Polymerization of Lactide to Polylactic Acid: Effect of Reaction Temperature

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***Abstract*— Polylactic acid (PLA) is one of biodegradable polymer produced from sustainable resources and have a few applications in various field. The reaction temperature is one of the factors that can affect the rate of reaction. From previous research, the inconsistent reaction temperature used for polymerization of lactide to PLA makes it difficult to identify which the best reaction temperature. Since the parameter involved is temperature, it is important to determine the value of the rate constant, frequency factor and the activation energy. Objectives of this study are to produce PLA at different temperatures and to characterize the PLA using Fourier transform infrared spectrometer and UV visible spectrophotometer. In this work, the polymerization of lactide to PLA used ring-opening polymerization (ROP) used lactide, lauryl alcohol and a thin layer of tin octoate. Reaction temperature in this experiment at temperature 110-130ºC. The PLA collected at the time interval and analyzed its characteristic. FTIR spectrum used to indicate the presence of -OH, -C=O and -CH_3. Based on FTIR result, the highest peak of -OH, -C=O and -CH_3 at temperature 130ºC. By comparing the reversible polymerization model to first-order reaction, the rate constant at 110, 120 and 130ºC obtained at 2.166, 3.012 and 4.236 s^{-1} while the value of frequency factor = $1.296 \times 10^6\ s^{-1}$ and activation energy = 42.68 kJ/mol.**

Keywords*— Characterization; FTIR; Lactide; Polylactic acid; Reaction temperature; Ring-opening polymerization; Stannous octanoate; UV visible spectrophotometer

INTRODUCTION

Polylactic acid or known as polylactide (PLA) is a thermoplastic aliphatic polyester from sustainable resources such as corn starch, tapioca roots, chips or sugarcane. PLA can apply for various applications such as in food packaging materials [1], biomedical products as matrices for drug delivery and bone fracture internal fixation devices in surgery [2], an agricultural plant growth promoter and non-woven applications such as geotextiles, wipes, diapers and more [3].

The reaction temperature is one of vital factor to make the rate of polymerization reaction of lactide faster. Many types of research done using a different range of reaction temperature for polymerization of lactide to PLA. Factors for having a different reaction temperature because of the equipment used, type and concentration of catalyst, type of solvent used and many. For example, Duda and Penczek [4] determined the thermodynamic parameters of L-lactide polymerization in dioxane at 80-130ºC. But, Sedush and Chvalun [5] produce PLA in differential scanning calorimetry at temperature 180-220ºC. The higher the temperature, reaction rate become increasing but too high processing temperature can increase the consumption of energy. Since this work dealing with the effect of reaction temperature, the rate constant, k and activation energy need to identify and compare with other researchers. For study the effect reaction temperature in polymerization of lactide to PLA used tin octoate catalyst and lauryl alcohol as an initiator at temperature 110-130ºC. Kinetic curves gained for experiments operated at different temperature. The activation energy determined using a model suggested by Witzke [6] and compared to first order reaction model from Petrucci [7].

METHODOLOGY

A. Materials

2-Ethylhexanoic acid tin (II) salt (Sn(Oct)2; Sigma Aldrich, 92.5-100% purity), 3,6-Dimethyl-1,4-dioxane-2,5-dione (Lactide; Sigma Aldrich, 99% purity) and 1-dodecanol (Lauryl alcohol; Merck) used for PLA production. For preparation tin octoate thin layer, the chemicals used are polyethylene glycol (Merck), ethylene glycol (Bendosen) and nitric acid (Merck, 65% purity). The chemicals used are polylactic acid (PLA; GoodFellow) and N, N-Dimethylformamide (DMF; Merck) for preparation of PLA sample for the calibration curve.

B. Preparation of thin layer of tin octoate

Nitric acid, ethylene glycol, polyethylene glycol (PEG) and tin octanoate used in this preparation. Ethylene glycol and tin octoate prepared by ratio 10: 1. Nitric acid added into the solution contain ethylene glycol and tin octoate and mixed for 30 minutes. After that, 10 ml of PEG added and stirred for 6 hours. Finally, the solution leaves for aging overnight.

C. Preparation for calibration curve

The standard sample of PLA prepared by melting the PLA pallet at temperature 90 ºC in DMF. After that, the stock sample diluted into 20 samples with different concentration. All the sample tested using UV visible spectrophotometer and the data obtained within the range 225nm recorded. Later, plotted the graph of absorbance versus concentration.

D. Production of PLA

For this production of PLA, the monomer that used was lactide, the initiator was lauryl alcohol and the catalyst used was tin octoate that prepared in a thin layer. Lactide and distilled water added into the mixer and heated until it reached temperature 90ºC. Next, the solution containing lactide and distilled water transferred into a batch reactor and ran for 3 hours at the temperature 110ºC. When the polymerization of PLA completed, the product collected and analyzed the PLA characteristic. The process of PLA production repeated at temperature 120 and 130°C.

D. FTIR Characterization

The functional groups of the PLA product characterized using a Fourier transform infrared spectrometer (Spectrum One FT-IR, PerkinElmer, USA). The spectra recorded within 4,000 cm^{-1} and 280 cm^{-1} frequency ranges, with 4 cm^{-1} spectral resolution.

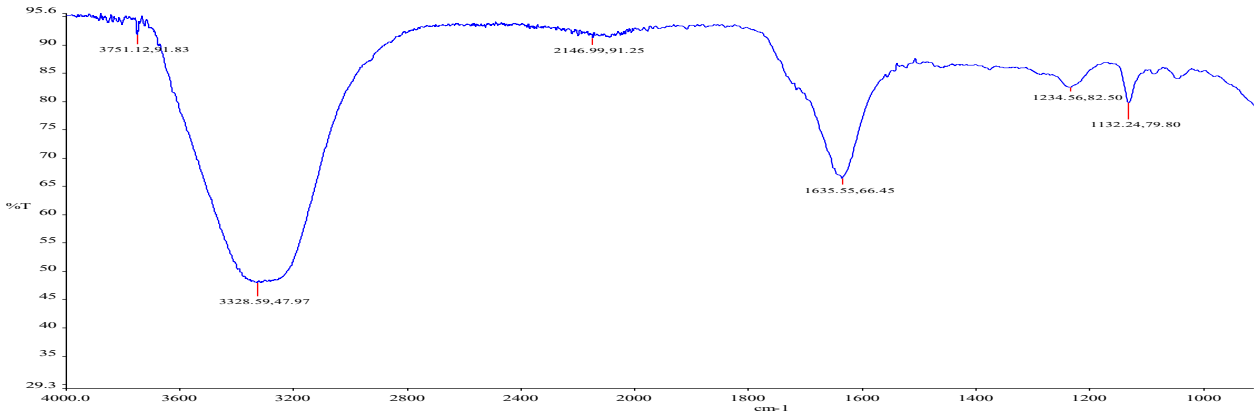
E. UV Visible Characterization

The concentration of PLA at different reaction temperature analyzed using UV visible spectrophotometer (LAMBDA 750 UV/Vis/NIR, PerkinElmer, USA). The absorbance recorded at wavelength range of 200-800 nm. Based on Auras et al. [8] and Goncalves et al. [9], the wavelength used to determine the absorbance of PLA at 225nm.

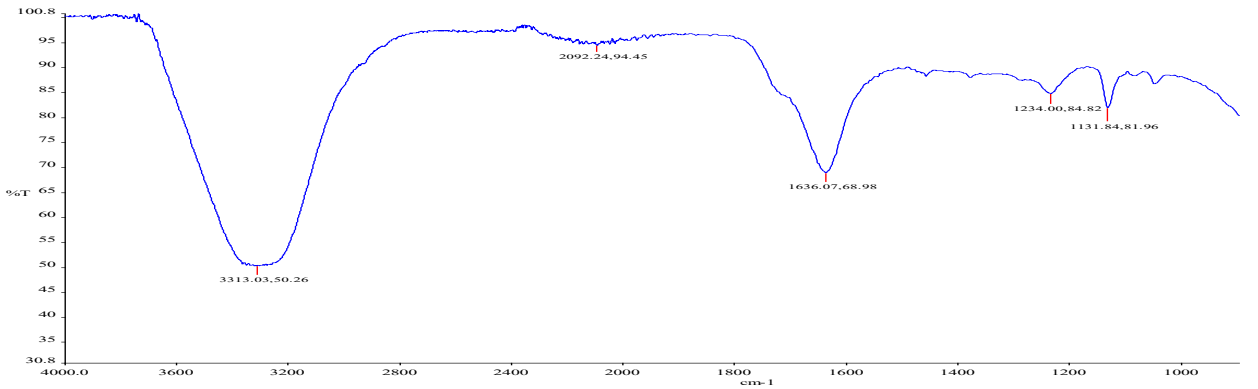
RESULTS AND DISCUSSION

A. Characterization of functional group of PLA using FTIR and UV visible

FTIR used in this work to verify the PLA produced. The presence of PLA confirmed when the value of peak compared with previous work. Table 1 showed a summary of peak band assignment for PLA at different temperature obtained from FTIR spectrum in Fig. 1.



[A]



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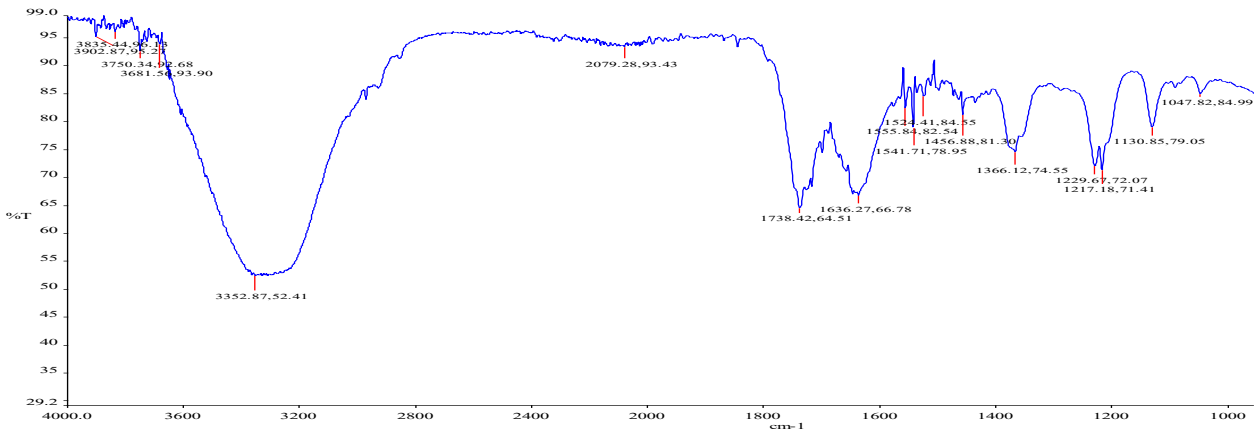

[C]

Fig. 1: The FTIR spectrum of PLA at temperature 110 [A],120 [B] and 130°C [C] at time 180 minutes.

Table 1: Summary of peak band assignment for PLA at different temperatures based on Fig. 1

Band assignment	Temperature (°C)		
	110	120	130
-OH	3328.59	3313.03	3352.87
-C=O	1635.55	1636.07	1636.27
$-CH_3$	1132.24	1131.81	1366.12

Table 1 showed that -OH peak at 3328.59, 3313.03 and 3352.87 cm^{-1} at temperature 110, 120 and 130°C. All value of -OH peak at different temperature within the range of band position of -OH stretching (hydroxyl and water) at 3571-3230 cm^{-1} referred to Wang et al. [10] and Garlotta [11] works. The highest -OH peak at temperature 130°C. The strong -OH peak indicated the terminal was -OH group and indicated the presence of water since it used as medium to melt the lactide to form lactide solution in this experiment. In Rahmayetty et al. [12] work, the lactide heated until it melted without using water. Therefore, the FTIR results from Rahmayetty et al. [12] showed the presence of -OH group but the weak peak indicated the -OH available as a terminal. The presence of hydroxyl group needs to be identified since the hydroxyl group part of building block that will differentiate between PLA and lactide.

The presence of -C=O peak shown at 1635.55, 1636.07 and 1636.27 cm^{-1} at temperature 110, 120 and 130°C. Based on Table 1, the highest -C=O peak at temperature 130°C. Those peaks about the range of -C=O stretch value based on data C=O stretching (carboxylic acid) cited in Wang et al. [10] which is 1694 cm^{-1}. But based on Garlotta [11], -C=O carbonyl stretch present at 1759 cm^{-1} which is the value higher compared to the result obtained from this experiment. The presence of carbonyl group needs to be identified since the carbonyl group part of building block for lactide and PLA.

The $-CH_3$ peak for temperature 110, 120 and 130°C at 1132.24, 1131.81 and 1366.12 cm^{-1}. From the data above, the peak of $-CH_3$ at temperature 130°C is highest compared to other temperature. From Wang et al. work [10], $-CH_3$ symmetric deformation vibration of PLA happened at spectra 1382 cm^{-1} and this value nearest to the $-CH_3$ at temperature 130°C which is 1366.27 cm^{-1}. For temperature 110 and 120°C, the value of $-CH_3$ peak nearest to data cited by Goncalves et al. [9] which is 1130 cm^{-1}. The presence of alkyl group needs to be identified since the alkyl group part of building block for lactide and PLA.

Overall result gained from FTIR spectrum showed the polymerization of lactide to PLA indeed produced PLA and it can be proven with presence of -OH, -C=O and $-CH_3$ as functional group for PLA.

UV visible used in this study to determine the concentration of PLA at wavelength 225 nm referred to Auras et al. [8] and Goncalves et al. [9]. Majority the reading of PLA absorbance in this study measured at of 220-230 nm to indicate the existence of PLA in the sample. From Fig. 2 and Fig. 3; the peak of the curve showed the absorbance of PLA produced at wavelength range of 220-230 nm. Thus, it proved the reference of PLA wavelength from Auras et al. [8] and Goncalves et al. [9] seem valid.

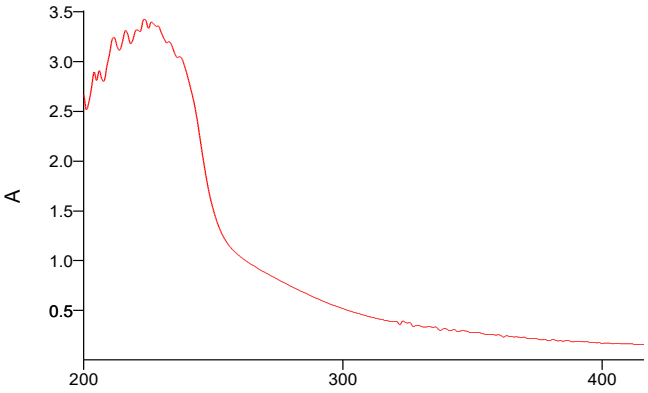

Fig. 2: Absorbance versus wavelength for PLA at temperature 120°C.

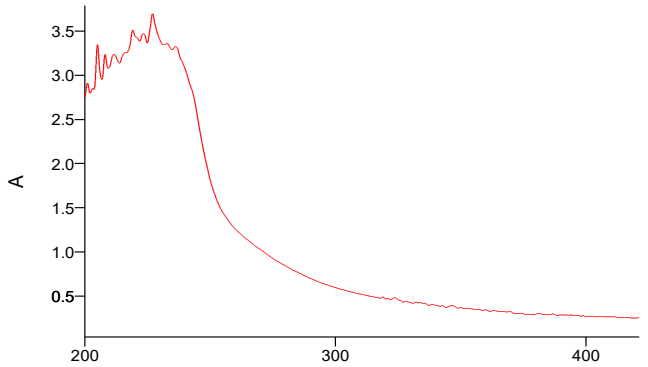

Fig. 3: Absorbance versus wavelength for PLA at temperature 130°C.

B. Effect of polymerization rate at different temperatures

Calibration curve method is an analytical chemistry technique to determine the concentration of unknown samples where the unknown sample is the concentration of PLA produced at temperature 110, 120 and 130°C at a certain time interval.

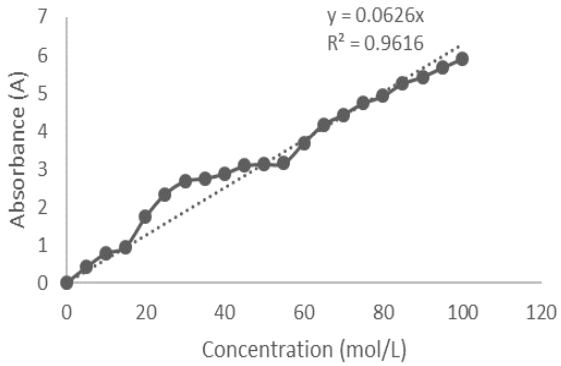

Fig. 4: Calibration curve of PLA standard sample

The information obtained from Fig. 4 is the equation of the straight-line and R-square value. The straight-line equation used to determine the concentration of PLA produced at different temperature. The R-square value significance to the quality of data obtained from the concentration of the sample. The most acceptable value usually more than 0.96. Since the R-square for this work is 0.9616, so this equation of straight line was valid to use to identify the concentration of PLA produced. The equation of the straight line applied to data obtained from Fig. 5 to plot graph of PLA concentration versus time taken at different temperature (Fig. 6).

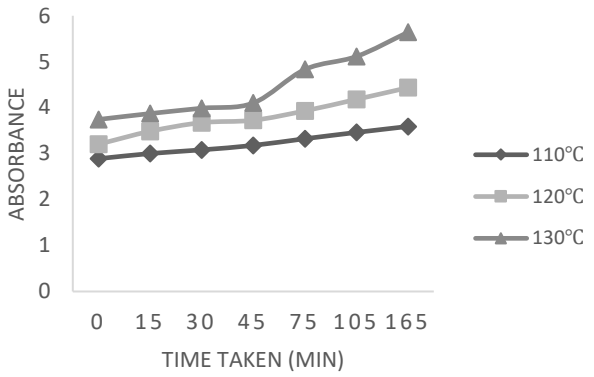

Fig. 5: Graph of absorbance versus time taken in different temperature.

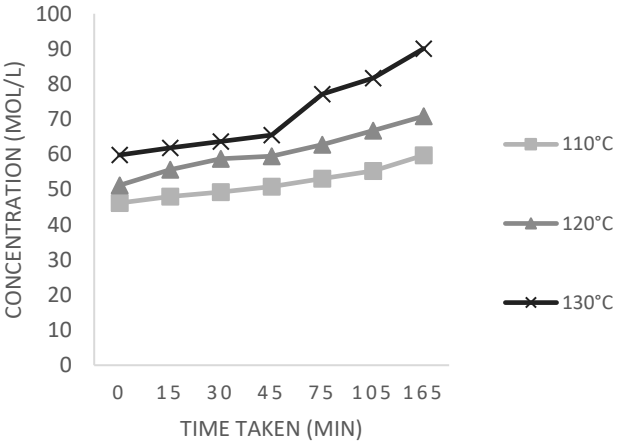

Fig. 6: Graph of PLA concentration versus time taken in different temperature.

Next, the order of reaction rate determined using model of reversible polymerization developed by Witzke [6]:

$$M = M_{eq} + (M_0 - M_{eq})e^{-kIt} \quad (1)$$

Where M - monomer concentration at time, Meq - equilibrium monomer concentration, M_0 - initial monomer concentration, k – polymerization rate constant, I - catalyst concentration.

The integrated rate law for a first-order reaction referred to Petrucci [7] that written in exponential form and logarithm form:

$$[A] = [A]_0 e^{-kt} \quad (2)$$

$$\ln[A] = \ln[A]_0 - kt \quad (3)$$

Where [A] – reactant concentration at time, $[A]_0$ – initial reactant concentration and k – rate constant. Eq. 1 compared to Eq. 2 and it showed the similarity in term of form. The negative value of k indicates the reactant concentration decreases with time. Thus, the reaction order from this experiment is first order of reaction.

Denote the concentration of lactide is [A] and the concentration of PLA is [B]:

$$[A] \rightarrow [B]$$

Hence, the first order of reaction from Eq. 3 written by replacing [A] to [B] and the positive value of k indicated the concentration of product increase with time as:

$$\ln[B] = \ln[B]_0 + kt \quad (4)$$

After the order of reaction determined, the rate constant at different temperature gained from slope based on Fig. 7. Table 2 showed the summary of rate constant obtained at temperature 110-130°C when temperature increase, the rate constant also increasing.

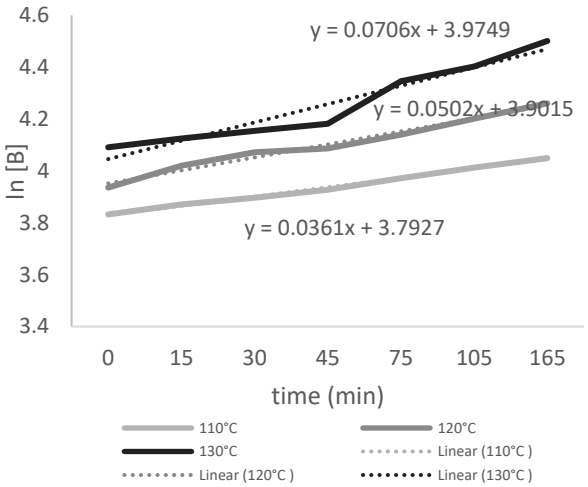

Fig. 7: Graph of natural logarithm of PLA concentration versus time at different temperature.

Table 2: Summary of rate constant at different temperature

Temperature (°C)	Rate constant, k (min^{-1})
110	0.0361
120	0.0502
130	0.0706

Arrhenius equation used in this work because this formula for temperature dependence reaction rates and the equation shown:

$$k_A(T) = Ae^{\frac{-Ea}{RT}} \quad (5)$$

Where A – frequency factor, Ea – activation energy (J/mol), R – gas constant (8.314 J/mol.K) and T – absolute temperature (K). When apply postulation to Eq. 5, the equation will become:

$$\ln k_A = \ln A - \frac{Ea}{R}\left(\frac{1}{T}\right) \quad (6)$$

Eq. 6 compared to $y = c + mx$, where by c= ln A and m=$\frac{Ea}{R}$. The straight line equation gave the value of slope that used to determine the activation energy and frequency factor. Arrhenius plot based on data from Table 2 and illustrated in Fig. 8. It can be seen from Fig. 8 that the data obtained fit into the straight line smoothly. Based on equation of straight line from Fig. 8:

$$\ln A = 14.075$$

$$\frac{Ea}{R} = 5134.6$$

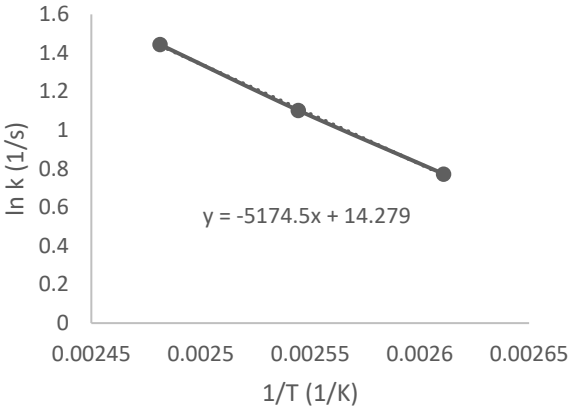

Fig. 8: Arrhenius plot for lactide polymerization

Therefore, the polymerization of lactide to PLA at temperature 110-130°C, the value of frequency factor, A = $1.296 \times 10^6\ s^{-1}$and activation energy, E_a=42.68 kJ/mol. Since this range of temperature used lower compared to other researchers, the value of frequency factor and activation also distinct. For examples, Yu [13] performed the polymerization at temperatures 130–180°C and based on his results, the value of E_a = 63 kJ/mol and the E_a value a little bit higher compared to result from this experiment. High activation energy means slower the polymerization rate. Sedush and Chvalun [5] conducted experiments at temperature 180-220°C, the value of frequency factor, A = $1.094 \times 10^6\ s^{-1}$and activation energy, E_a= 50 ± 5 kJ/mol. Since Sedush and Chvalun [5] also performed their experiment at different parameter such as concentration of catalyst, for that reason the value of frequency factor and activation energy quite distinct.

Conclusion from this work showed that increase the reaction temperature can speed up the rate of reaction. Yu et al. [13] and Karande et al. [14] also stated in their work that polymerization rate increases with temperature.

In future research, the polymerization of lactide to PLA need to study of the effect reaction temperature in term of molecular weight of PLA produced, the type and concentration of catalyst and initiator and more. Those parameters also influence the kinetic and thermodynamic data of polymerization reaction. The significance of this study to provide kinetic and thermodynamic data and the characterization of PLA using FTIR and UV visible to be used as a reference for other studies.

CONCLUSION

The polymerization of lactide to PLA with effect of reaction temperature well conducted. The functional group of PLA successfully determined from data obtained from FTIR and UV visible then compared to other previous work. FTIR results showed all the reaction in different temperature produced PLA. UV visible result showed all the reaction determined at selected wavelength. By comparing the reversible polymerization model to first-order reaction, the rate constant at 110, 120 and 130ºC obtained at 2.166, 3.012 and 4.236 s^{-1} while the value of frequency factor = $\mathbf{1.296 \times 10^6\ s^{-1}}$ and activation energy = 42.68 kJ/mol.

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MANUSCRIPT APPROVAL FORM FOR RESEARCH PROJECT II

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Student's Name : Amira Amiza Aminudin Matric No. : 2015429651

Project Title : Polymerization of lactide to PLA: Effect of reaction temperature

Supervisor's/ Examiner's comments:
CORRECTIONS HAVE BEEN MADE ACCORDINGLY.

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