water efficiently is needed during the polycondensation process. Thus, the apparatus is absolutely designed to resolve this problem. Besides that, the use of solvent during the polycondensation was also making easier to remove water due to it decreased the solution viscosity. Marques *et al.* [6] reported that the use

of high boiling point of solvent was efficiently removing produced water.

Stannous chloride as a catalyst in polycondensation was proven to allow achieving high molecular weight of poly (lactic acid) [5, 7]. Moon *et al.* [4] optimized this catalyst performance through screening various metal-alkoxides as co-catalysts. The result showed that Ti(OⁱPr)₄ as the co-catalyst of SnCl₂·2H₂O was allowing poly (lactic acid) with average molecular weight of 57000 g/mole with low yield (38%). In another investigation, stannous chloride was activated by various proton acids [8]. The stannous chloride activated by *p*-toluene sulfonic acid (TSA) was allowing average molecular weight of 43000 Da with high yield (95%). It can be highlighted that the performance of catalyst can be achieved by different treatments. Both activation and impregnation are well acknowledged to improve the catalyst performance. Thus, it is needed to investigate the performance of treated catalyst in direct polycondensation.

Poly (lactic acid) has two active end-groups, acid (-COOH) and hydroxyl (-OH), which make it feasible to be copolymerized or grafted with other chains. Wang *et al.* [9, 10] succeeded to copolymerize poly (lactic acid) with glycolic acid and ethylene glycol via direct melt polycondensation. These copolymers enhanced the hydrophilicity and biodegradability of poly (lactic acid).

Glycerol has three hydroxyl groups. This group gives an opportunity to be substituted with the other groups. The hexamethyl diisocyanate (HMDI) was proven its performance as a chain extender of poly (lactic acid) [11]. Diisocyanate groups (CNO) can react with hydroxyl groups by forming urethane bonds. The glycerol can be



prepared as a backbone by reacting hydroxyl group of glycerol and isocyanate group of HMDI. By preparing glycerol as active sites of backbone, poly (lactic acid) can be attached in and the average molecular weight of the copolymer could be expected three times than that of poly (lactic acid).

This article reports the characterization of poly (lactic acid) and graft copolymer of glycerol-g-poly (lactic acid) synthesized via direct polycondensation with solvent of *m*-xylene and treated catalyst of SnCl₂. The three different treatments of stannous chloride in this investigation were in a hydrous form, an anhydrous form and an impregnated form. Further, the molecular weight, molecular structure and thermal properties of poly (lactic acid) were investigated. The purification method of obtained poly (lactic acid) was analyzed by x-ray diffraction (XRD).

EXPERIMENTAL PART

Materials

Monomer *l*-lactic acid in 88-92% aqueous solution was kindly supplied by Scharlau (Spain) with density of 1.20 (20^o/4^o). *M*-xylene (96%), glycerol and chloroform were ordered from Sigma Aldrich. Methanol AR (99.5%) was purchased from Avonchem (UK). Stannous (II) chloride dihydrate (98%) and activated gamma alumina (γ-Al₂O₃) were ordered from LOBA Chemie (India) and Strem chemicals (USA), respectively. PLI003, a commercial name of poly (lactic acid) was kindly supplied by NatureplastTM (France). Characteristics of PLI003 are transparent, density of 1.25 g/mL and melt flow index (MFI) of 12-20 g/10 mins (190 °C/2.16 kg) as reported by supplier. Further, all chemicals were used in this investigation without any purification.

Preparation of catalysts

The three different treatments of stannous chloride were prepared as follows: (i) A hydrous form: the stannous chloride AR from the supplier is in a hydrous form (SnCl₂·2H₂O). Further, this catalyst form was called as a precursor. Without any purification and treatment, it was directly used as the catalyst in the direct polycondensation. (ii) An anhydrous form: the anhydrous form was obtained by placing the amount of SnCl₂·2H₂O to oven at 120 °C for 5 hours. In this process, hydrates (two water/H₂O molecules) could be removed and the catalyst became in an anhydrous form (SnCl₂). (iii) An impregnated form: the impregnation treatment was carried out by impregnating gamma alumina (γ-Al₂O₃) support with SnCl₂·2H₂O. The composition of precursor is 10 wt% to the catalyst support. In this treatment, the precursor was dissolved in distilled water and then, mixed with the support properly. The mix of catalyst and its support was dried at 120 °C for 4 h prior to be calcined at 600 °C for 5 h [12].

Preparation of backbone

The backbone was prepared by reacting 1 mole glycerol and 3 mole hexamethyl diisocyanate. This reaction is carried out for 2 hours at 80 °C. The schematic of this reaction as follows:

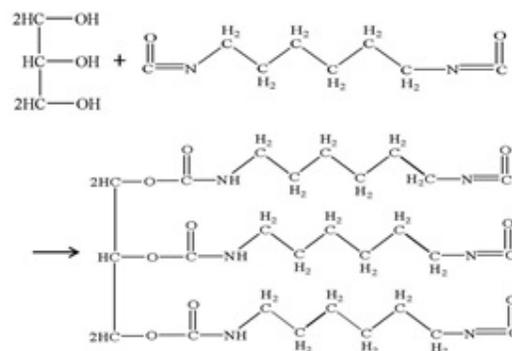


Figure-1. Reaction scheme of attaching isocyanate of HMDI chains into glycerol.

Then, the other end-isocyanate groups will be reacted with hydroxyl groups of synthesized poly (lactic acid) for certain reaction times at 138 °C.

Synthesis

The synthesis of poly (lactic acid) was performed in the 500 ml round bottom three necked flask equipped with a dean stark trap, a capillary inlet for nitrogen and a thermocouple. The initial concentration of *l*-lactic acid was 150 gr in 200 ml of solution. The catalyst was introduced about 0.1 wt% (calculated according to the amount of *l*-lactic acid) and the rotation speed of a stirrer was set at 150 rpm. Reaction temperature was controlled at boiling point of *m*-xylene as solvent (138 °C) using a heating bath above heat magnetic stirrer RCT basic IKAMAG (USA). During the reaction, nitrogen gas was flowed with rate of 100 ml/min in atmospheric pressure.

For each reaction time (24, 48 and 72 h), chloroform was poured into the mixture to isolate the catalyst and discard it. Then, the resulting mixture was added into methanol. Precipitated poly (lactic acid) was collected by filtration, dried and obtained white powder was characterized its molecular weight and structure, intrinsic viscosity and thermal properties.

For graft copolymerization, poly (lactic acid) was first synthesized for 24 h using SnCl₂/γ-Al₂O₃ as a catalyst with conditions as mentioned earlier. Then it was mixed with the glycerol as a backbone after reacted with hexamethyl diisocyanate. The molar ratio between backbone and poly (lactic acid) is 1:3.

Characterization

Average molecular weight (Mw) was determined by an Alliance GPCV 2000 (Waters, US) at 30 °C. Tetrahydrofuran (THF) as mobile phase was set at flow rate of 1 ml/min. The calibration curve was obtained from polystyrene standards. The infrared spectra were recorded



using a Vertex 70 (Bruker, Germany). Scanning was performed 32 scans at a resolution of 4 cm^{-1} for each sample and then, collected and averaged as the result data of FTIR.

Thermal properties of obtained poly (lactic acid) was performed using a Shimadzu DSC60 (Japan) with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. X-ray pattern was determined using a XMD 300 (Unisantis, Germany) with Cu-K α radiation (wavelength, $\lambda=1.5406\text{ \AA}$), operated at 45 kV and 0.8 mA. The scanning rate was operated at $0.16^{\circ}/\text{sec}$ with angle scanning from 5 to 80° .

Determination of viscosity was measured using viscometers Cannon-Fenske with type of 520 00 and k constant of 0.002061 (Schott Geräte, Germany). The intrinsic viscosity $[\eta]$ was determined in chloroform ($c=2\text{ g/dl}$) at $25\text{ }^{\circ}\text{C}$ and calculated using a single-point determination, namely: Solomon-Cuita equation [13] as presented in equation (1):

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \quad (1)$$

Where $\eta_r = t/t_0$ and $\eta_{sp} = \eta_r - 1$ are the relative and the specific viscosity, respectively. c is the concentration of poly (lactic acid). Further, the viscosity molecular weight (M_v) of poly (lactic acid) was calculated using Mark-Houwink-Sakurada relation [13] as presented in equation (2):

$$[\eta] = K \bar{M}_v^a \quad (2)$$

Where K is the parameter related to the stiffness of the chain and a is representing the type of polymer, solvent and temperature.

RESULTS AND DISCUSSION

Molecular weight

Three different treated catalysts were utilized for polycondensation of lactic acid. The performance of these catalysts with various times was summarized in Table 6.1 with average yield of 85%. It can be seen that increasing reaction time resulted in higher molecular weight of obtained poly (lactic acid). For example: average molecular weight increased from 4,459 to 18,121 and 21,083 Da when reaction time was increased from 24 to 48 and 72 hrs with precursor $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as a catalyst. This phenomenon was also occurred in the other catalysts. The increasing of Mw was still ongoing during the time range of 24-72 hrs at reaction temperature of $138\text{ }^{\circ}\text{C}$. Exhibiting the decomposition of poly (lactic acid) has not occurred. In a contrary, Bai and Lei [14] reported the decomposition occurred in reaction time over than 13 hrs with reaction temperature of $180\text{ }^{\circ}\text{C}$. Kim and Woo [5] also reported the decomposition of obtained poly (lactic acid) that addressed by the decreasing rapidly of Mw at reaction temperature of $154\text{ }^{\circ}\text{C}$ over 48 hrs. Although, the polymerization rate in this temperature was faster than that at $138\text{ }^{\circ}\text{C}$. It can be

highlighted that temperature not only stimulates the polymerization but also the decomposition of obtained poly (lactic acid).

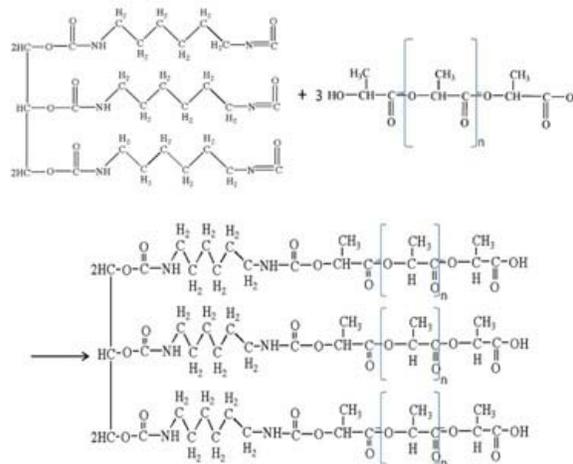


Figure-2. Schematic graft copolymerization of glycerol-glycol (lactic acid).

Based on average molecular weight, impregnation of SnCl_2 on $\gamma\text{-Al}_2\text{O}_3$ had a good performance as a catalyst in direct polycondensation. For reaction time of 72 hrs, the Mw of poly (lactic acid) closed relatively to the commercial one (PLI003). And also, the average polydispersity index (PDI) was lower than the others. It could be explained that $\gamma\text{-Al}_2\text{O}_3$ as the support catalyst was giving the stability of SnCl_2 during the polycondensation at 138°C . This statement was confirmed with another investigation that the selection of appropriate supports would keep the stability of catalyst and also enhance its performance [12].

The graft copolymerization of PLA31 into glycerol backbone produced the graft poly (lactic acid) with Mw of 110,054 Da (see PLAG1 in Table-1). This result was also found in the graft copolymer PLAG2. It has Mw about three times higher than that of PLA32. This indicated that the attaching poly (lactic acid) chains into the backbone were done successfully. The molecular structure of the graft copolymer can be depicted in Figure-2. This structure will be proven later in the FTIR section

The intrinsic viscosity was calculated using Solomon-Cuita equation (Equation.1). This equation is a simple and more suitable for fast determination. The intrinsic viscosity data (see Table-1) was taken from average values of three measured viscosity. Mello *et al.*[13] employed this equation and showed that the results were not much different than those calculated by graphic extrapolation. Furthermore, the intrinsic viscosity ($[\eta]$) data employed to estimate the viscosity molecular weight (M_v) of poly (lactic acid) using Mark-Houwink-Sakurada relation (Equation. 2). The parameters of 'K' and 'a' for poly (lactic acid) in chloroform at 25°C are 5.45×10^{-4} and 0.73, respectively [15, 16].



Table-1. Polycondensation processes and characterization of obtained poly (lactic acid).

Sample	Catalyst	Time h	Product				
			M_w^a	PDI ^b	$[\eta]^c$	M_v^d	Appearance
PLA11	SnCl ₂ , 2H ₂ O	24	4,459	1.8	0.23	3,948	white powder
PLA12	SnCl ₂ , 2H ₂ O	48	18,121	2.6	0.69	17,780	white powder
PLA13	SnCl ₂ , 2H ₂ O	72	21,083	2.6	0.74	19,568	white powder
PLA21	SnCl ₂	24	9,794	1.9	0.39	8,138	white powder
PLA22	SnCl ₂	48	21,965	2.4	0.76	20,296	white powder
PLA23	SnCl ₂	72	44,193	2.3	1.31	42,789	white granule
PLA31	SnCl ₂ / γ -Al ₂ O ₃	24	36,425	1.8	1.13	34,946	white powder
PLA32	SnCl ₂ / γ -Al ₂ O ₃	48	78,774	1.7	2.00	76,394	white granule
PLA33	SnCl ₂ / γ -Al ₂ O ₃	72	104,392	1.5	2.48	102,573	white granule
PLAG1 ^e	SnCl ₂ / γ -Al ₂ O ₃	24	110,054	1.7	2.57	107,707	white granule
PLAG2 ^e	SnCl ₂ / γ -Al ₂ O ₃	48	195,795	1.6	3.65	174,162	white granule
PLI003 ^f	-	-	146,059	1.4	3.11	139,863	transparent pellet

^a Average molecular weight determined by GPC

^b Polydispersity index (PDI) determined by GPC

^c Intrinsic viscosity calculated by Solomon-Ciuta equation

^d Viscosity molecular weight calculated by Mark-Houwink equation

^e Graft copolymer of poly (lactic acid) and glycerol

^f Poly (lactic acid) from commercial market.

As presented in Table-1, the increasing molecular weight of poly (lactic acid) by reaction time was always followed by an increase of the intrinsic viscosity. It could be explained that intrinsic viscosity was reflecting the contribution of solute to the viscosity of solution. Thus, the higher molecular weight which also has longer chains would greatly affect to the intrinsic viscosity. Comparison between the average molecular weight (M_w) obtained by GPC and the viscosity molecular weight (M_v) obtained by viscometry also can be seen in Table-1 and it has a similar tendency.

The appearance of obtained poly (lactic acid) was in the form of white powder or granule. The granule form was found in average molecular weight more than 42,789 Da. The solubility test of products showed that they had a similar tendency to dissolve in nonpolar solvent, like: chloroform. Further, the pouring ethanol into poly (lactic acid) solution gradually exhibited the presence of fractional sedimentation. Probably, it was due to the various molecular weight of obtained poly (lactic acid). This result was also confirmed from the polydispersity index (PDI) as presented in Table-1. The PDI of all synthesized poly (lactic acid) was about 2.

Table 6.1 also showed that the obtained poly (lactic acid) has lower average molecular weight (M_w) than that of the commercial one. The highest M_w was

104,392 Da closing to the commercial one (146,059 Da), relatively. It was obtained by using SnCl₂/ γ -Al₂O₃ as a catalyst for 72 hrs. Generally, low grade of poly lactic acid was obtained in this investigation due to its molecular weight. It may be unsuitable for application which requires high mechanical strength such as: for packaging application, etc. However, this product has high biodegradation rate which can be used in a polymeric drug delivery system.

Molecular structure

Figure-3 shows the infrared (IR) spectra of obtained poly (lactic acid) with different treatments of catalyst in the same reaction time (72 hours). The similar IR spectrum of samples was obtained that indicating the same of their molecular structure. The absorption band data of obtained poly (lactic acid) was summarized in Table-2. The hydroxyl group (-OH) appeared in weak intensity as showed at wave number 3568 cm⁻¹. It indicated that the presence of the hydroxyl group was diminishing due to the polymerization process.

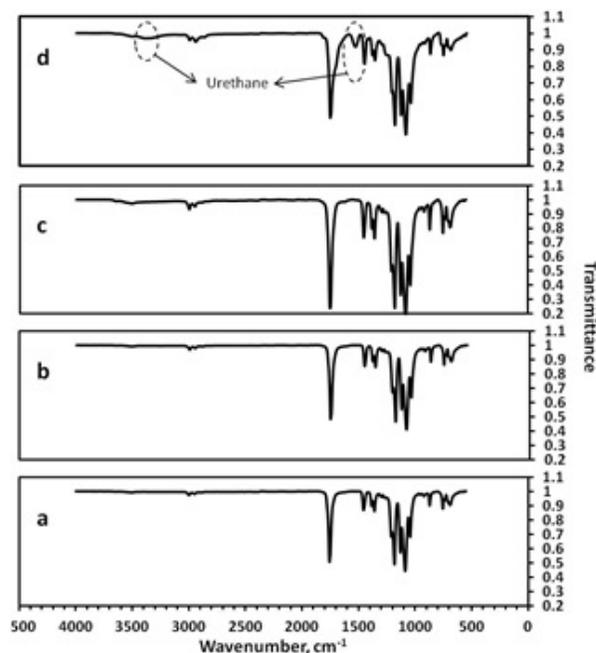


Figure-3. Infra-red spectra of obtained poly (lactic acid) and with different treatment of catalyst and copolymer poly (lactic acid): (a) PLA13, (b) PLA23, (c) PLA33 and PLAG1.

The methyl group as stretching -CH- appeared at 2997 and 2946 cm⁻¹ with different intensity. The intensity in these wave numbers was becoming stronger from Figure-3(a) to 6.3(c). It could be explained that the stronger intensity showed more the presence of stretching -CH- in samples. Later, this phenomenon would be confirmed with average molecular weight (M_w) of samples.



The presence of a carboxyl group was detected in the wave number of 1756 cm^{-1} as stretching $\text{C}=\text{O}$. Those three groups exhibited that poly (lactic acid) can be obtained via direct polycondensation of lactic acid. For sample PLAG1 as a copolymer glycerol-g-poly (lactic acid), an $\text{C}-\text{NH}-$ stretching peak was monitored at 3325 and 1580 cm^{-1} which clearly show the formation urethane linkage. This statement was also supported by Garlotta [17] and Khan *et al.* [18] in their investigation and presented in Table-2. The presence of the urethane group indicated that the synthesized poly (lactic acid) could be attached to the backbone as depicted in Figure-2.

Based on Younes and Cohn report [19], the crystalline or amorphous phase of poly (lactic acid) can be determined from the wave number of $\text{C}-\text{C}-$ bond. The obtained poly (lactic acid) in this investigation was in amorphous phase due to the $\text{C}-\text{C}-$ bond was found in the wave number around of 869 cm^{-1} . This result was confirmed by X-ray diffraction to elaborate its crystallinity degree.

Table-2. Comparison of absorption band between poly (lactic acid) from this synthesis, Garlotta's and Khan's report.

Wave number of poly (lactic acid)		Chemical bonding	Mode	Notification
Synthesis	Garlotta [17]			
3568	3571	OH	Stretching	Weak intensity
3325 ^(a) [18]		$\text{C}-\text{NH}-$	Stretching	
2997, 2946	2995, 2944	CH	Stretching	asymmetric, symmetric
1756	1759	$\text{C}=\text{O}$	Stretching	
1580 ^(a)		$\text{C}-\text{NH}-$	Stretching	
1455	1453	CH_3	Bending	
1383, 1360	1382, 1362	CH	Deformation	asymmetric, symmetric
1278	1268	$\text{C}=\text{O}$	Bending	
1210, 1183, 1131	1194, 1130, 1093	$\text{C}-\text{O}-$	Stretching	
1088, 1044	1047	OH	Bending	
871	926, 868	$\text{C}-\text{C}-$	Stretching	

^(a) It is only found in copolymer glycerol-g-poly (lactic acid) that refers to urethane linkage [18]

Explicitly, Figure-3 and Table-2 showed that there are no wave numbers for the catalyst. Indicating the catalyst can be removed properly from product by extraction as employed in this investigation. When chloroform added in obtained poly (lactic acid) solution, it only dissolved the poly (lactic acid) and abandoned the catalyst crystal. Thus, it was easy to discard catalyst from the poly (lactic acid) solution.

Thermal characterization

The thermal characteristics of some obtained and commercial poly (lactic acid) are shown in Table-3. The temperature range which analyzed in this investigation is between 25 to $200\text{ }^\circ\text{C}$ with heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) of PLA13 was not detected while the others varied from 43.5 to $46.5\text{ }^\circ\text{C}$. Explicitly, poly (lactic acid) which has higher average molecular weight, it has also higher glass transition temperature. This phenomenon was also stated by Hiltunen *et al.* [20]. For PLA13, the disappearance of T_g may be due to its T_g is lower than the temperature range of the heating scan (25 - $200\text{ }^\circ\text{C}$) or this product is very brittle.

From Table-3, the enthalpy of melting (ΔH_m) is increasing as well as the degree of crystallinity increases. It can be explained that the melting peak shows a condition which the existing crystalline structure of polymer is destroyed. Thus, it is requiring more energy to melt the higher crystallinity of sample. Flory and Vrij [21] explained that increasing degree of polymerization (molecular weight) correlates with higher melting temperature. It was also occurred as presented in Table 3 that melting temperature is improving as well as the average molecular weight increases.

Table-3. Thermal characteristics of obtained and commercial poly (lactic acid).

Sample	T_g^{\pm} 2%	T_{cc}^{\pm} 2%	ΔH_{cc}^{\pm} 1.5%	T_m^{\pm} 2%	ΔH_m^{\pm} $\pm 1.5\%$	X_c^d	
						DSC	XRD
PLA13	ND ^e	89.4	29.44	131.8	-32.05	2.79	4.21
PLA23	43.5	97.6	32.13	146.9	-39.76	8.14	9.73
PLA33	44.6	96.9	31.22	154.9	-43.32	12.91	14.56
PLAG1	44.5	98.2	27.02	160.4	-40.43	14.32	15.53
PLI003	46.5	102.9	29.79	170.1	-49.27	20.79	21.89

^a Glass transition temperature, $^\circ\text{C}$

^b Cold crystallization temperature (T_{cc} , $^\circ\text{C}$) and cold crystallization enthalpy (ΔH_{cc} , J/mol)

^c Melting temperature (T_m , $^\circ\text{C}$) and melting enthalpy (ΔH_m , J/mol), the negative sign refers to the endothermic peak and ignored in the calculation of crystallinity.

^d Degree of crystallinity (%) obtained by calculation using DSC data and analysis of XRD diffractograms using a software Xpovder ver. 2004.04.08 PRO.

^e ND = Not detected

The appearance of cold crystallization peak during the heating scan, indicating the poly (lactic acid) undergoes rearranging the amount of crystalline structures in amorphous phase. Thus, the calculation degree of crystallinity was not neglecting this peak. The equation can be seen in our previous work [22]. The minimum and maximum degree of crystallinity was found at 2.79 and 14.32% for PLA13 and PLAG1, respectively. Compared



to the commercial one, the obtained poly (lactic acid) is more amorphous.

Comparison degree of crystallinity obtained from DSC and XRD was also seen in Table-3. The values of crystallinity calculated from XRD were always higher than those calculated from DSC (Table-3). This attributed to the difference scanned areas of the same sample. XRD diffractograms just scanned the sample surface, while the DSC evaluated the bulk crystallinity. Therefore, the crystallinity values of XRD scan were strongly influenced by the compaction process of powder samples. It provoked morphology of surface and shear zones, thus leading to higher crystallinity, as a result of the orientation.

X-ray diffraction was performed on different zones of each sample. Figure-4 shows the XRD scans of obtained poly (lactic acid) in the range of $2\theta = 10- 80^\circ$. The poly (lactic acid) shows major diffraction peaks at $2\theta = 16.4^\circ$ ascribed to the crystal planes (2-0-0) or (1-1-0), indicating that the crystal of PLA has the typical orthorhombic structure. Another less intense peak also appeared at $2\theta = 18.6^\circ$ corresponded to the crystal plane (2-0-3). This also indicates that the crystal structure is also orthorhombic. The similar result was also reported by other [23, 24].

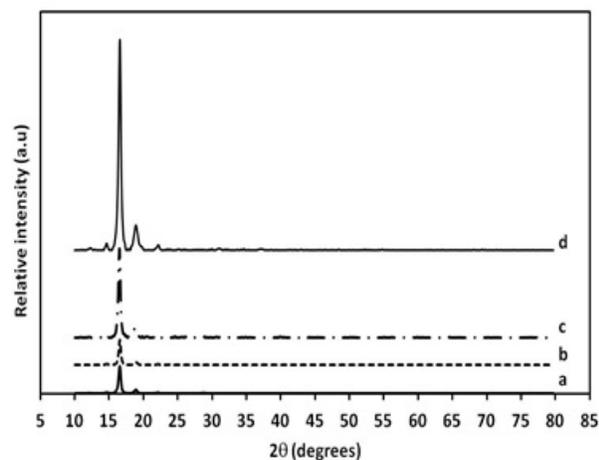


Figure-4. Typical x-ray diffraction scans of obtained poly (lactic acid): (a) PLA13, (b) PLA23, (c) PLA33 and (d) PLAG1.

CONCLUSIONS

High molecular weight of poly (lactic acid) can be synthesized by direct polycondensation in solution with average yield of 85%. The performance of catalyst during the polycondensation was significantly affecting the obtained poly (lactic acid). Impregnation of SnCl_2 on $\gamma\text{-Al}_2\text{O}_3$ showed a better performance to produce high molecular weight (Mw) and low polydispersity index (PDI) than other treatments. This catalyst was also successfully employed to graft obtained poly (lactic acid) chains into glycerol as a backbone. The extraction method using chloroform was a proper technique to remove the catalyst from the product. Characterization of samples

showed the obtained poly (lactic acid) was more amorphous and lower molecular weight than those of commercial one. Due to the low molecular weight, the application of obtained poly (lactic acid) was restricted by lack mechanical properties.

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