The production poly(L-lactic acid) from direct polycondensation in mass scale

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Abstract— *To investigate the potential to produce poly(L-lactic acid), PLLA from direct polycondensation and solid state polymerization, SSP in mass scale, PLLA were synthesized via direct polycondensation and SSP in both lab and mass scale. The synthesized PLLA from both lab and mass scale shows the comparable melting temperature, T_m and MW at the similar polymerization conditions. The appearances of synthesized PLLA are yellow-white solid powder. Thus there are high potential to produce PLLA from new process which is environmental friendly and non-complex facilities process.*

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Keywords— poly(L-lactic acid), mass scale production, direct polycondensation, solid state polymerization

1. INTRODUCTION

Recently, many countries and state are banning petroleum based plastic grocery bags due to its non-degradable in environment, so biodegradable polymer has attracted much attention as the biodegradable plastic bag for the replacement of petroleum based plastic bag. Polyesters such as polyhydroxyalkanoates (PHA), polyhydroxybutyrates (PHB) and polylactic acid (PLA) play a predominant role as biodegradable plastics due to their potentially hydrolysable ester bond [1]. Poly(L-lactic acid) PLLA is widely used to produces the biodegradable plastic bag, since the raw materials can be produced on a mass scale by the microbial fermentation of agricultural by products mainly the carbohydrate rich substances. PLA have the outstanding mechanical properties over other biodegradable polyester and in absence of enzymes or catalyst, PLLA degrade to lactic acid by simple hydrolysis[2]. In commercial production of PLLA is performed by using the ring opening polymerization (ROP) of the dimmer of L-lactic acid, L-lactide. The synthesized PLLA from ring opening polymerization of lactide, a process that uses catalysts such as tin, zinc, aluminum and lead, initiators such as n-, sec- and tert-butyl lithium, and solvent such as diphenyl ether, toluene and chloroform. Many of these components are toxic or flammable. As a result, this process requires purification to remove the unwanted materials from the product, which requires complex facilities [3]. The alternative route to produced PLLA is the direct polycondensation of L-lactic acid or oligomer of PLLA. However the synthesis of high molecular weight PLLA by this method is considered to be difficult, because of instability of the lactic acid oligomer and the difficulty in removing the water produced in the polymerization, which can encourage the depolymerization [4, 5]. Thus, PLLA synthesized with the organic solvent and via melt-solid polymerization have been investigated.

In this present work, PLLA was synthesized via direct polycondensation and solid state polymerization in lab and mass scale to determine the potential of produce PLLA via environmental friendly and non-complex facilities process. The thermal properties and ^{1}H-NMR of synthesized PLLA from both scales were investigated.

2. METHODOLOGY

Materials

L-lactic acid (Galactic) with a monomer concentration of 90% w/w was used as received. p-Toluenesulfonic acid, PTSA was used as catalyst and used as received. Chloroform was used as the eluent in gel permeation chromatography (GPC). The polystyrene standard for GPC calibration was supplied by Sigma Aldrich Chemical Co. (USA).

Synthesis of PLLA

In this work PLLA were synthesized by direct polycondensation polymerization to obtain the PLLA oligomer and further polymerization by solid state polymerization to obtain high molecular weight PLLA.

Lab scale

Direct polycondensation polymerizations were conducted in 25 ml custom made test tube with a mechanical stirrer and condenser connected to an inline cold trap and a vacuum pump. Thermometer was used to measure the exterior oil temperatures of the test tube. The reactor pressure was measured and controlled by vacuum controller (VCN500, OKANO). The pressure in the reactor was lower incrementally using a vacuum pump (G-50DA, ULVAC-KIKO).

Five grams of L-LA and 0.5%w/w of PTSA were added to reactor (test tube), PLLA was synthesized by direct polycondensation (DP) through three operations: distillation, oligomerization and polymerization. The temperature and pressure during the polymerization were precisely controlled at 150 ^{o}C 30 torr for 4 hr. At the end of the reaction, the products were poured in the plastic tube and allowed to cool to room temperature. After solidification, the product was grinded and annealed at 100 ^{o}C for 2 hr. Annealed product was further solid state polymerized in the reactor to obtain high molecular

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weight PLLA as 3 following steps: step1 110 ^{o}C 10 torr 5 hr, step 2 130 ^{o}C 10 torr 5 hr and step 3 150 ^{o}C 10 torr 5 hr.

Mass scale

For study the potential to produce PLLA in mass scale from direct polycondensation polymerizations, the similar reaction condition of lab scale was selected to compare the thermal properties and molecular weight of synthesized PLLA on the effect of reactor size. The reaction was conducted in 100 L reactor with a paddle and condenser connected to an inline cold trap and a vacuum pump. Thermocouple was used to measure the internal of reactor and exterior oil temperatures. The reactor pressure was measured and controlled by vacuum controller (VCN500, OKANO). The pressure in the reactor was lower incrementally using a rotary vacuum pump (K7503, OSAKA VACUUM ltd.)

One hundred kilograms of L-LA and 0.5%w/w of PTSA were added to reactor, PLLA was synthesized by direct polycondensation (DP) through three operations: distillation, oligomerization and polymerization. The temperature and pressure during the polymerization were precisely controlled. Polymerization was done for 4 hr at 30 torr after reaching 150^{o}C. At the end of the reaction, the products were discharged at 150 ^{o}C in stainless bats and allowed to cool to room temperature for 7 hr and were kept in dry ice. After solidification, the product was grinded and annealed at 90 ^{o}C for 2 hr. Annealed product was further solid state polymerized in the reactor to obtain high molecular weight PLLA. The reaction temperature has to lower than melting temperature, T_m of sample to prevent the molten of PLLA [6]. Thus, the temperature was gradually increase step by step as following steps: step1 100 ^{o}C 10 torr 23 hr; step 2 115 ^{o}C 10 torr 8 hr; step 3 120 ^{o}C 10 torr 14 hr. and step 4 135 ^{o}C 10 torr 6 hr.

Analytical method

The PLA's weight average molecular weight (MW), number average molecular weight (Mn) and Mw/Mn ratio were determined using a gel permeation chromatography (GPC) system equipped with two chromatography columns and a RI detector. Chloroform was used as the eluent at a flow rate of 1 mL/min, and the molecular weight were calibrated to a polystyrene standard at 40 ^{o}C. The thermal properties (melting temperature, T_m and glass transition temperature, T_g) were measured by using DSC at heating rate 20 ^{o}C/min under N_2 atmosphere.

3. RESULTS AND DISCUSSION

Thermal and physical properties of synthesized PLLA

The PLLA oligomer, that obtained from direct polycondensation were annealed and further polymerized solid state polymerization, SSP, respectively as previously described. In SSP, the polymerization temperatures have to lower than melting temperature, T_m to maintain the reaction in solid phase. Thus the reactions were stopped to sampling the synthesized PLLA for determining T_m by DSC before further polymerization. The physical and thermal properties of synthesized PLLA from both lab scale and mass scale are tabulated in Table 1 and 2, respectively. For both scale, thermal and physical properties show the similar results. After direct polycondensation, the low molecular weight PLLA or PLLA oligomer are obtained. Then synthesized PLLA oligomers were further polymerized via SSP at temperature below T_m. As longer solid state polymerization time, higher MW of PLLA is obtained due to the longer time and higher probability of oligomer to interact each other [7-8]. Melting temperatures, Tm also show the similar results, Tm of synthesized PLLA gradually increase with increasing SSP time as shown in Figure 1 and 2 for lab scale and mass scale, respectively. For lab scale, Tm of polymerized PLLA are 137, 140, 150, 162 and 172 ^{o}C for direct polycondensation, annealing, SSP step1, SSP step 2 and SSP step 3, respectively. For mass scale, Tm of polymerized PLLA are 130, 131, 130, 143, 150, 150 and 157 ^{o}C for direct polycondensation, annealing, SSP step1, SSP step 2, SSP step 3 and SSP step 4, respectively. As longer SSP time, higher and shaper DSC thermograms are obtained due to the increasing of reaction time [9]. The Tm and MW values of the synthesized PLLA from lab scale and mass scale are comparable at the same conditions. Thus the size of reactor does not show the effect on the Tm and MW of synthesized PPLA. For the physical characteristic also show the similar characteristic which are yellow-white solid power.

For mass scale, there are comments involved bumping of lactic acid during direct polycondensation and the agglomerations of molten PLLA during SSP due to low molecular weight of PLLA oligomer. To avoid bumping of lactic acid during direct polycondensation, gradually adjust temperature and pressure are required. For preventing the agglomeration of PLLA in SSP, pre-anealling reaction at 40-50 ^{o}C is needed.

Table1 Thermal and physical properties of synthesized of PLLA from lab scale

Step	Conditions	%Yield	T_c (°C)	T_m (°C)	MW	PDI	Characteristics	
							Appearance	color
Melt Polymerization	150 °C 30 torr	62.75%	96	137	3730	2.37	Solid-powder	white
Annealing	100 °C atm		56	140	4220	2.08	Solid-powder	white
Solid state Polymerization/5h	110°C 10 torr 5 hr			150	7160	2.44	Solid-powder	white
Solid state Polymerization/10h	130°C 10 torr 5 hr			162	21300	2.17	Solid-powder	white
Solid state Polymerization/15h	150°C 10 torr 5 hr			151,172	32400	2.19	Solid-powder	Yellow-white

Table2 Thermal and physical properties of synthesized of PLLA from mass scale

Step	Conditions	%Yield	Tc (°C)	Tm (°C)	MW	PDI	Characteristics	
							Appearance	color
Melt Polymerization	150 °C 30 torr	75.25	92	130	3160	2.41	Solid-powder	white
Annealing	90 °C Atm 3 hr			131	3570	1.93	Solid-powder	white
Solid state Polymerization/10 hr	110°C 10 torr 7 hr			130	3790	1.89	Solid-powder*	Yellow-brown
Solid state Polymerization/26 hr	100°C 10 torr 16 hr			143	7050	2.14	Solid-powder, Rock of melt part Grinding by hand in reactor	Yellow-white
Solid state Polymerization/34 hr	115°C 10 torr 8 hr			150	10800	2.14	Solid-powder, Small rock	Yellow-white
Solid state Polymerization/47 hr	120°C 10 torr 13			150	20200	2.36	Solid-powder, Small rock	Yellow-white
Solid state Polymerization/53 hr	135°C 10 torr 34 hr 6 hr			157	24000	2.16	Solid-powder, Small rock	Yellow-white

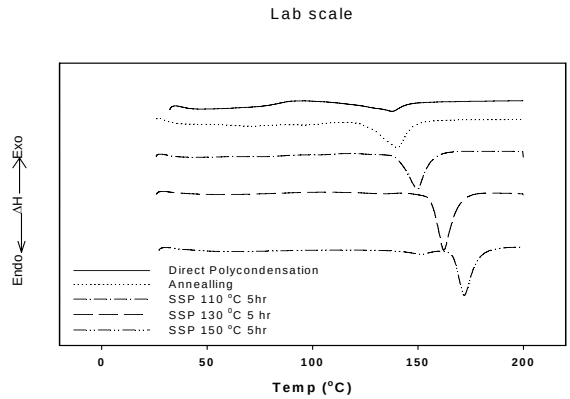

Figure 1. DSC thermogram of synthesized PLLA from mass scale.

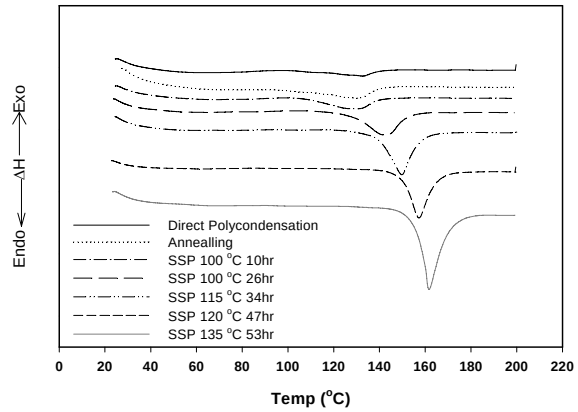

Figure 2. DSC thermogram of synthesized PLLA from mass scale.

4. CONCLUSIONS

To develop the environmental friendly and non-complex facilities process of PLLA production. In this work, PLLA was successfully synthesized via direct polycondensation and solid state polymerization in lab and mass scale and confirmed by using ^{1}H-NMR. The synthesized PLLA from both lab and mass scale shows the comparable melting temperature, T_m and MW. Thus there are high potential to produce PLLA from new process. The investigations of effect of time and reaction condition for high efficiency and economized reaction are required in future works.

5. ACKNOWLEDGMENT

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