



# Poly lactic acid production using the ring opening polymerization (ROP) method using Lewis acid surfactant combined iron (Fe) catalyst ( $\text{Fe}(\text{DS})_3$ )

T. Widjaja<sup>\*</sup>, N. Hendrianie, S. Nurkhamidah, A. Altway, Bayu Yusuf, Fakhrizal F, Aisyah Alifatul, Atha Pahlevi

Chemical Engineering Department, Institut Teknologi Sepuluh Nopember, Sukolilo, Surabaya, 60111, Indonesia

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## ABSTRACT

LASC catalyst synthesis process was carried out using iron metal (Fe) and its characterization properties were tested. There are five stages carried out, namely, the manufacture of the LASC  $\text{Fe}(\text{DS})_3$  catalyst, lactic acid dehydration, polycondensation of lactic acid into L-lactic acid oligomers (OLLA), depolymerization of oligomers into L-lactide, and the ROP process to convert L-lactide into Polymers. L-lactic acid (PLLA). The analysis used is as follows, Karl-Fisher; Spectroscopy Fourier Transform Infrared (FTIR); and Nuclear Magnetic Resonance (HNMR); Gel Permeation Chromatography (GPC); Thermogravimetry Gravity Analysis (TGA) and X-Ray Diffraction (XRD). Based on the experimental results, the catalyst  $\text{Fe}(\text{DS})_3$  has a crystallinity value of 24% which indicates an amorphous nature and is easy to react. The value of the thermal stability of the catalyst is at 180 °C where the catalyst is able to process up to a temperature of 180 °C. Each step of the ROP is validated by FTIR analysis which shows that the components of the group are in accordance with the expected product. The comparison of the crystallinity values of PLA produced with  $\text{FeCl}_3$  and  $\text{Fe}(\text{DS})_3$  were 37.5 and 49%, respectively. Melting temperature ( $T_m$ ) values are 111 and 107 °C, respectively,  $T_d$  values are 327 and 352 °C, and the resulting molecular weights are 23,720 and 20,232 g/mol. Based on the results obtained, it can be seen that the use of a LASC catalyst in the form of  $\text{Fe}(\text{DS})_3$  is more effective than without using a LASC catalyst.

## 1. Introduction

Poly lactide or Poly(Lactic Acid) (PLA) is one of the most promising plastic biopolymers for various applications due to its competitive cost, biocompatibility, biodegradability, low environmental impact, excellent transparency, good processability and good mechanical properties. Thermal stability. In addition, this biopolymer has also been commercialized by NatureWorks™ and the global demand for PLA was estimated around 500 kton in 2022 (Jem and [68]). In general, there are three methods of synthesizing PLA with a molecular mass in the range of 8000–150,000 g/mol, including polycondensation, condensation dehydration azeotropic polymerization through the formation of lactide or so-called ring-opening polymerization (ROP). The most important method for the synthesis of PLA with high molecular weight yields is ring-opening polymerization [1]. In the PLA synthesis process, the ring-opening polymerization method is generally assisted by metal catalysts such as Zn(II), Ti(IV), and Sn(Oct)<sub>2</sub> is often used [2]. In general, the

<sup>\*</sup> Corresponding author.

E-mail addresses: [triw@chem-eng.its.ac.id](mailto:triw@chem-eng.its.ac.id) (T. Widjaja), [sasya22aisyah@gmail.com](mailto:sasya22aisyah@gmail.com) (A. Alifatul).

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polymerization method with ring opening requires organic solvents, such as toluene, PEG, TSA, and others [3] which, when viewed, the solvent used is quite harmful to the environment when used and can cause health problems such as respiratory and respiratory complaints. Complaints of eye irritation [4].

One of the catalysts that is quite promising lately is Lewis Acid Surfactant Combined Catalyst (LASC), where the catalyst is starting to be widely used as a catalyst for fast reactions with aqueous solvents. The use of LASC as a heterogeneous catalyst also has economic advantages because the deactivation of the catalyst takes a long time and can be used for several reaction cycles. LASC as a green catalyst is expected to be used as a substitute for tetraphenyltin  $\text{Sn}(\text{C}_6\text{H}_5)_4$  which has been approved by the Food and Drug Administration (FDA). Tetraphenyltin contains metal Sn which when the concentration of Sn increases will also increase the level of toxicity, although the resulting Molecular Weight (Mw) will be higher, but the product cannot be used for medical and food packaging purposes [5].

Several previous studies discussing LASC catalysts including Zhang and Wu [6] have carried out further research on LASC catalysts by conducting Friedlander synthesis from quinoline using scandium tris(dodecyl sulfate)  $[\text{Sc}(\text{O}_3\text{SOC}_{12}\text{H}_{25})_3]$  catalyst. Then, research conducted by Pradhan et al., in 2013 by synthesizing chromeno[4,3-*b*]chromene using different LASC catalysts, it was found that Fe (DS)<sub>3</sub> catalyst has a high yield of 93%. In terms of other synthesis, this catalyst is still rarely discussed in research, but there are several studies that have tested this catalyst, including the synthesis of quinazoline derivatives [7] and the synthesis of hexamethylcyclisiloxane [8]. In the LASC catalyst lactic acid polymerization has been tested by [9], but the polymerization method used is not ring-opening polymerization but the lactic acid polycondensation method.

Based on several advantages and previous studies, this research will make PLA with the ROP method with various types of catalysts so that it is hoped that in this study the results of PLA with better characteristics and are more environmentally friendly.

## 2. Materials and methods

### 2.1. Research material

The materials to be used in this study include Lactic Acid 88–92% purchased from Merck,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  purchased from EMSURE,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Sodium Dodecyl Sulfate (SDS) 98% purchased from Aldrich.

### 2.2. Research procedure

#### 2.2.1. Preparation of Lewis Acid Surfactant Combined Catalyst (LASC) $\text{Fe}(\text{DS})_3$

First, 1.063 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were weighed then, 20 ml of distilled water was heated at a temperature of  $\pm 60^\circ\text{C}$ . It aims to increase the solubility of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . After the distilled water was heated, the  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  powder was put into a glass beaker containing aquadest and stirred using a glass stirrer until dissolved. At the same time, 3.4 g of SDS were weighed to make a surfactant solution. After that, measure 100 ml of distilled water which is used as SDS solvent. Aquadest is heated to a temperature of  $60^\circ\text{C}$  with the aim of increasing and accelerating the solubility of SDS. After the Lewis acid solution and surfactant solution are made, first the two solutions are put into the refrigerator for about  $\pm 3$  h, because the reaction between Lewis acid solution and surfactant solution is an endothermic reaction [10]. Cold, then prepare an ice bath by storing ice water into a basin. Then, these two solutions were mixed in an ice bath, then the stirrer was turned on and stirred at 150 rpm for 30 min. After that, the LASC solution was filtered with filter paper to form a precipitate. The precipitate is then cleaned with aquadest to form coarse crystals. Then the precipitate is placed in an oven with a temperature of  $60^\circ\text{C}$  for  $\pm 24$  h. After being heated in the oven, the precipitate is put into a desiccator until it is ready to use. In addition, the catalysts used will be subjected to qualitative tests in the form of FTIR, TGA, and XRD.

#### 2.2.2. Stage of dehydration or reduction of moisture content of lactic acid

50 ml of lactic acid was measured using a measuring cup, then put into a four-neck flask and a stirrer was added. Then, the four-neck flask is connected to the equipment that has been installed. After the set of tools has been installed, the flask is heated in an oil bath at a temperature of  $120^\circ\text{C}$  and stirred at a speed of 150 rpm, after the thermometer shows a temperature of  $120^\circ\text{C}$ , nitrogen gas is flowed into a four-neck flask with a low flow for 2 h, this aims to push water vapor, a vacuum pump also ignited occasionally with the aim of lifting water vapor instantly. After 2 h of the dehydration process, the sample was taken with a dropper for the purposes of Karl-Fischer test analysis and to calculate its density with the help of a pycnometer, then the FTIR test to see the groups of the sample.

#### 2.2.3. Polycondensation stage of lactic acid to oligomer *l*-lactic acid (OLLA)

After the first step has been carried out, the next step is the process of polycondensation of lactic acid into OLLA. In this process, an esterification reaction occurs from lactic acid which is a type of carboxylic acid to OLLA which is a type of ester [69]. In this process, lactic acid whose water content has been reduced is then heated using the previous set of tools at a temperature of  $150^\circ\text{C}$  for 2 h followed by reheating at a higher temperature of  $180^\circ\text{C}$  for the next 2 h [70]. In this process, it is carried out at atmospheric pressure. The results that will be obtained are OLLA products that are cloudy in color with sticky properties. This oligomer will be analyzed by GPC to see the molecular weight, FTIR test to see the group based on the wave value and supported by the NMR test which specifically observes the proton position of the group.

#### 2.2.4. Steps of oligomer depolymerization to *l*-lactide

After the polycondensation stage was completed, the depolymerization stage was started by preparing 0.1%  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  catalyst

and then put into a four-neck flask. After that, the flask was heated again at a temperature of 210 °C. Then, after the temperature was reached the sample was conditioned in a vacuum by turning on the vacuum pump. The valve at the bottom is treated open and closed to lift the lactide vapor instantly. The raised lactide vapor will harden in the condenser because at temperatures below 10 °C, the lactide will be solid, therefore, the condenser water is kept at a low temperature [71]. This continues until the lactide vapor is exhausted or no longer formed because the condenser is clogged or something. After that, the process is stopped, and the four-neck flask will contain a residue of lactic acid which must be removed quickly because the residue will harden at room temperature. Meanwhile, the accumulated lactide is transferred to an empty container and stored in the freezer. After that, the lactide will be analyzed by FTIR and HNMR. tests.

### 2.2.5. ROP step to convert L-lactide to PLLA

In this last stage, namely the open ring polymerization stage, initially the variable types of catalysts were prepared, including the previously prepared FeCl<sub>3</sub> and Fe(DS)<sub>3</sub> catalysts. These two catalysts were weighed by mass 0.2% by weight of lactide. The collected lactide was removed from the freezer and heated in a four neck flask at 160 °C for 4 h with 150 rpm stirring. After this process, the product obtained was crude PLA. This result is then placed in a porcelain dish and allowed to cool to room temperature. After the crude PLA is dry, it is taken using an iron stirrer because the resulting PLA will stick to the porcelain cup. The PLA will be subjected to qualitative tests in the form of FTIR and DSC, as well as quantitative tests in the form of GPC tests.

## 2.3. Characterization analysis

In this study, the characterization of ROP results using LASC was carried out by testing to determine the qualitative and quantitative results of each PLA synthesis process obtained, including: Karl-Fisher test in PT. Angler BioChemLab; Spectroscopy Fourier Transform Infrared (FTIR) in Laboratory of Water Technology and Industrial Consulting ITS; Proton Nuclear Magnetic Resonance (H NMR) Airlangga University Laboratorium; Differential Scanning Calorimetry (DSC) in Diponegoro University Laboratorium; Gel Permeation Chromatography (GPC) in Diponegoro University Laboratorium; Thermogravimetry Gravity Analysis (TGA) in Laboratorium of Energy ITS; and XRD in Material and Metalurgi ITS Laboratorium.

## 3. Results and discussion

### 3.1. LASC production

In this study, the LASC catalyst used was based on Lewis acid FeCl<sub>3</sub> combined with SDS surfactant to obtain a LASC catalyst in the form of Fe(DS)<sub>3</sub>. The purpose of the combination of Lewis acids with surfactants is to overcome the natural nature of Lewis acids which are labile to water so that the Lewis acid catalyst will not react with the expected substrate but reacts with water and the surfactant itself functions as a solvent for organic compounds through the formation of colloids that protect the reaction. synthesis of organic compounds with Lewis acid catalyst from water [11,72]. The following is the analysis result of Fe(DS)<sub>3</sub> compared to SDS surfactant.

Fig. 1 shows the FTIR spectrum of SDS and LASC in the form of Fe(DS)<sub>3</sub>. SDS has peak wave numbers in the alkyl group, among others 2957 cm<sup>-1</sup>, 2870 cm<sup>-1</sup> which indicates the formation of strain and vibration of the CH<sub>3</sub> group [12]; 2922 cm<sup>-1</sup> and 2853 cm<sup>-1</sup> for the strain vibration CH<sub>2</sub>; 1466 cm<sup>-1</sup> and 721 cm<sup>-1</sup> which show bending (CH<sub>2</sub>) and rocking vibrations of CH<sub>2</sub>; 1080 cm<sup>-1</sup> shows the C–C strain vibration [73]. Meanwhile, the peak wave numbers on the anion head from SDS include strain vibrations and stress on the anion head group at 823 cm<sup>-1</sup> (symmetrical strain S–OC); 982 cm<sup>-1</sup> (asymmetric strain S–OC); 1069 cm<sup>-1</sup> (OSO<sub>3</sub> symmetric decreasing strain); and 1215 cm<sup>-1</sup> (symmetrically decreasing strain OSO<sub>3</sub>). In the LASC spectra, there is a significant shift and splitting of wavenumber values in the anion head compared to SDS spectra. This shift is caused by the interaction of the dodecyl sulfate anion

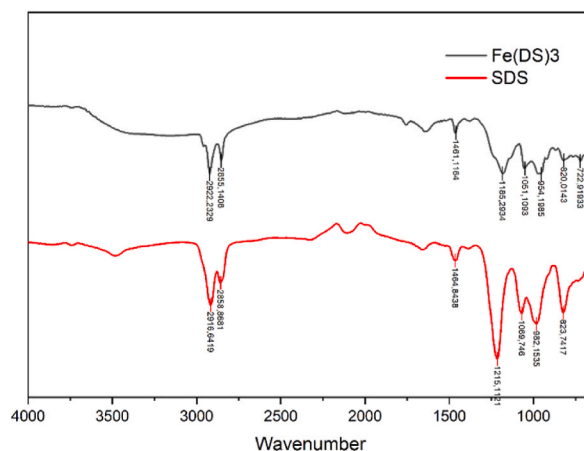


Fig. 1. FTIR Fe(DS)<sub>3</sub> compared to SDS.

with the Lewis metal cation (Fe(III) [9] and is in line with that reported by [74] which states that Fe(III) is bound to surfactants via sulfate ions. The results of the LASC and SDS spectra also have similarities with studies conducted by [9,12,74].

Furthermore, the synthesis of the LASC catalyst was carried out by XRD. Based on the calculations performed in Fig. 2, the crystallinity of Fe(DS)<sub>3</sub> is 24%. The degree of crystallinity indicates whether a catalyst is good in a synthesis process because the more amorphous a catalyst is, the better the performance. In addition, the degree of crystallinity of a catalyst affects its catalytic activity, if the catalyst used in a synthesis is more amorphous, the catalytic activity will also be better because the number of catalytic surfaces and sites of catalytic activity of the catalyst is also greater [13].

Based on TGA analysis, Fig. 3 shows the decomposition took place in 2 stages, according to [14,75], and [12], the mass decomposition of the LASC consists of several stages, namely the first stage shows elimination water and the formation of anhydrous compounds from LASC which took place at room temperature up to 100 °C. This was also confirmed by research conducted by [74] which showed that in the combination of Fe(III) with surfactants there are water molecules bound to Fe metal. (III) in the synthesized LASC catalyst. This is also reinforced by Fig. 1 graph of Fe(DS)<sub>3</sub> which shows a lower transmittance value than the SDS precursor at a wave number of around 3500 cm<sup>-1</sup>, where the wave number is the existence of -OH origin in a compound. The next stage is the endothermic reaction of releasing alkyl chain molecules, and SO<sub>3</sub> on the substrate which takes place at a temperature of 100 °C–278 °C. The last stage is the exothermic combustion of carbon residues that takes place above a temperature of 278 °C. Shown in Fig. 3 There is a residue remaining from the exothermic combustion of carbon residues, the residue is the residue of dodecyl sulfate molecules that form strong bonds with Lewis acid metals [9]. Based on Fig. 3 it can be seen that the largest decomposition temperature of Fe(DS)<sub>3</sub> occurs at 180 °C so that this catalyst can still be used in the open ring polymerization process in this study. Based on the analysis results from FTIR, XRD, and TGA, the LASC catalyst obtained is a combination compound of Lewis acid FeCl<sub>3</sub> with SDS surfactant which forms Fe(DS)<sub>3</sub> where this catalyst is suitable for the polymerization process which takes place at a temperature of 160 °C.

### 3.2. Lactic acid polymerization results

The lactic acid dehydration process aims to remove impurities in the form of water vapor. In the polycondensation process, water is in equilibrium with lactic acid in the reaction for oligomer formation, so that if water is not eliminated, the oligomer formation process will be hampered [76]. Therefore in this study the feed water was eliminated as much as possible to optimize the lactic acid polycondensation process. In this study, the dehydration process was carried out by heating the feed until it passed the boiling point of water, which is 120 °C to evaporate the water in the feed and the flask was fed with N<sub>2</sub> gas continuously to push the water to the condenser.

Based on Table 1 it appears that the water content of lactic acid was reduced by 6.3% which indicates that the dehydration process was successfully carried out to eliminate water so that the polycondensation reaction shifted towards oligomeric products. However, it appears that the elimination process can only eliminate about 50% of water from lactic acid, this is due to the strong affinity of lactic acid to water due to the hydrogen bonds formed and its low volatility making it difficult to separate water from lactic acid [77–79]. After analysing the water content of lactic acid, then measuring the density of lactic acid before and after dehydration as an approach to measure the purity of lactic acid that will be used in this study.

Based on Table 1 The density of lactic acid before the dehydration process has a smaller density with the density of lactic acid that has gone through the dehydration process where the density of lactic acid after going through the dehydration process has a value that is quite close to the literature from [76] which states that The density of lactic acid in general is 1.224 g/ml.

#### 3.2.1. Lactic acid polycondensation results

Polycondensation is a reaction that combines two lactic acid monomers into dimers, trimers, and oligomers. This reaction involves the incorporation of 2 carboxylic acid groups into an ester group which is characterized by the formation of water vapor [76]. Therefore, in this study, feed water was first eliminated to shift the polycondensation reaction towards the formation of oligomers. The following is the result of product analysis of lactic acid polycondensation using the FTIR instrument.

Based on Fig. 4 There are wavelength values for lactic acid and oligomers, including 3377 cm<sup>-1</sup> and 3496 cm<sup>-1</sup> for the strain vibration of the OH group; 2989 cm<sup>-1</sup> and 2995 cm<sup>-1</sup> for the C–H strain vibration; 1714 cm<sup>-1</sup> and 1747 cm<sup>-1</sup> for the C=O group; and

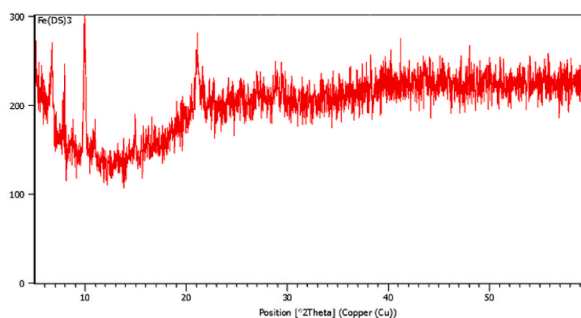


Fig. 2. Xrd result for Fe(DS)<sub>3</sub>.

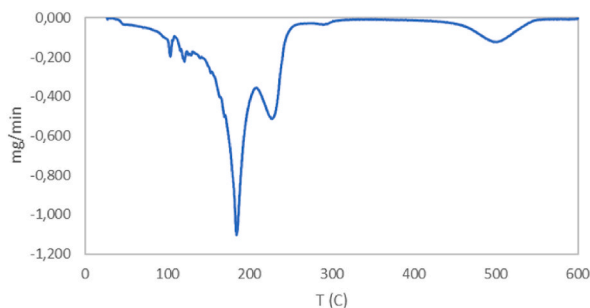


Fig. 3. TGA graphic for Fe(DS)<sub>3</sub>.

Table 1

Comparison of results of analysis of water content and density of lactic acid solution using the Karl-Fischer test before dehydration after dehydration.

Objective	Before dehydration	After Dehydration
Water Content (%)	13,6	6,3
Density (g/mL)	1188	1227

1182  $\text{cm}^{-1}$  for the C–O strain. In Fig. 4 There are identical peak values in the range (1700  $\text{cm}^{-1}$  – 1750  $\text{cm}^{-1}$ ) for lactic acid and oligomers where in that range there are peaks for the carbonyl group of carboxylic acids at 1700–1720  $\text{cm}^{-1}$  while for the ester group there are at 1720–1750  $\text{cm}^{-1}$  [80]. In Fig. 4 shows a shift in the peak from the original 1714  $\text{cm}^{-1}$  in lactic acid to,  $\text{cm}^{-1}$  in the oligomer which indicates the occurrence of an esterification reaction of lactic acid into lactic acid oligomers. Based on this evidence, it can be concluded that the lactic acid polycondensation process succeeded in converting lactic acid into oligomers.

In addition, in Fig. 4 There is also a peak –OH origin at wave number 3496  $\text{cm}^{-1}$  which should experience a significant reduction due to the dehydration process and the consumption of –OH groups in the lactic acid polycondensation process appears in oligomers [81,82]. The peak appearance at the –OH origin is caused by the presence of short oligomeric chains and the presence of unreacted lactic acid residues that increase the hydroxyl group [83]. Based on [1,2,81,84], the wavelength values of the clusters obtained have a value that is quite close in this study so it can be concluded that the polycondensation process obtained in this study succeeded in converting lactic acid into oligomers. The results of the polycondensation process were also analyzed using H Atomic Nuclear Magnetic Resonance to strengthen the FTIR results that have been obtained. The following is an analysis of the product resulting from polycondensation using a Core Magnetic Resonance instrument.

Based on Fig. 5 The shift values for lactic acid oligomeric compounds from the polycondensation results in this study are: 1.38–1.41 ppm; 1.46–1.51 ppm; 4.26–4.3 ppm; and 5.01–5.17 ppm. The first two chemical shift signals (c and b) are H doublet signals which indicate the protons of the CH group atoms which are neighboring atoms of the CH<sub>3</sub> group of oligomers. While the next two chemical shift signals (a and d) are the H quartet signals which indicate protons from the CH<sub>3</sub> group which are neighboring atoms of the CH group of the oligomer.

Based on the chemical shift values it has been shown, both the CH<sub>3</sub> group and the CH group are in 2 different chemical environments, one of which is on the main chain of the oligomer while the other is next to the –OH terminal group of the oligomer. This is reinforced by the intensity shown in Fig. 5 which shows one region has a greater intensity than the others, indicating that one of them is in the oligomeric main chain [85]. The chemical shift values obtained in this study are different from those reported by [70,85]

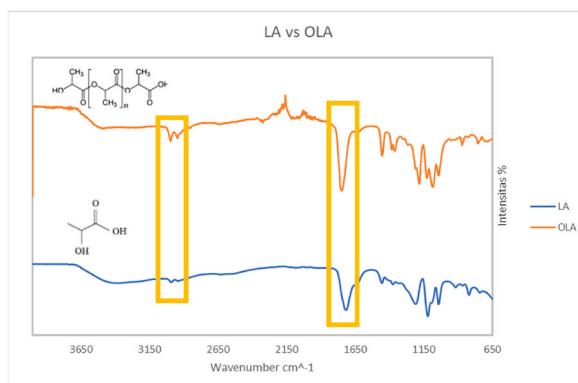


Fig. 4. FTIR results comparison of lactic acid and lactic acid oligomers.

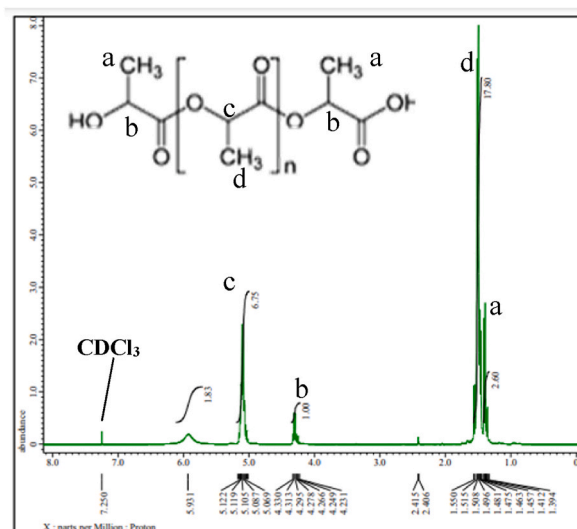


Fig. 5.  $^1\text{H}$  NMR result of lactic acid oligomer.

where this difference may be due to the influence of residual lactic acid that does not react to form oligomers.

### 3.2.2. Oligomeric depolymerization results

In this study, the depolymerization process is a lactide ring formation process obtained through the interaction reaction between dimer molecules (*trans*-esterification reaction) to become lactide, where the interaction between these molecules is caused by the thermal degradation of lactic acid oligomers into short oligomeric chains or lactide rings (Rahmayetty et al., 2018; [86]). This process takes place at temperatures above  $180^\circ\text{C}$  [87] and based on [88] the optimum temperature of the depolymerization process using an  $\text{SnCl}_2$  catalyst is at  $210^\circ\text{C}$ . The following are the results of lactide analysis from the depolymerization process in this study.

In Fig. 6 it can be seen that oligomers and lactides have wave numbers that are close to each other, where the wave numbers of each group on lactide are  $2996\text{ cm}^{-1}$  and  $2931\text{ cm}^{-1}$  which indicate the presence of CH groups;  $1265\text{ cm}^{-1}$  and  $1094\text{ cm}^{-1}$  which show the vibrational valence of asymmetric COC and symmetrical lactide ring;  $1752\text{ cm}^{-1}$  which shows C=O lactide;  $1455\text{ cm}^{-1}$  and  $1354\text{ cm}^{-1}$  which show asymmetric and symmetrical bend vibrations of CH originating from  $\text{CH}_3$ ;  $933\text{ cm}^{-1}$  which shows the O=C-O lactide ring. Seen from Fig. 6 There is a peak appearance at the wave number of  $933\text{ cm}^{-1}$  which previously did not appear in the oligomer. In the literature it is stated that the appearance of the peak in the wavenumber is an indication of the O=C-O lactide ring shown at the wavenumber of  $936\text{ cm}^{-1}$  [89,90]. The slight difference with the literature may be due to differences in the lactide isomer where in the literature it is D,L-Lactide while in the synthesis it is L-Lactide. The results of the depolymerization are further strengthened by Fig. 7 which shows the comparison of the FTIR graph of the synthesized lactide with the standard (commercial) lactide which is shown in Fig. 7 shows the overall identical wavenumber for both the synthesized and standard lactides. There is an appearance of wave numbers around  $3500\text{ cm}^{-1}$  in the synthesized lactide which is thought to come from the -OH origin [91]. This is caused by the presence of impurities such as the remaining oligomers that do not react to form a lactide ring so that the -OH group on the oligomer is detected [92]. Based on Fig. 6 and 7. Lactide FTIR charts obtained in this study also have similarities with those reported by [90,92-94] and Banu et al. , 2009.

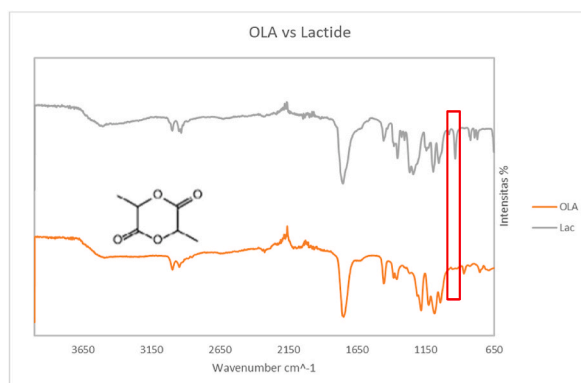


Fig. 6. FTIR results comparison of lactide with lactic acid oligomers.

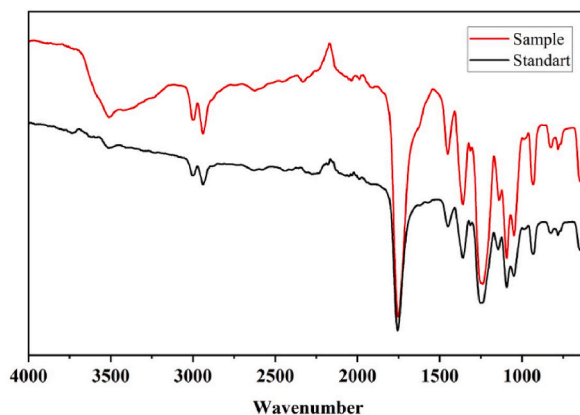


Fig. 7. Comparison of FTIR result of synthesized lactide with standard lactide.

After analysis using FTIR, the depolymerized product was also analyzed using a Core Magnetic Resonance instrument to strengthen the FTIR analysis results obtained. The following is the result of the Core Magnetic Resonance analysis of the depolymerized product.

Based on Fig. 8 The chemical shift values for depolymerized lactide compounds in this study were 1.5–1.6 ppm and 5.0–5.1 ppm. The first chemical shift signal (b) is a doublet H which indicates the number of protons from the CH group which is a neighbor of the CH<sub>3</sub> group while the second signal (a) shows the H quartet which indicates the proton from the CH<sub>3</sub> group which is a neighbor of the CH group. The value of the chemical shift in the H doublet and the H quartet in this study is slightly different from that reported by [76]. This can result in impurities remaining in lactide.

Based on the results of the analysis that has been obtained, it can be concluded that the oligomer depolymerization process has succeeded in converting the oligomers into lactide rings which will be used in the ring opening polymerization process.

### 3.2.3. Comparison of polymerization results

The polymerization process is a process in which monomers combine in large amounts of two or more types of monomers to form long-chain polymers. In research, the polymerization process takes place through the opening of the lactide ring so that it can form a long chain of lactic acid polymer. The following are the results of the obtained PLA analysis.

Based on Fig. 9 shows a difference at the peak of the 933 cm<sup>-1</sup> wave number that appears on the lactide graph, while the polymerized PLA product does not show a peak at that wave number. The disappearance of the peak in the wavenumber indicates that the lactide monomer ring has opened and polymerized. The results obtained are also in line with those reported by [95] which stated that the loss of the peak at the wave number of 933 cm<sup>-1</sup> is an indication of the opening of the lactide ring. The results of the synthesis are also strengthened by Fig. 10 which compared standard (commercial) PLA with synthetic PLA in this study. Based on the FTIR graph shown, it appears that the wave numbers between standard (commercial) PLA and the PLA synthesized in this study have identical wave numbers. Based on this, it shows that the lactide polymerization process has succeeded in opening the lactide ring to combine

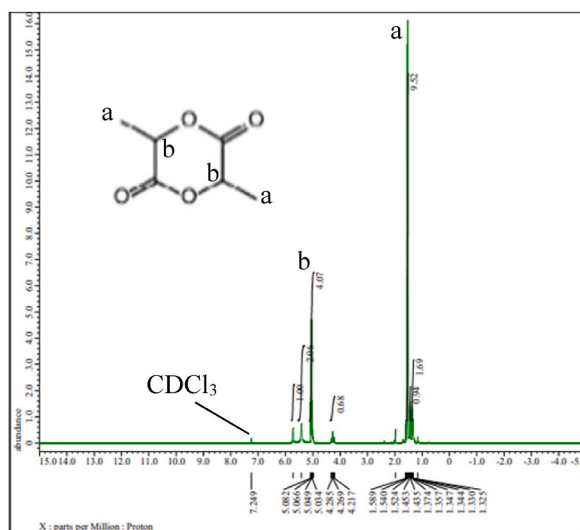


Fig. 8. Lactide H NMR chart.



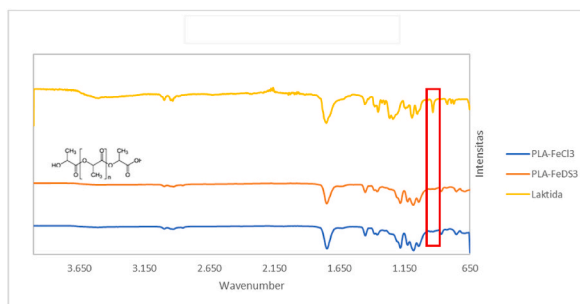


Fig. 9. Comparison of FTIR results of synthesized PLA with lactide.

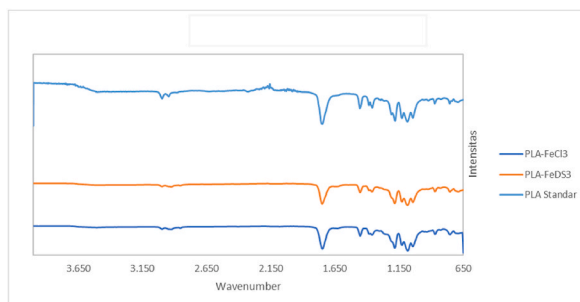


Fig. 10. Comparison of synthesized PLA FTIR results with commercial PLA

lactide monomers into polymers with long chains to form poly lactide or poly lactic acid so that the final product of this polymerization is PLA.

Based on Fig. 11 shows 2  $2\theta$  peaks in PLA polymerized with  $\text{FeCl}_3$  catalyst and PLA polymerized with  $\text{Fe}(\text{DS})_3$  which is  $16.79^\circ$ ;  $16.74^\circ$  and  $19.08^\circ$ ;  $19.13^\circ$ . The results obtained in the study also have similarities with those reported by [76,96]. From Fig. 11. Furthermore, calculations were carried out to determine the degree of crystallinity of PLA obtained from the synthesis and the values obtained were 37.5% for PLA polymerized with  $\text{Fe}(\text{DS})_3$  catalyst and 49% for PLA with  $\text{FeCl}_3$  catalyst. Based on the crystallinity value of  $\text{FeCl}_3$  catalyst is higher than  $\text{Fe}(\text{DS})_3$ , it is reinforced by the high intensity shown in the  $\text{FeCl}_3$  graph while  $\text{Fe}(\text{DS})_3$  is much lower. The degree of crystallinity of a polymer indicates that the regularity of the polymer compound is getting better, if a polymer has a high degree of crystallinity, the polymer is denser so the resistance is getting better. In addition, high crystallinity also indicates that the molecular weight of the polymer is getting higher due to the regularity of the polymer structure [97]. It can be concluded that the surfactant catalyst combined with Lewis acid Fe (III) reduces the degree of crystallinity of the obtained PLA so that a suitable application for polymers with a low degree of crystallinity is film application while  $\text{FeCl}_3$  is more suitable for temporary storage in the future.

Thermal property and crystallinity of PLA have a direct influence on its degradation. In general, the physical and mechanical properties of a polymer are determined based on its stereochemistry. The degree of crystallinity of PLA depends on the type and

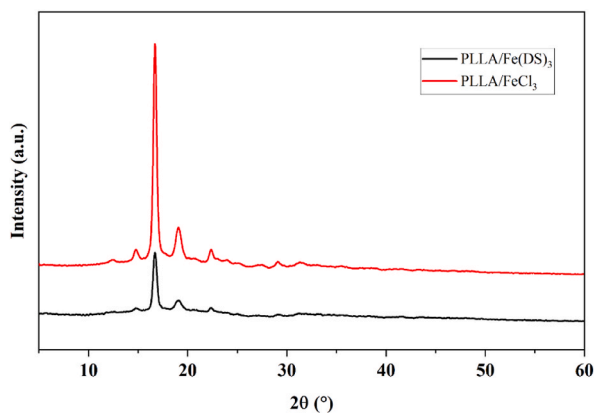


Fig. 11. Comparison of XRD results of PLA using  $\text{FeCl}_3$  catalyst with  $\text{Fe}(\text{DS})_3$ .



composition of the stereoisomer of the lactic acid monomer. The regulation of physical properties and biodegradability of PLA can be obtained by resemizing D isomers and L isomers (PDLLA), the more D-isomers, the more amorphous PLA will be and the less the amount will increase the degree of crystallinity of PLA. The degree of crystallinity of PLA affects the melting point, glass transition point and mechanical properties of PLA. So that the increase in the composition of the D-isomer will further reduce its thermal stability due to its more amorphous nature. On the other hand, the presence of an amorphous domain that increases the rate of degradation of PLA also has the advantage of being a product that is easily decomposed so that it is more friendly to the environment. In industrial applications. In this research, the basic material used is lactic acid with L-isomer to increase its thermal properties and degree of crystallinity. PLA with high crystallinity is expected to increase its durability for long-term use due to its high thermal and chemical resistance [98]. The glass transition temperature of a polymer is a macro manifestation of the flexibility of a polymer chain, where when the density of a polymer increases, the glass transition temperature increases [99]. The following is the result of the DSC analysis of the PLA synthesized in this study.

When a polymer is heated to a temperature that exceeds the  $T_g$  of the polymer, a polymer transition occurs from the original stiff to rubbery-like and softened. In addition to  $T_g$ , another parameter that is no less important is the melting temperature of the crystalline polymer ( $T_m$ ), when a polymer is heated to exceed the  $T_m$  of the polymer, a phase change occurs from a solid to a viscous liquid [100]. Parameters  $T_g$  and  $T_m$  of a polymer are very important to determine how the polymer will be applied in everyday life. According to [101] the thermal performance of commercial PLA obtained from Natureworks with an average molecular weight of 160,000 g/mol was 52 °C for the  $T_g$  value and 152 °C for the  $T_m$  value with a degree of crystallinity of 12.9%. As a comparison, PLA synthesized using a lipase catalyst with a molecular weight of around 5400 g/mol reported by [76] has a PLA crystallinity degree of 31% with  $T_g$  and  $T_m$  obtained at 65 °C and 119 °C. Based on Fig. 12 it appears that the PLA synthesized in this study has  $T_m$  and  $T_d$  values in PLA using  $FeCl_3$  and  $Fe(DS)_3$  respectively 107 °C; 111 °C and 352 °C; 327 °C. Based on the results of DSC analysis, it can be concluded that the thermal properties The PLA synthesized in this study has a performance that is still far below commercial PLA, this indicates that the molecular weight of PLA in this study is still far below that of commercial PLA. This low molecular weight also causes low thermal resistance so that the  $T_g$  value of the PLA synthesized in the study was not recorded. In addition, the results of the PLA obtained in the study are still in the form of crude PLA, so there are still many impurities that can reduce the properties of the synthetic PLA. There is a unique phenomenon in the  $T_d$  value of PLA synthesized using  $Fe(DS)_3$  which has a  $T_d$  value compared to PLA synthesized using  $FeCl_3$ . This seems to be caused by the presence of micellar micromolecules that still surround crude PLA, causing the  $T_m$  value of PLA synthesized using  $Fe(DS)_3$  catalyst to be higher.

In addition, polymers with higher molecular weights will have much better mechanical properties. Generally, the mechanical properties of polymeric materials increase with increasing molecular weight to a certain extent, where the mechanical properties are independent of the polymer chain length. High molecular weight polymers are generally required to obtain good mechanical properties and high thermal stability. Higher molecular weight polymers also mean that there is an increase in chain bonding, which leads to an increase in the tensile strength and modulus of elasticity of the polymer. The limit values at high molecular weights will vary depending on the particular polymer [102].

Research conducted by Hyon et al., in 1997 aimed to determine the effect of variations in the concentration of stannous octoate catalyst from 0.003 to 0.8 wt% on the molecular weight of PLLA. Data obtained that to produce PLLA with optimal molecular weight requires an optimal concentration of catalyst which at the time of catalyst concentration of stannous octoate is 0.05% wt. In addition, a study conducted by Domb & Langer in 1987 tested several catalysts used for polymerization of 1,3 bis(*p*-carboxyphenoxy)propane sebacic acid (CPP-SA). The highest molecular weight value was found in the addition of a cadmium acetate catalyst with Mw 245,010 from the original variable without a catalyst to produce Mw 116,800. In addition, the addition of cadmium acetate catalyst which is a heterogeneous catalyst has the highest viscosity compared to other catalyst variables. The GPC result of PLA synthesized in this study was shown in Fig. 13 then tabulated in Table 2.

Based on Table 2 it appears that the molecular weight of PLA synthesized using  $FeCl_3$  catalyst has a slightly higher molecular weight than using  $Fe(DS)_3$  catalyst. It appears that in the reaction conditions without water solvent and the reactor atmospheric conditions which are not inert  $FeCl_3$  still has a performance that is above  $Fe(DS)_3$ . This is because the performance of the Lewis acid  $FeCl_3$  catalyst is water-labile so that the reaction conditions without solvent indicate that the  $FeCl_3$  catalyst has slightly superior performance to the  $Fe(DS)_3$  catalyst. This is supported by research conducted by [11,15] which showed that the LASC catalyst had better performance results when the reaction conditions had water as a solvent than without using water as a solvent. In addition, the atmospheric conditions of the polymerization reaction also have an influence where according to [103] the polymerization reaction using a LASC catalyst is a radical polymerization reaction that requires inert atmospheric conditions in the process to produce better performance. Atmospheric conditions that are not inert cause the radical polymerization reaction process to be inhibited, this is due to the presence of oxygen which is an inhibitor in radical polymerization so that the formation of long polymer chains is terminated. In addition, the molecular weight value of synthesized PLA in this study is still far below the molecular weight value of commercial PLA. This was caused by imperfect reactor conditioning, where the reactor was only isolated from the air but no inert atmosphere conditioning was carried out in the reactor, namely  $N_2$  gas flowed. According to [104] this thermal oxidation causes a decrease in the properties of the polymer so that the molecular weight of the PLA obtained is of low value. This is supported by research conducted by [105] which shows the results of PLA with high molecular weight when the reactor conditions are inert by flowing nitrogen gas. In addition to these two factors, another cause of the low molecular weight of PLA is synthetic PLA which is still in the form of crude PLA, so that the impurities contained in PLA also seem to have an effect on PLA properties. According to [98] the presence of impurities in the form of catalyst residues, even though the amount is very small, can reduce the thermal properties of the obtained PLA, so based on this, a PLA purification process is needed to remove impurities in PLA.

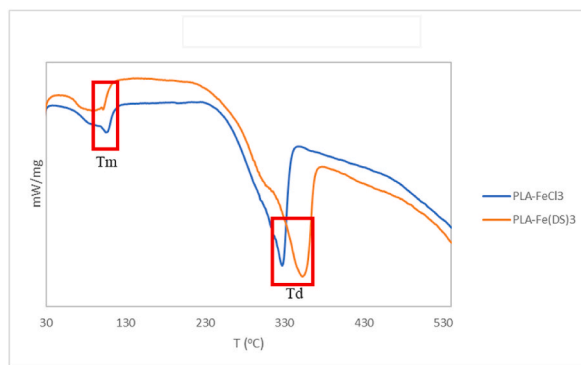


Fig. 12. Comparison of DSC result of PLA using FeCl<sub>3</sub> with Fe(DS)<sub>3</sub>.

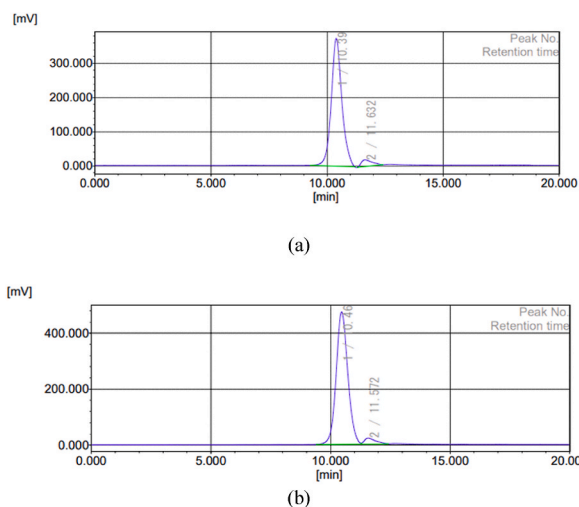


Fig. 13. Gpc result of synthesized PLA (a) catalyzed by FeCl<sub>3</sub> and (b) catalyzed by Fe(DS)<sub>3</sub>.

Table 2

Comparison of the molecular weight of PLA synthesis using FeCl<sub>3</sub> catalyst with Fe(DS)<sub>3</sub> Specimen-catalyst Mw, Mn, and PDI

Catalyst-specimen	Area of each peak (%)	MW (g/mol)	Mn (g/mol)	PDI
PLA-FeCl <sub>3</sub>	94.97	23,720	16,591	1.430
	5.03	235	66	3.546
PLA-Fe(DS) <sub>3</sub>	95.93	20,232	13,622	1.485
	4.07	301	80	3.778

#### 4. Conclusion

The synthesis of the Lewis Acid catalyst combination of Surfactants was carried out by dissolving SDS and FeCl<sub>3</sub>.6H<sub>2</sub>O then mixing the two solutions under cold conditions with stirring then the precipitate formed was then filtered and then put in an oven and desiccator. In the synthesis of PLA, there are four stages of the process, namely the stage of dehydration of lactic acid, the stage of polycondensation of lactic acid, the stage of oligomer depolymerization, and the stage of open ring polymerization where the research succeeded in converting lactic acid into a polymer that was strengthened by the results of FTIR and XRD analysis. The LASC catalyst obtained in this study has a crystallinity characteristic of 24% so that the catalyst is amorphous and thermal stability up to 180 °C. The PLA results obtained in this study between the FeCl<sub>3</sub> and Fe(DS)<sub>3</sub> catalysts were the crystallinity degrees of 49% and 37.5%, Tm values are 111 °C and 107 °C, Td values are 327 °C and 352 °C, and molecular weights are 22,540 g/mol and 19,420 g/mol.

#### Author contribution statement

Tri Widjaja, N. Hendrianie, S. Nurchamidah, A Altway: Conceived and designed the experiments; Contributed reagents, materials,

analysis tools or data. Aisyah Alifatul, Bayu Yusuf, Fakhrizal F, Atha Pahlevi: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

### Data availability statement

Data included in article/supplementary material/referenced in article.

### Additional information

No additional information is available for this paper.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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