Molecular Weight and Structural Properties of Biodegradable PLA Synthesized with Different Catalysts by Direct Melt Polycondensation

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Abstract. Production of biodegradable polylactic acid (PLA) from biomass-based lactic acid is widely studied for substituting petro-based plastics or polymers. This study investigated PLA production from commercial lactic acid in a batch reactor by applying a direct melt polycondensation method with two kinds of catalyst, γ-aluminium(III) oxide (γ-Al_2O_3) or zinc oxide (ZnO), in reduced pressure. The molecular weight of the synthesized PLA was determined by capillary viscometry and its structural properties were analyzed by functional group analysis using FT-IR. The yields of polymer production with respect to the theoretical conversion were 47% for γ-Al_2O_3 and 35% for ZnO. However, the PLA from ZnO had a higher molecular weight (150,600 g/mol) than that from γ-Al_2O_3 (81,400 g/mol). The IR spectra of the synthesized PLA from both catalysts using polycondensation show the same behavior of absorption peaks at wave numbers from 4,500 cm^{-1} to 500 cm^{-1}, whereas the PLA produced by two other polymerization methods – polycondensation and ring opening polymerization – showed a significant difference in % transmittance intensity pattern as well as peak area absorption at a wave number of 3,500 cm^{-1} as –OH vibration peak and at 1,750 cm^{-1} as –C=O carbonyl vibrational peak.

Keywords: *biodegradable PLA; polycondensation; catalyst; molecular weight; FT-IR.*

1   Introduction

Recently, the demand and development of biomass based plastics has rapidly increased. It could provide a solution to many world issues, such as global warming as the largest one. Plastics made from biomass can reduce global warming by diminishing carbon emissions. This is because the synthesis process and raw materials of biomass based plastics do not require any fossil fuel resources. Other environmental problems, such as air pollution or earth pollution caused by conventional petroleum based plastics, can also be reduced with biomass based plastics. Biodegradable polymers as an alternative plastic material have been used to replace conventional plastics. Poly-lactic acid (PLA) is a biodegradable polymer from the polyester group with excellent

characteristics. PLA has a high tensile modulus, which leads to high thermal stability.

Poly-lactic acid (PLA) can be synthesized from lactic acid by two general methods: direct condensation polymerization and ring-opening polymerization. PLA is typically synthesized by ring opening polymerization (ROP) of lactide, a process that uses catalysts such as tin, zinc, aluminum and lead; initiators such as n-, sec- and tert-butyl lithium; and solvents such as diphenyl ether, toluene and chloroform [1,2]. However, direct condensation polymerization of L-lactic acid like bulk polymerization, azeotopic dehydration, and enzymatic polymerization have been known to produce PLA with a molecular weight in the order of only $\sim 10^4$ g/mol due to the unfavorable reaction equilibrium constant of L-lactide [3]. In comparison with the well-established method for the catalytic ring-opening polymerization of L-lactide [4-7], the direct polycondensation of L-lactic acid has received much less attention. Studies of direct polycondensation of L-lactic acid with various catalysts [8,9], melt/solid polycondensation [10], and direct condensation polymerization of L-lactic acid in bulk state [11] have been conducted in order to investigate the production of PLA with a high molecular weight. In recent years, a breakthrough was reported by Kimura, *et al.* [12] and Gao, *et al.* [13], who produced high molecular weight PLA by direct melt polycondensation using binary catalysts system stannous(II) chloride dihydrate/para-toluene sulphonic acid monohydrate ($SnCl_2$/TSA) in a relatively short reaction time.

This paper reports the synthesis of poly(lactic acid) from commercial lactic acid monomer using two different catalysts – γ-aluminium(III) oxide (γ-Al_2O_3) and zinc oxide (ZnO) – by melt-polycondensation. The average molecular weight of the synthesized PLA samples was measured by capillary viscometry. The structural properties of the synthesized PLA were analyzed by functional group analysis using FT-IR.
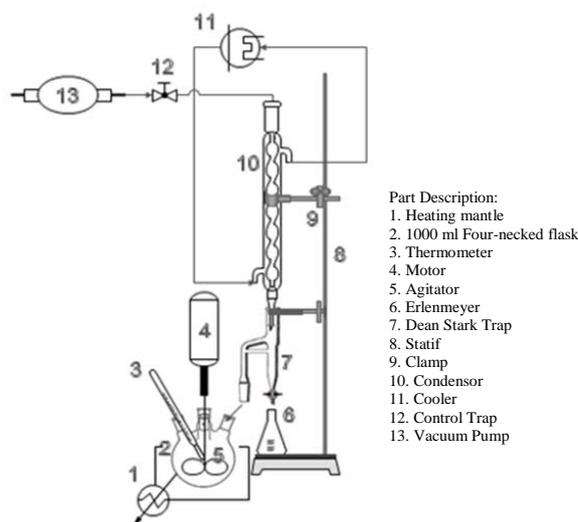
2   Experiment

2.1   Materials

Pharmacy grade lactic acid (LA) was supplied by Purac with a monomer concentration of 88.10 wt.% and density of 1.119 g/ml. γ-aluminum(III) oxide (γ-Al_2O_3) with a pore volume of 0.14 ml/g as catalyst was synthesized using the hydrothermal method from aluminum nitrate kindly donated by the catalyst laboratory at the Department of Chemical Engineering, ITB, Indonesia. The other catalyst, zinc oxide (ZnO) of 99.9% purity, was purchased from Sigma-Aldrich. Chloroform and methanol as solvent for PLA isolation were purchased from Merck.

2.2   Direct Melt Polycondensation and Characterization

A 1-liter four-necked flask was equipped with a mechanical stirrer and a reflux condenser connected to a vacuum system through a cold trap (Figure 1). PLA melt-polycondensation was conducted in three steps in the following order: preheating, oligomerization, and polymerization. First, 200 ml of a 88.10 wt % aqueous solution of LA was dehydrated in the flask at 120°C and at atmospheric pressure for 2 hour in order to remove water from the LA monomer. Then, for oligomerization, the preheated LA was reduced to a pressure of 10 torr at 100°C for 2 h and then continually heated to 150°C under a pressure of 10 torr for another 2 h. In the polymerization period, the predetermined catalyst was added to the flask and the reaction mixture was stirred by mechanical stirrer at 180°C under a pressure of 10 torr for 30 h. During polymerization, the solution of lactic acid darkened into old-greenish and gradually became viscous. After polymerization, the flask was cooled down and the viscous solution was dissolved in chloroform. The product was precipitated in methanol, filtered and dried slowly at 60°C to vaporize the remaining methanol after filtration.

The molecular weight of the PLA produced was measured by capillary viscometry using chloroform as solvent and calibrated according to PLA standards of 137,000, 148,000, 182,000, and 237,000 g/mol [14]. These standard PLA samples were procured from LG Chemical. To determine the PLA structure, we conducted functional group analysis using a Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrophotometer (FT-IR).

Part Description:
1. Heating mantle
2. 1000 ml Four-necked flask
3. Thermometer
4. Motor
5. Agitator
6. Erlenmeyer
7. Dean Stark Trap
8. Statif
9. Clamp
10. Condensor
11. Cooler
12. Control Trap
13. Vacuum Pump

Figure 1 Experimental apparatus for direct methyl-polycondensation.

3 Results and Discussion

3.1 Polymerization of PLA under Various Temperature and Time

Table 1 shows the polymerization results under various temperatures and the reaction times of the lactic acid through a direct polycondensation with ZnO catalyst. As for the temperature of polymerzation, the polymerization at 160°C yielded the highest value of lactic acid conversion, i.e. about 71%, while the PLA obtained at the 180°C polymerization condition showed a higher molecular weight of 79,400 g/mol compared to the 56,600 g/mol of PLA produced at 160°C. However, at a polymerization temperature of 200°C, the experiment of polymerization had to be stopped after 4 hours because gelation occurred in the reator. Hence, we found that the optimum condition for lactic acid polycondensation was at a temperature of 180°C.

Table 1 Reaction Conditions[a] and Experimental Data of PLA Polymerization.

Experiment	Temperature (°C)	Time (hours)	Mv (g/mol)	Yield (g)	Conversion (%)
1	160	30	56,600	119	71
2	180	30	79,400	106	63
3	200	4	-	-	-
4	180	20	68,800	104	62
5	180	40	84,300	109	65

[a] Lactic acid 2.31 mol, pressure 50 torr, and catalyst ZnO 0.1 g

From this consideration, another time-various experiment was conducted to optimize the Mv and yield. The highest value for both Mv and yield was obtained at 40-hour polymerization. Meanwhile, the 20-hour polymerization yielded the lowest value for both Mv and yield under the same temperature. It seems that the longer the reaction time, the higher the molecular weight of PLA is produced.

3.2 Molecular Weight of PLA Synthesized with Different Catalysts

Poly lactic acid (PLA) was synthesized with two kinds of catalyst – γ-Al_2O_3 and ZnO – using the direct melt polycondensation method. Table 2 shows the reaction conditions and the results of yield and molecular weight of the synthesized PLA. From Table 2, the molecular weight of the PLA synthesized using ZnO was greater than that of the PLA synthesized using γ-Al_2O_3. This may be related to active sites on the surface of the two different catalysts used

to synthesize PLA by melt-polycondensation. The ZnO catalyst seems to have a greater active site surface area so the polymerization can go further than that of the γ-Al$_2$O$_3$ catalyst, making the polymer chain of the product longer.

Table 2   Reaction Conditions[c] and Experimental Data of PLA Polymerization.

Type of catalyst	Amount of Catalyst (g)	Yield (g)	Conversion (%)	Mv (g/mol)
γ-Al$_2$O$_3$	8.5	80	47	81,400
ZnO	0.1	58	35	150,600

[c] Lactic acid 2.31 mol, temperature 180°C, pressure 10 torr, and time 30 hr

The reaction rate of lactic acid polycondensation is generally determined by the amount of water (H$_2$O) produced as byproduct. During polymerization, the longer the length of the PLA polymer chain, the more water produced. On the other hand, the existence of water molecules leads to depolymerization of the PLA. As reported in Moon, *et al*. [10], the best PLA product was produced using SnCl$_2$ catalyst. The catalyst mechanism of SnCl$_2$/TSA during polymerization showed that SnCl$_2$ has high solubility in water and is first activated by water molecules after which the polymerization rate increases. This means that interaction between catalyst and water contained in the system is also important for an effective polymerization. On the other hand, the use of water molecules for catalyst activation also reduces the number of water molecules, which causes depolymerization of the PLA. ZnO catalyst is more soluble in water (0.16 mg/100 mL at 30°C) than γ-Al$_2$O$_3$, which should be advantageous for ZnO catalyst to make longer PLA chains during polycondensation. Unfortunately, γ-Al$_2$O$_3$ is insoluble in water, so in this case it is difficult to reduce the number of water molecules. Also, the chance of removing water molecules from the system greatly depends on vacuum pressure of the system. During the experiment, the γ-Al$_2$O$_3$ catalyst tended to settle at the bottom of the flask reactor, so its distribution in the system decreased gradually, whereas the ZnO catalyst was well distributed in the whole reaction system under mechanical stirring.

The use of different catalysts during polymerization also influences the yield results of PLA product. In this paper, PLA synthesis using γ-Al$_2$O$_3$ had a greater yield than using ZnO but molecular weight decreased. This means that the product from polymerization using γ-Al$_2$O$_3$ contained many short PLA chains, whereas ZnO catalyst produced a lower amount of PLA but with longer chains.

3.3 Structural Properties of Synthesized PLA using FT-IR Analysis

Figure 2 shows that the IR spectrum of lactic acid has specific broad and strong absorption of carboxylate acid group between 2,900 cm^{-1} and 3,500 cm^{-1}. This represents the absorption of –OH bond stretching mode. Vibration of carbonyl in lactic acid (-C=O) appears to have strong intensity at wave numbers of 1,700-1,725 cm^{-1}. The –C-O- bond absorbs the IR at 1,210-1,320 cm^{-1}.
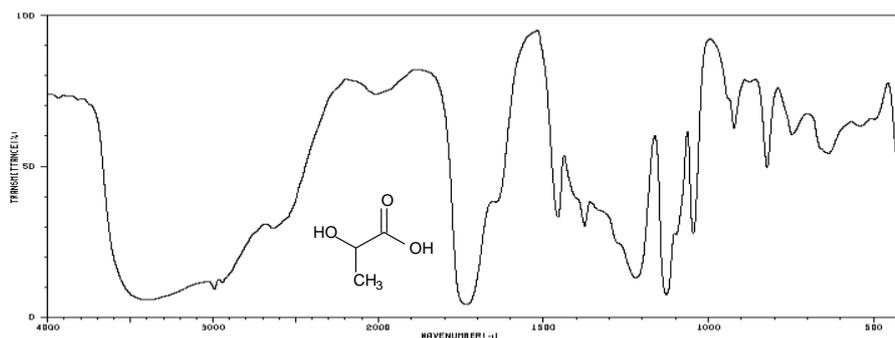
Figure 2 IR spectrum of lactic acid [18].

As shown in Figure 3, the area of IR absorption peaking at 3,500 cm^{-1} in Figure 2 decreases as the IR intensity transmittance increases. This is because of decreasing –OH group vibration. During polymerization, lactic acid monomers have intermolecular interaction thus resulting in the formation of new bonds between –OH attached to the carboxylate group and –OH attached to methyl groups of other monomers. The –OH group is reduced as a result of a condensation reaction and in exchange dimers, trimers, oligomers and polymers are created. The –C=O absorption peak at 1,700 cm^{-1} from lactic acid sharpened after polymerization as ester bonds (-COO-R) form in the PLA chains, thus the PLA's IR spectra show a shift of the –C=O absorption peak at 1,757 cm^{-1}. Another specific indication of ester group formation is the peak shift from 1,210-1,320 cm^{-1} to 1,100 cm^{-1} as a result of the absorption of –C-O- stretch in the ester group.

The IR spectra of the synthesized PLA using both catalysts show similar behavior as those of the standard PLA. No significant peak change was found in the two IR spectra from Figure 3. From Table 3, the IR peak wave numbers of the synthesized PLA from both catalysts were similar to the PLA absorption characteristics from reference [15]. This means that the product of the lactic acid polymerization was polylactic acid. There is no catalystic effect on the

changes in the PLA structure. The catalysts only play a role in accelerating the polymerization.
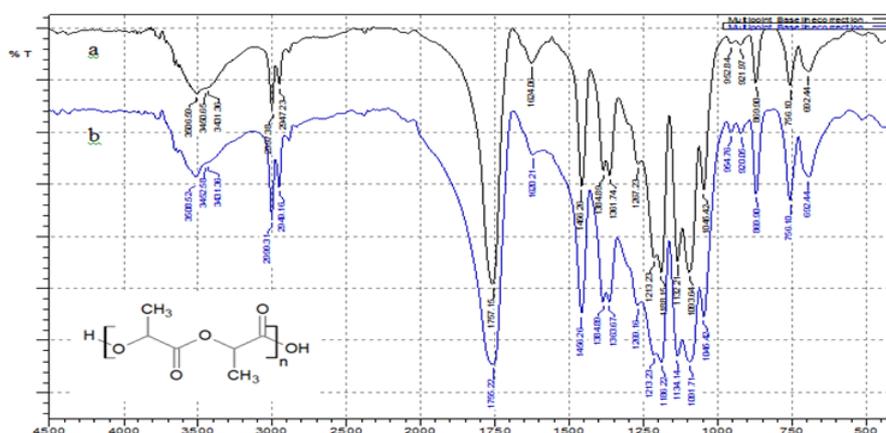

Figure 3 IR spectra of (a) PLA using γ-Al₂O₃ and (b) PLA using ZnO.

Table 3   IR Absorbtion Peaks of PLA Samples.

Functional Group	Wave number (cm⁻¹)			
	PLA (γ-Al₂O₃)	PLA (ZnO)	PLA ROP	PLA ref. [15]
-OH stretch	3506.59	3508.52	3504.66	3571
-CH- stretch	2997.38, 2947.23	2999.31, 2949.16	2995.45, 2945.30	2995, 2944
-C=O carbonyl stretch	1757.15	1755.22	1757.15	1759
-CH₃ bend	1456.26	1456.26	1454.33	1453
-CH- deformation	1384.89, 1361.74	1384.89, 1363.67	1361.74, 1381.03	1382, 1362
-C=O bend	1267.23	1269.16	1267.23	1268
-C-O stretch	1132.21, 1093.64	1134.14, 1091.71	1186.22, 1130.29, 1091.71	1194, 1130, 1093
-OH bend	1045.42	1045.42	1047.35	1047
-C-C- stretch	952.84, 921.97	954.76, 920.05	954.76, 867.97	926, 868

Figure 4 shows a comparison of the IR spectra between two different polymerization methods, i.e. ring opening polymerization of lactide and melt-polycondensation of lactic acid. Standard PLA from LG Chem. was produced by ring opening polymerization of lactide and had molecular weight 148,000 g/mol. Significant differences were found in the % transmittance intensity

pattern as well as in the peak area absorption at a wave number of 3,500 cm^{-1} as –OH vibration peak and at 1,750 cm^{-1} as –C=O carbonyl vibrational peak. At a wave number of 3,500 cm^{-1}, the standard PLA showed smaller –OH peak area vibration than the PLA synthesized using ZnO catalyst. This was caused by the different PLA molecular weight affected by the different length of the PLA chains. The higher the molecular weight of the PLA, the longer the PLA chains. With increasing the length of the PLA chains, the content of -OH bonds contained in the PLA backbone becomes lower. Hence, the IR beam that is used for -OH bond vibration will be lower and a higher transmittance will be recorded in the spectra. On the other hand, ring opening polymerization yields a better PLA product with higher molecular weight than melt-polycondensation. The IR spectra also indirectly show that PLA synthesized by melt-polycondensation has a higher amount of short PLA chains that have many –OH groups at the end of the chain.
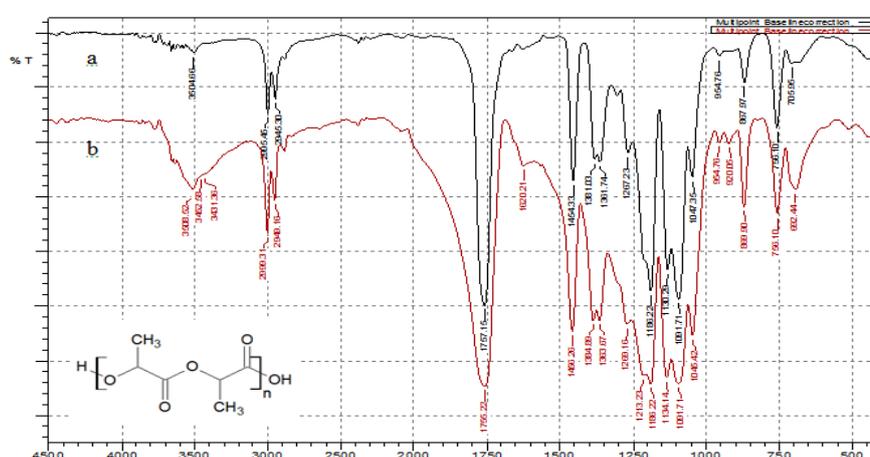
Figure 4 IR spectra of (a) PLA made by ring opening polymerization and with 148,000 g/mol molecular weight, (b) PLA made by direct melt polycondensation using ZnO and with 150,600 g/mol molecular weight.

From the work of Kister, *et al*. [16], morphology, conformation and configuration of PLA chains can be studied by interpreting the IR and Raman spectra. Using analysis of the sensitive band at absorption peak wave numbers around 1,300 cm^{-1}, the crystallinity and tacticity of the PLA chain can be qualitatively determined. Amorphous and atactic PLA will be indirectly identified by a lower %IR transmittance than that of semicrystalline and syndyotactic PLA. The IR spectra from Figure 4 show that the synthesized PLA had a lower %IR transmittance than the standard PLA at wave number 1,300 cm^{-1}. This means that the structure of the synthesized PLA may not be better

oriented than that of the standard PLA. A crystallinity analysis using IR spectroscopy was conducted by Younes, *et al*. [17]. They reported that two bands in the IR spectra related to the crystalline and the amorphous phase of PLA. These specific characteristics were found at 755 cm^{-1} and 869 cm^{-1}. The peak at 755 cm^{-1} can be assigned to the crystalline phase, while the peak at 869 cm^{-1} can be assigned to the amorphous phase [15]. From Figure 4, both IR spectra show peaks at 755 cm^{-1} and 869 cm^{-1}. This means that both PLA samples had crystalline and amorphous phase. But the synthesized PLA had a lower %IR transmittance at wave number 869.90 cm^{-1} than the standard PLA at wave number 867.97 cm^{-1}. Although it is not directly related, the amorphous phase of synthesized PLA may be higher than that of standard PLA.

4   Conclusion

Polylactic acid produced by applying direct melt polycondensation with two kinds of catalyst, γ-aluminium(III) oxide (γ-Al$_2$O$_3$) and zinc oxide (ZnO), was characterized for both molecular weight and structural properties. The molecular weight of the PLA synthesized from ZnO catalyst was higher than that of the PLA synthesized from γ-Al$_2$O$_3$ catalyst. This difference is caused by the solubility of the catalyst in water and the distribution of the catalyst in the reactant for polymerization. The IR spectra of the synthesized PLA from both catalysts using polycondensation showed similar behavior with the PLA absorption peak at wave numbers from 4,500 cm^{-1} to 500 cm^{-1}. This means that the different types of catalyst do not influence the structural properties of the PLA during polycondensation. However, the different polymerization methods of either polycondensation or ring opening polymerization showed significant differences in behavior of the PLA absorption IR peak. The different structural properties of PLA according to different polymerization methods may be due to various factors, such as molecular weight, crystallinity of polymer or catalyst. Therefore, further research is needed to find out the effect of various reactionconditions and catalyst types on molecular weight, structural properties, thermal properties, and mechanical properties of PLA.

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