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Effect of Temperature and Concentration of SnCl₂ on Depolymerization Process of L-Lactide Synthesis from L-Lactic Acid via Short Polycondensation

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Abstract

Lactide is a group of cyclic ester, which is used to synthesize polylactic acid (PLA) by ring opening polymerization method. The properties of PLA depend strongly on the quality of the lactide monomer from which it is synthesized. In this research, lactide was synthesized from L-lactic acid through short polycondensation process without catalyst and depolymerization process with SnCl₂ catalyst. The influences of temperature and catalyst concentration on the depolymerization were investigated to achieve high yield, high concentration and exact stereoform of the lactide produced. Polycondensation process of L-lactic acid was carried out gradually at 120 to 180°C for 5 h. Polycondensation produced oligomer with molecular weight (Mn) 2272-2390, (Mw) 2699-2911 and PDI 1.03 to 1.24. Yields of oligomer were between 79.63-83.64%. Depolymerization process was carried out at 76 torr for 3 h with variation of temperature of 190-220°C and concentration of SnCl₂ 0.05-0.2 % (w/w). The crude lactide yield increased with the raising of SnCl₂ concentration and temperature up to 210°C. At temperature of 220°C, the reaction rate of oligomerization for heavy residue was much faster than the depolymerization for lactide produce, which resulted in a lower yield of lactide and more residu obtained. The highest yield of crude lactide was 78.8% with mass of SnCl₂ catalyst used 0.1 (w/w) and temperature 210°C. Lactide was characterized by using fourier-transform infrared (FT-IR) spectroscopy and proton nuclear magnetic resonance (^{1}H NMR). From ^{1}H NMR analysis, optical purity of lactide produced in depolymerization process confirmed to be L-lactide and no stereoform of racemic formed. Temperature and catalyst concentration did not influence to stereoform of lactide but it affected to L-lactide concentration in crude lactide produced. The highest L-lactide concentration obtained in this study was 81.03%.

Keywords: Depolymerization, Lactic acid, Lactide, Oligomer, Polycondensation

Introduction

Polylactic acid (PLA) is a great potential to be developed as a replacement for conventional plastic. PLA is a versatile polymer, biodegradable and derived from renewable resources [1]. PLA can be obtained from lactic acid derived from sugar, starch, cellulose, and glycerin waste of biodiesel [2]. PLA can be produced through various polymerization processes from lactic acid including: polycondensation, ring opening polymerization, and direct method such as azeotropic dehydration and enzymatic polymerization [3]. Ring-opening polymerization is the best method to produce polymers with high molecular weight. Lactide is used in production of high molecular weight PLA in the ring-opening polymerization route and is therefore an important intermediate in the industrial production of PLA [4]. Optical purity in lactide determines the quality of the resulting PLA. The synthesis of high optical pure lactides is thus of practical importance for the development of high performance materials based on PLA. Lactide has three stereoisomers, L-, D-and L, D-lactide. Therefore, the product polymer can be synthesized in the form of poly (L-lactic acid) (PLLA), poly (D-lactic acid) (PDLA), or racemic product (PDLLA) [1, 2].

L-lactide from L-lactic acid is produced through two-stage processes, polycondensation and depolymerization. Polycondensation of L-lactic acid produces oligomers in the form of short chain PLA and depolymerization of oligomer produces a cyclic ester, lactide. Polycondensation of lactic acid can be carried out without using catalyst because the acid can be a self-catalysator. Lactic acid molecules have some functional groups, such as hydroxyl (OH) and carboxylic acid (-COOH), a typical of esterification reactions as a result of intermolecular and intramolecular interactions. Intermolecular interaction of lactic acid in the polycondensation reaction causes the formation of dimers, trimmers, oligomers and produces water molecule (H₂O), while the intramolecular interactions lead to changes in the form of a dimer of lactic acid into lactide [5].

Depolymerization reaction is strongly influenced by temperature, pressure, molecular weight of oligomers and catalyst. Several catalysts have been used for the synthesis of lactide to produce high yield products and to minimize the formation of rasemic. Lactide formation involves back-biting reaction refers to the formation of cyclic compounds via intra-molecular reactions between carboxylic groups at the end of the chain and the ester bond in the first group in the PLA chains [6]. Muller et al. (1993) developed a tin catalyst in a continuous and semi-continuous process to lactide production at industrial scale. Sn catalyst can produced lactide of high optical purity [7]. The synthesis of lactide was done by Yoo et al. (2006) who studied the effect of temperature, pressure and

different catalyst from tin (SnO, Sn(II)Oct and SnCl₂) in the synthesis of lactide from oligomeric PLA. The oligomeric PLA was synthesized via polycondensation at 200°C under nitrogen atmosfer for 6 h [6].

The properties of the crude lactide depend on the quality of the oligomer as well as on the depolymerization reaction parameter. Previous studies have not yet reported the synthesis of L-lactide from L-lactic acid with a shorter polycondensation at gradually temperature. In this study, the oligomeric PLA was synthesized from L-lactic acid via polycondensation. It was carried out gradually at 120-180°C for 5 h. The aim of this study was to determine the effect of temperature and concentration of SnCl₂ catalyst on depolimerization process of oligomer produced toward optimum yield and optical purity of the crude lactide produced.

Materials and Methods

Materials: L-lactic acid (90%) and SnCl₂ were purchased from Merck (Indonesia). Chloroform, tetramethylsilane (TMS) and tetrahydrofuran (THF) for analysis were purchased from Sigma Aldrich.

Polycondensation of L-Lactic Acid

L-lactic acid (50 ml) was put in a four-necked flask equipped with a magnetic stirrer, a temperature controller, and a condenser, which was connected to a collector distilled. The reaction was carried out at 120°C for 1 h with continuous nitrogen gas flow to push evaporative water into the condenser. Afterwards, the oligomerization stage held gradually at 150°C for 2 h and at 180°C for 2 h without nitrogen gas flow.

Depolymerization of Oligomer

The oligomer synthesized from L-lactic acid was depolymerized in a four-necked flask. The flask was equipped with a magnetic stirrer, a temperature controller, and a distillation column, which was connected to a vacuum pump. The reaction was carried out at temperature variations: 190; 200; 210; 220°C, variation weight of SnCl₂ 0.05; 0.1; 0.2% (w/w) and 76 Torr. The Oligomer was heated until it stopped producing distillate. Subsequent to the depolymerization process completed, the vacuum valve was closed slowly. Then lactide was collected on the sample container.

Analytical methods

Molecular bonding was analysis by using FT-IR (Agilent Technologies type Cary 630). The chemical structure of product was determined by ¹H NMR spectra recorded on a JEOL spectrometer operating at 500 MHz. In the process of proton investigation chloroform was used solvent and tetramethylsilane as an internal standard. The number-average molar mass (Mn, Mw) and polydispersity index (PDI) of the oligomer were determined by using GPC-8025. Tetrahydrofuran (THF) was used as mobile phase at flow rate of 1.0 ml/min with a column temperature of 40°C. Calibrations were fulfilled with narrow-molecular-weight distributed polystyrene standards. The yield of crude lactide in the depolymerization process was calculated by using eq.1.

$$\text{Yield of crude lactide (\%)} = \frac{\text{crude Lactide product (gr)}}{\text{Oligomer in reactor (gr)}} \times 100\% \qquad (1)$$

Results and Discussion

Polycondensation of L-Lactic acid

L-lactic acid polycondensation was carried out without catalyst and gradually increased at temperature (120 to 180°C) for 5 h. Oligomer was very viscous at 150°C and harden at room temperature. Oligomer was a solid translucent white, brittle and unhygroscopic. The FT-IR spectra of lactic acid and oligomer is shown in Figure 1. The FT-IR spectrum of lactic acid showed the existence of the-OH stretching vibration at 3403 cm⁻¹ wave number, C-H stretching vibration at 2988 cm⁻¹, carbonyl group (C=O) at 1718 cm⁻¹, C-H bending vibration at 1456, 1375 cm⁻¹ and C-O stretching at 1207 cm⁻¹. Changes that occur after the L-lactic acid transformed into oligomers, identified by significant reduce of the –OH stretching vibration in the oligomer. The reduce of –OH absorbance was due to the evaporation of water at 120°C and the polycondensation process that consumes the OH groups to form the ester bond with the acid group. The final statement is similar as described by Nikolic et al. (2010) [8]. In the FT-IR spectrum of oligomer, carbonyl group (C=O), C-H bending vibration and C-O stretching were found at 1747, 1452 and 1180 cm⁻¹, respectively.
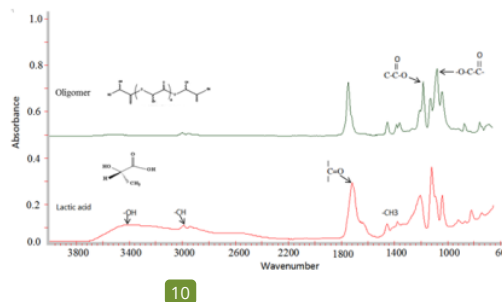

**Figure 1. The FT-IR spectra of L-lactic acid and oligomer**

The ¹H NMR spectrum of oligomer was measured during its synthesis process. It was shown in Figure 2. The ¹H NMR spectrum of oligomer showed a doublet at 1.58 ppm for the methyl group (CH₃ protons) and quartet at 5.16 ppm for the main chain methine proton of PLLA. The results of this study corresponded to which reported by Yoo & Kim (2006); Tsukegi (2007) where the CH₃ signal oligomer is at 1.45-1.64 ppm [6, 9]. This ¹H NMR spectrum of oligomer is similar with spectrum of PLLA that reported by Ding et al. (2011) [10].

Figure 3 shows the molecular weight of oligomer which produced from polycondensation process of L-lactic acid. The yield of oligomer in the polycondensation stage was 79.63-83.64% with molecular weight of oligomer produced (Mn) 2272-2390 Da, (Mw) 2699-2911 Da and PDI 1.03-1.24. Yield of oligomer obtained in this study is similar to those reported Pravin et al (2014) by using Pb-based oxide and Sn (Oct)₂ catalyst with total oligomerization longer time was 9 hours. Mw generated this study is much higher than the research

Pravin et al (2014) that produce oligomers with Mw in 1380 [11].
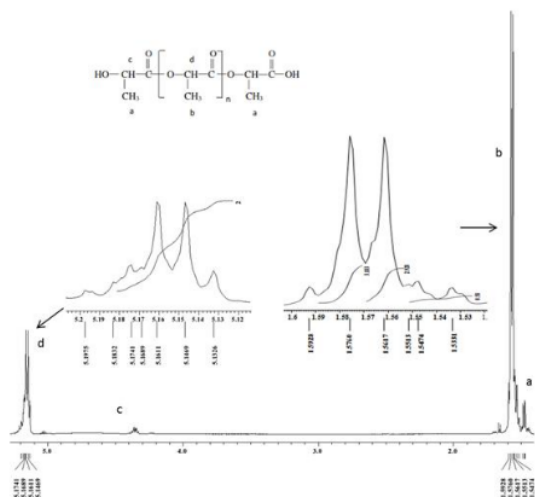
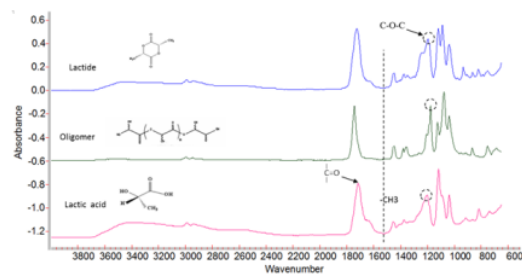**Figure 2. The ^{1}H NMR spectrum of oligomers**
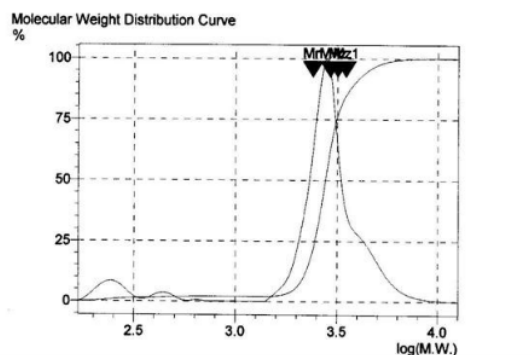
The peak is Mw/Mn (PDI), Mn, Mw, Mz/Mw

Figure 3. The molecular weight distribution of oligomer Depolymerization

Effect of temperature and SnCl$_2$ concentration

Lactide formation of oligomers by a trans-esterification intramolecular reaction is known as back-bitting reaction. This phenomenon occurs at high temperature and long reaction time. Lactide product was a white solid powder, hygroscopic and crystallized at room temperature. FT-IR spectra from lactic acid, oligomer and lactide produced is shown in Figure 4. The differences in wave numbers of lactic acid, oligomer and lactide from FT-IR spectra are not significant, because all of these compounds have the same functional group. From the results of FT-IR analysis, C = O stretch in lactic acid, oligomer and lactide gave peaks at wave number in sequence 1718, 1747 and 1720 cm^{-1}. CH$_3$ peak for lactic acid, oligomer and lactide showed in 1456, 1452, 1454

cm^{-1}, C-O stretching showed in 1207, 1180 and 1201 cm^{-1} for lactic acid, oligomer and lactide. This result has similarities with the research results by Achmad et al. (2009) [12].

Figure 4. The FT-IR spectra of lactic acid, oligomer and lactide

The ^{1}H NMR spectrum of lactide consisted of two patterns of segregation, doublet and quartet. Doublet peak shows a proton which has one proton neighbor non-equivalent with it. Quartet peak shows a proton which has 3 protons neighbors. Figure 5 shows that the spectrum consists of two peaks, the highest peak is the doublets and the left shift is quartet. The spectrum quartet consists of four peaks that are on the proton shift 5.07-5.02 ppm and the spectrum doublets consist of two protons shift peak at 1.65-1.68 ppm.
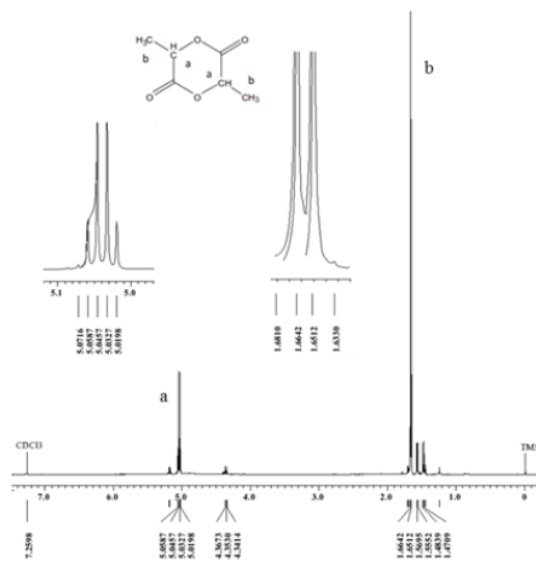

Figure 5. The ^{1}H NMR spectrum of crude lactide

Result of this study is different from that reported by Yoo (2009). The use of SnO catalyst produced D,L-lactide with the-CH signal at 1.72 ppm [6]. The third doublet spectrum of ^{1}H NMR proved the methyl group consisted at L, L / D, D-

lactide, meso-lactide and oligomer, thus can be seen in sequential chemical shift at 1.65-1.68; 1.70-1.75; and 1.45-1.64 ppm [8]. Based on the literature, the resulting lactide product is at stereoisomers L, L / D, D-lactide. ^{1}H NMR spectrum could not distinguish the form of L-or D-lactide as the two types of these isomers have the same spectrum. Raw material for making lactide in this experiment is L-lactic acid, thus it stands to the reason that the product is L-lactide.

The effect of temperature and concentration of $SnCl_2$ can be seen in the yield of crude lactide and concentration of L-lactide produced. Crude lactide yield from depolymerization process was calculated using eq.1 and showed in Figure 6. Crude lactide yield was influenced by the reaction temperature. The result from temperature variation at 190-210°C, shows the higher the temperature, the higher the yield of crude lactide generated. At each variation of the catalyst concentration, the highest crude lactide yield obtained at 210°C. The highest crude lactide yield obtained at 210°C with the addition of the catalyst 0.1% (w/w) is 78.8%. At temperatures of 220°C and the addition of the catalyst 0.2% (w/w), crude lactide yield was decreased significantly. In this condition, the reaction rate of esterification for heavy residue was much faster than the depolymerization for lactide produce, which resulted in a lower yield of crude lactide and more residue obtained. This event was marked by a color change from the original oligomer yellow-brown to black. The loss in yield was likely due to the formation of heavy residues, which would have remained in the flask after the depolymerization.
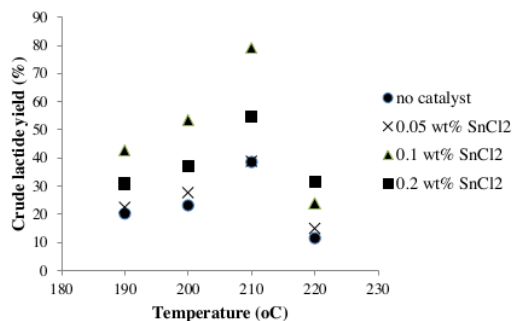

Figure 6. Effect of temperature and $SnCl_2$ concentration on the yield of crude lactide

Concentration of L-lactide in crude lactide was determined by using eq.2 from ^{1}H NMR spectrums of crude lactide, as seen in Figure 7.

$$L - Lactide\ concentration\ (\%) = \frac{L - Lactide}{L - Lactide + a + b + c} \times 100\% \tag{2}$$
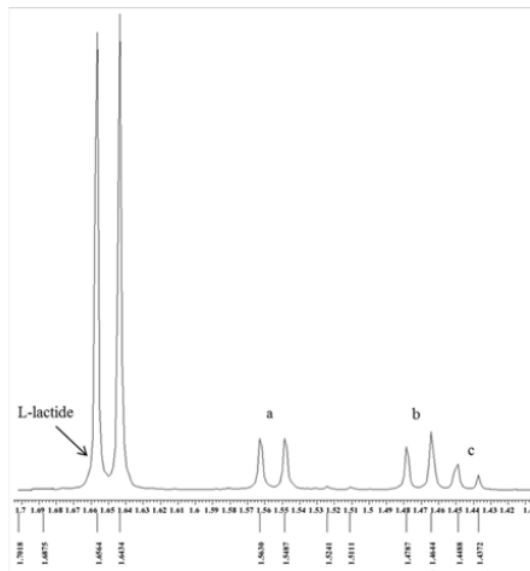

Figure 7. The ^{1}HNMR spectrum doublet of crude lactide

The results of this study obtained the ^{1}H NMR spectrum of lactide product with various temperature reactions shows peak at 1.68-1.65 ppm and 1.56-1.43 ppm of impurities such as oligomers. Temperature and catalyst concentration has no effect on the optical purity of the resulting lactide but its influence to L-lactide and impurity concentration in the crude lactide. Figure 8 shows the effect of $SnCl_2$ concentration on the % L-lactide concentartion produced when the depolymerization process was carried out at 210°C and 76 torr. The highest L-lactide concentration was obtained with using 0.1 % (w/w) of $SnCl_2$. L-lactide concentration decreased from 81.03 to 64.2% when using of 0.2 % (w/w) $SnCl_2$ catalyst because the higher catalyst concentration increased the occurence of side reaction. L-lactide concentration decreased with increasing levels of impurities in the crude lactide.
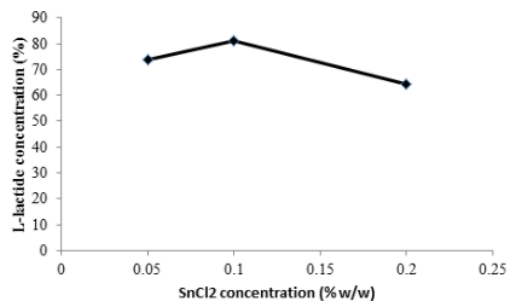

Figure 8. L-Lactide concentration in the crude lactide

Conclusion

^{1}H NMR spectrums of lactide product were doublet in the range 1.67-1.65 ppm and quartet at 5.07-5.02. The optical purity of lactide produced was L-lactide. Temperature and $SnCl_2$ concentration have no influence on the optical purity of lactide produced. At a pressure of 76 Torr the production of L-lactide increased with the increasing temperature and catalyst weight. The highest yield of crude lactide was 78.8% and the L-lactide concentration was 81.03%. This result was achieved at depolimerization temperature of 210^oC and the amount of $SnCl_2$ catalyst of 0.1 % (w/w).

References

[1]   Lopes, M.S., A. Jardini, and R. Maciel Filho., 2012, "Poly (lactic acid) production for tissue engineering applications," Procedia Engineering., **42**: p. 1402-1413.

[2]   Lasprilla, A.J., et al., 2012, "Poly-lactic acid synthesis for application in biomedical devices—A review," Biotechnology advances., **30**(1): p. 321-328.

[3]   Garlotta, D., 2001, "A literature review of poly (lactic acid)," Journal of Polymers and the Environment., **9**(2): p. 63-84.

[4]   Inkinen, S., et al., 2011, "From lactic acid to poly (lactic acid)(PLA): characterization and analysis of PLA and its precursors," Biomacromolecules., **12**(3): p. 523-532.

[5]   Groot, W., et al., 2010, "Production and purification of lactic acid and lactide. Poly (lactic acid): Synthesis, Structures, Properties, Processing, and Applications," p. 1-18.

[6]   Yoo, D.K., D. Kim, and D.S. Lee., 2006, "Synthesis of lactide from oligomeric PLA: Effects of temperature, pressure, and catalyst," Macromolecular research., **14**(5): p. 510-516.

[7]   Muller, M., et al., 1993, "Meso-lactide," Google Patents.

[8]   Nikolic, L., et al.,2010, "Novel microwave-assisted synthesis of poly (D, L-lactide): the influence of monomer/initiator molar ratio on the product properties," Sensors., **10**(5): p. 5063-5073.

[9]   Tsukegi, T., et al., 2007, "Racemization behavior of l, l-lactide during heating," Polymer degradation and stability, **92**(4): p. 552-559.

[10]   Ding, L., et al.,2011, "Bulk solvent-free melt ring-opening polymerization (ROP) of L-lactide catalyzed by Ni (II) and Ni (II)–Ln (III) complexes based on the acyclic Salen-type Schiff-base ligand," Inorganic Chemistry Communications., **14**(8): p. 1274-1278.

[11]   Upare, P.P., et al., 2012, "Synthesis of lactide from alkyl lactate via a prepolymer route," Industrial & Engineering Chemistry Research, **51**(13): p. 4837-4842.

[12]   Achmad, F., et al., 2009, "Synthesis of polylactic acid by direct polycondensation under vacuum without catalysts, solvents and initiators," Chemical Engineering Journal, **151**(1): p. 342-350.

Acid in biorefinery of palm oil waste using Response Surface Methodology", IOP Conference Series: Materials Science and Engineering, 2018
Publication

7   Pravin P. Upare, Maeum Lee, Dong Won Hwang, Young Kyu Hwang, Jong-San Chang. "New heterogeneous Pb oxide catalysts for lactide production from an azeotropic mixture of ethyl lactate and water", Catalysis Communications, 2014
Publication
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8   Sung Il Moon, Yoshiharu Kimura. "Melt polycondensation ofL-lactic acid to poly(L-lactic acid) with Sn(II) catalysts combined with various metal alkoxides", Polymer International, 2003
Publication
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9   A Bello, K Morales, L Sánchez, V Lidueñez, A Leal, G Gelves. " Computational Implementation of Required Industrial Unit Operations for Bio-Plastic Production From Starch Extracted from Banana Peels by Aerobic Fermentation using ", Journal of Physics: Conference Series, 2020
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