Effect of temperature and time for the production of polylactic acid without initiator catalyst from lactide synthesized from ZnO powder catalyst

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Abstract. Polylactic acid (PLA) is a biodegradable polymer that most importance at the present due primarily to its properties as biological degradation and biocompatibility derived from renewable resources. This study investigated the role of zinc oxide powder and tin(II) 2-ethylhexanoate as the catalysts for lactide and PLA synthesis, respectively. Polylactic acid was obtained by four stages: dehydration, oligomerization, depolymerization and ring opening polymerization. The catalyst was added and water was removed at the first stage then the reactions are carried out at different temperatures and reaction time on the other stages. The ratio of lactic acid and zinc oxide powder was 1000:3 for lactide synthesis, the ratio of lactide product and tin(II) 2-ethylhexanoate was 1000:4 for PLA synthesis without any initiator. The PLA products were analysed for the yield, some chemical and physical properties such as functional group, decomposition temperature, melting temperature of synthesized PLA. It is found that at reaction temperature of 160°C and reaction time for 5 h gave the highest yield PLA of 64.5% with its decomposition temperature of 311°C and melting point temperature at 152°C. There are two main mechanisms, polymerization and depolymerisation occurring in reaction and each mechanism plays a major role with respect to the reaction condition. At higher reaction temperature and longer time, the rate of depolymerisation is higher than that of polymerization leading to the lower of decomposition and melting temperature of synthesized PLA.

1. Introduction

Polylactic acid (PLA) is one of the most well-known biodegradable and biocompatible polymer produced in small and large quantities [1]. It’s interesting biopolymer in recently for the other applications because of its excellent mechanical properties and compatibility with the environment. PLA is one of the most appropriate polymers to replace non-biodegradable synthetic polymers based on fossil fuel [2]. Polylactic acid (PLA) is a highly versatile material, which can be obtained from the renewable resources such as garbage, potato, sugars in corn starch, cassava or sugar cane and glycerin waste of...
biodiesel and other agricultural products [3]. PLA is widely used for various applications, in the medical field using as tissue engineering, implants, drug delivery systems etc. It can be used for food packaging and textiles [4]. The low molecular weight PLA is appropriate for drug delivery, which has a long history of safety in humans [5, 6]. PLA can be prepared by different ways from lactic acid such as direct condensation polymerization, ring opening polymerization and azeotropic condensation polymerization [5]. Ring-opening polymerization (ROP) of lactic acid is the most commonly route to achieve high molecular weight and consists of three steps: polycondensation, depolymerization and ring opening polymerization [1, 5]. PLA can be produced by using of different organometallic compounds as catalysts for aluminum, zinc, tin, etc. However, tin(II) 2-ethylhexanoate (Sn(Oct)2) is the most common catalyst for the synthesis of high molecular weight PLA [7]. Tin(II) 2-ethylhexanoate was approved for surgical and pharmacological applications and widely utilized initiator due to give the high molecular weight polymers in ring opening polymerization rout [8]. The catalyst aqueous dispersion of zinc oxide nanoparticles was used in lactide synthesis and could lead to highly efficient production of high molecular weight PLA by using PGL-10 as an initiator in the process [9]. Zinc oxide was an alternative catalyst for lactide synthesis to 72% yield after the process at 230 - 240°C [10].

In this work, we investigated the polymerization of lactide synthesized by using ZnO as a catalyst in the presence of tin(II) 2-ethylhexanoate without any initiator. The objective of this study was to determine the effect of reaction temperatures and time in the polymerization stage on the yield, and some of physical and chemical properties such as functional group, degradation temperature, melting point of produced PLA.

2. Material and methods

2.1. Chemicals

Commercially available L-lactic acid (liquid, 88%) was obtained from Purac Co., Rayong, Thailand. Catalysts zinc oxide, tin(II) 2-ethylhexanoate and organic solvents methanol, ethyl acetate, chloroform were purchased from Italmar Co., Bangkok, Thailand. Nitrogen gas was obtained from Linde Co., Rayong, Thailand.

2.2. Methods of lactide and PLA synthesis

2.2.1. Lactide synthesis. Lactic acid (liquid, 88%) (400 ml) with zinc oxide as a catalyst were added into a 1000 mL three necked flask, which were equipped with a magnetic mixer, a thermocouple and a condenser connected to a vacuum system. The process performed under a pressure of 60 kPa at temperature 80°C for 2 h in order to remove water content. After the dehydration the product was further oligomerized, the temperature was slowly adjusted up to 150°C under pressure 20 kPa for 3 h without catalyst was added at this stage. After 3 h of oligomer stage, lactide was produced through depolymerization, which carried out at 170°C, pressure 2 kPa and maintaining for 3 h. After the completion of the depolymerization process the crude lactide was cooled to room temperature.

2.2.2. Lactide purification. The crude lactide was preheated at 70 - 80°C then dissolved in ethyl acetate with ratio of crude lactide and ethyl acetate (1:1.5 w/v) by stirring for 10 min. The undissolved impurities were then separated by vacuum filtration, the filtrate was cooled down to room temperature prior to the recrystallization at 4°C for 24 h. The recrystallized lactide was then isolated from ethyl acetate by vacuum filtration and the filtrate was further dried in a vacuum oven at 40°C, pressure 100 Pa for 24 h. The purified lactide was then collected in the sample container. After completing the process, the quantity of lactide was weighed and conversion yield of lactide was calculated by Eq. (1).

\[
\text{Lactide yield (\\% w/w)} = \frac{\text{Mass of lactide (g)}}{\text{Mass of lactic acid (g)}} \times 100
\]  

(1)
2.2.3. **PLA synthesis by ring-opening polymerization of lactide.** The purified lactide was weighed then placed in a three-neck flask, which was equipped with a magnetic stirrer, thermocouple with nitrogen gas flow at 1.5 mL min\(^{-1}\). The tin(II) 2-ethylhexanoate as a catalyst was added into the reactor while lactide was heated until it melted with ratio of lactide produced and tin(II) 2-ethylhexanoate was 1000:4. The mixture was carried out by varying at 140, 160 and 180°C for different duration time 5, 8, and 10 h. Upon completely this stage, the product mixture was cooled to room temperature.

2.2.4. **PLA purification.** After the PLA synthesis process, crude PLA was cool to room temperature and collected to sample container then chloroform was added to dissolve crude PLA with 1:1 w/v for 30 min. After that, allow to the purification which precipitated into excess cold methanol, and then white solid PLA gradually formed and separated by vacuum filtration. The filtrate was dried in a vacuum oven with pressure 100 Pa at 45°C for 24 h. After completely the process, the quantity of PLA produced was weighed, and its conversion yield was calculated by Eq. (2).

\[
\text{PLA yield (}\%\text{w/w}) = \frac{\text{Mass of PLA produced (g)}}{\text{Mass of lactide input (g)}} \times 100
\]  

2.3. **Methods of lactide and PLA characterization**

2.3.1. **FTIR Characterization.** The functional groups of the products were characterized using a fourier transform infrared spectrometer (FT-IR, TENSOR 27, Germany). Before measurement, lactide and PLA were prepared to dry in vacuum oven at 45°C, and 100 Pa for 24 hours then made the sample to be powder. The measurement was performed at a resolution of 4 cm\(^{-1}\) in the range of 4000-400 cm\(^{-1}\) for a total of 64 scans.

2.3.2. **Polarimeter characterization.** Lactide synthesized from lactic acid was detected for its stereoforms and optical purity by polarimeter (BELLINGHAM & STANLEY P20 POLARIMETER, United Kingdom). Lactide was prepared and the optical rotation was measured in toluene solution at concentration of 1.0 % (w/v) at 20°C, and a 200 mm cell length. The specific rotation, and enantiomer excess were calculated by Eq. (3) and (4), respectively.

\[
[\alpha]_{D}^{20^\circ C} = \frac{\alpha}{c \times l}
\]

\[
\%ee = \frac{\alpha}{(\alpha)_{\text{pure}}} \times 100
\]

Where,

- \([\alpha]_{D}^{20^\circ C}: specific\ rotation, (degree)\]
- \(\alpha: observed\ rotation, (degree)\]
- \((\alpha)_{\text{pure}}: pure\ rotation\ of\ sample, (degree)\]
- \(c: concentration\ of\ sample, (g/ml)\]
- \(l: cell\ length, (dm)\]
- \(ee: enantiomer\ excess, (%)\]

2.3.3. **NMR Characterization.** Synthesized PLA was characterized its molecular structure using a nuclear magnetic resonance spectrometer (NMR 500 MHz Bruker AVANCE III HD, Germany). Proton NMR was obtained by using deuterated chloroform as a solvent, and tetramethylsilane was used as the internal standard.
2.3.4. TGA Characterization. The decomposition and the melting behaviour of samples were characterized by thermogravimetric analyser (Mettler Toledo TGA/DSC1, Switzerland) with the heating scan from 25 to 800°C. The heating rate was 10°C min\(^{-1}\) and the flow rate of nitrogen gas was 50 mL min\(^{-1}\).

3. Results and discussion

The production of lactide from lactic acid involves a three-stage processes, namely dehydration, oligomerization and depolymerization, and PLA synthesis relates to the ring-opening polymerization of lactide product, which carried out as previously described.

3.1. Synthesis of lactide and PLA

Lactide yield obtained from the stage of lactide synthesis by using zinc oxide as catalyst was 31.25% determined by Eq. (1) and PLA yields at the various temperatures and durations were calculated by the Eq. (2) as shown in Figure 1. PLA products yield using tin(II) 2-ethylhexanoate 0.4 wt% as a catalyst in the processes, which carry out for 5 h at temperatures of 140, 160, and 180°C were 49.62 %, 64.5%, and 50.39%, respectively. Increasing the duration of 8 h, PLA yield 53.1% and 62.06% of temperature 140 and 160°C, respectively. For increasing time of 10 h, yield of PLA are 58.73%, 55.7%, and 49.04% at temperatures of 140, 160, 180°C, respectively. The maximum yield was found at 160°C for 5 h. The result is shown that the increasing temperature for a long time does not improve the product yield [5].

![Figure 1](image)

**Figure 1.** Effect of reaction temperature and time on PLA synthesis.

3.2. Characterization of lactide and PLA

3.2.1. Functional group of lactide and PLA. The product of lactide and PLA were analysed the functional group determine by FTIR and shown that the products for both lactide and PLA were the same compared to the commercial PLA, as shown in Figure 2. The bonds of carbonyl stretch and oxy carbonyl (ester) were observed at wave number 1748 cm\(^{-1}\) and 1181 cm\(^{-1}\), respectively. The \(-\text{CH}\) bond was observed at 2996 cm\(^{-1}\), and \(-\text{OH}\) bond stretching was observed at wavenumber 3530 cm\(^{-1}\), which is characteristic of a carboxylic acid. Alcohol bond was higher than that of \(-\text{OH}\) stretching from the carboxylic acid due to very strong hydrogen bonds in carboxylic acids. However, at the lower wavelengths of bond are tended to show considerable overlap because it is difficult for the characterization. The infrared spectroscopy wavenumbers (cm\(^{-1}\)) for the bonds and products functional groups were as follows: \(-\text{OH}\) stretch (free): 3100; \(-\text{CH}\)-stretch: 2996 (asymmetric), 2946 (symmetric), 2877; \(-\text{C}=\text{O}\) carbonyl stretch: 1748; \(-\text{CH}_3\) bend: 1452; \(-\text{CH}\)- symmetric and asymmetric: 1382 and 1360; \(-\text{C-O}\)- stretch: 1181, 1083; \(-\text{OH}\) bend: 1042 [3].
3.2.2. Stereoisomer of lactide. In general, stereoisomer of lactide provided in three stereoforms as L-lactide, D-lactide, and optically inactive meso-lactide form which is an equimolar (racemic) mixture of D and L isomers [11]. The lactide product was detected, the resulting observed rotation $\alpha = -13.4^\circ$ was used to calculate by Eq. (3) to obtain the specific rotation was $([\alpha]_D^{20})_{L,LA} = -291^\circ$. This result to confirm the stereoform of lactide synthesized was L-stereoisomer as L-lactide. Determination of enantiomer excess value of synthesized lactide was calculated by eq. (4), to find its percentage stereopurity. While the neat optical rotation of L- and D-lactides were $([\alpha]_D^{20})_{L,LA} = -298.8^\circ$ and $([\alpha]_D^{20})_{D,LA} = +298.8^\circ$ at 20 °C in a toluene solution, respectively [12]. The value of enantiomer excess of synthesized lactide was obtained for 4.5%, and the stereopurity of synthesized lactide was 52.25% of L-stereoisomer.

3.2.3. Molecular structure of PLA. The molecular structure of PLA produced was evaluated by $^1$H NMR and $^{13}$C NMR as shown in Figure 3(a) and 3(b), respectively. The PLA powder was considered for the analysis obtained at 160°C by using tin(II) 2-ethylhexanoate 0.4 wt% as a catalyst for 5 h in polymerization stage. Figure 3(a) shows the $^1$H NMR as H-doublet signal for methyl proton resonance in the main chain at 1.57 ppm. The spectrum shows signal of methine proton resonances in the main chain of PLA at 5.19 ppm. The $^1$H NMR spectrum of PLA at 2.6 and 4.37 ppm was assigned to the methine proton next to the terminal hydroxyl group and carboxyl group, respectively. The result from analysed of $^1$H NMR, the spectrum of PLA was similar to that reported by other works [3, 13]. Figure 3(b) shows the $^{13}$C NMR spectrum of PLA product. The $^{13}$C NMR spectrum of PLA signals visible for molecular structure of methyl carbon, carbon methane and carbon ester assigned at 16.75, 69.12 and 169.73 ppm, respectively. The resulting synthesized PLA was shown that PLA is formed in the present study for $^{13}$C NMR evaluated similar to that reported by other works [3, 14].
3.2.4. Thermal stability of PLA. The thermal stability of the lactide and PLA were determined by TGA/DSC. The profiles of decomposition temperature obtained from TGA are shown in Figure 4(a-d), whereas the melting temperature from DSC is displayed in Figure 4(e). These results of commercial lactide and PLA are also included in those figures to compare with the synthesized samples. Synthesized lactide was obtained decomposition, and melting point of 240°C and 94°C, respectively is related to commercial lactide shown in Figure 4(a) and 4(e). The temperature of decomposition and melting point of PLA samples were concluded and exhibited in Figure 5(a-b), respectively. Decomposition and melting temperature of commercial PLA were analysed of 338°C and 153°C, respectively. It is found that the overall trend of decomposition and melting temperature of synthesized PLA tends to increase with an increasing of reaction temperature to reach a maximum point at 160°C, then decreasing in higher reaction temperature. The increasing of decomposition and melting temperature implies that the
increasing of molecular weight of synthesized PLA. In general, during the reaction there is a competition reaction between polymerization and depolymerization of lactide monomers to obtain PLA products. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The polymerization was proposed to describe by the insertion-coordination mechanism as shown in Figure 6 [11, 15]. For the effect of reaction time, it is shown that the decomposition and melting temperature mostly decreases with an increasing of reaction time for all reaction temperature except at the 140°C. This could be explained by the depolymerisation play a major role of reaction. It is observed at reaction temperature 140°C, the melting temperature increases with an increasing in reaction time. This result could be due to at this low reaction temperature the shorter chain molecules may occur in higher amount in bulk phase thus the melting temperature may be increased. The optimum condition in this work was found that at reaction temperature 160°C with 5 h, which obtained the decomposition and melting temperature of 311°C and 152°C, respectively. The melting temperature of 152°C is comparable to commercial PLA of 153°C as shown in Figure 5 (b), which is nearly to the range of commercial PLA pellet supplied by Nature Works, with T_m at 155 - 170°C [9].
Figure 4. Analysis thermal stability results of (a-d) TGA and (e) DSC of synthesized lactide and PLA and commercial samples.

Figure 5. The decomposition and melting temperature of commercial PLA and synthesized PLA in different reaction temperature and time: (a) decomposition temperature and (b) melting temperature.
4. Conclusion
The tin(II) 2-ethylhexanoate was used as a catalyst in ring-opening polymerization of synthesized lactide with concentration of 0.4% (w/w) at a temperature of 160°C and reaction time for 5 h gave the highest yield PLA of 64.5% with its decomposition temperature of 311°C and melting point temperature at 152°C which is comparable to the commercial one. The reaction temperature and time are significant variables, there is a competition between polymerization and depolymerisation mechanisms occurring in reaction and each mechanism plays a major role with respect to the conditions. At higher reaction temperature and longer time, the rate of depolymerisation is higher than that of polymerization leading to the lower of decomposition and melting temperature of synthesized PLA.

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References
[1] A.J. Lasprilla, G.A. Martinez, B.H. Lunelli, A.L. Jardini, R.M. Filho, Poly-lactic acid synthesis for application in biomedical devices - a review, Biotechnol Adv 30(1) (2012) 321-8.
[2] C.L. Sungyeap Hong, An Overview of the Synthesis and Synthetic Mechanism of Poly (Lactic acid), Modern Chemistry & Applications 02(04) (2014).
[3] Rahmayetty, Y. Whulanza, Sukirno, S.F. Rahman, E.A. Suyono, M. Yohda, M. Gozan, Use of Candida rugosa lipase as a biocatalyst for L-lactide ring-opening polymerization and polylactic acid production, Biocatalysis and Agricultural Biotechnology 16 (2018) 683-691.
[4] H.R. Kricheldorf, S.M. Weidner, About the influence of salicylic acid on tin(II)octanoate-catalyzed ring-opening polymerization of l-lactide, European Polymer Journal 119 (2019) 37-44.
[5] Y. Hu, W.A. Daoud, K.K.L. Cheuk, C.S.K. Lin, Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly(Lactic Acid), Materials (Basel) 9(3) (2016).
[6] S. Pivsa-Art, N. Phansroy, W. Thodsaratpiyakul, C. Sukkaew, W. Pivsa-Art, S. Lintong, T. Dedgheng, Preparation of Biodegradable Polymer Copolyesteramides from L-Lactic Acid Oligomers and Polyamide Monomers, Energy Procedia 56 (2014) 648-658.
[7] A.V. Yarkova, V.T. Novikov, V.N. Glotova, A.A. Shkarin, Y.S. Borovikova, Vacuum Effect on the Lactide Yield, Procedia Chemistry 15 (2015) 301-307.
[8] S.C. Alaa, Toshio Masuda, Christoph Weder, Poly(lactic acid) Science and Technology Processing, Properties, Additives and Application, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK, 2015.
[9] Y. Hu, W.A. Daoud, B. Fei, L. Chen, T.H. Kwan, C.S. Ki Lin, Efficient ZnO aqueous nanoparticle catalysed lactide synthesis for poly(lactic acid) fibre production from food waste, Journal of Cleaner Production 165 (2017) 157-167.
[10] C.H.K. Hong, S.H.; Seo, J.Y.; Han, D.S., Manufacturing Method of Lactide from Lactic Acid. CN Patent 102,796,071A, (2012).
[11] K. Masutani, Y. Kimura, Chapter 1. PLA Synthesis. From the Monomer to the Polymer, Poly(lactic acid) Science and Technology 2014, pp. 1-36.
[12] L. Feng, X. Bian, Z. Chen, S. Xiang, Y. Liu, B. Sun, G. Li, X. Chen, Determination of D-lactide content in lactide stereoisomeric mixture using gas chromatography-polarimetry, Talanta 164 (2017) 268-274.
[13] B. Choubisa, M. Patel, B. Dholakiya, Synthesis and characterization of polylactic acid (PLA) using a solid acid catalyst system in the polycondensation method, Research on Chemical Intermediates 39(7) (2012) 3063-3070.
[14] L. Ding, W. Jin, Z. Chu, L. Chen, X. Lü, G. Yuan, J. Song, D. Fan, F. Bao, 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) (2011) 1274-1278.
[15] L. Fang, R. Qi, L. Liu, G. Juan, S. Huang, Synthesis of Poly(L-lactide) via Solvothermal Method, International Journal of Polymer Science 2009 (2009) 1-7.