# Fermentation of Lactic Acid to Polylactic Acid: A Study

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***Abstract*—Polylactic acid (PLA) is one of the major commercially available polymers which widely used in the food packing materials, fibers, agricultural films and biomaterials. Synthesis of PLA from fermentative lactic acid is another new alternative substrate which it is contributes to the reduction of production cost, increase the renewable resources value, and development of bioplastic that is environmentally friendly materials. PLA was synthesis in a direct polycondensation method with suitable chosen catalyst which is p-toluenesulfonic acid (PTSA) to obtained higher molecular weight (Mw). The fermentative lactic acid was prepared from Lactobacillus rhamnosus TISTR 108 and used as a monomer of polymerization. The number average molecular weight (Mn) and molecular weight (Mw) of PLA products were analyzed by end-group analysis and High Performance Liquid Chromatography (HPLC). From the results, high molecular weight of PLA were obtained from commercial lactic acid by direct polycondensation under appropriate conditions which are 0.25 wt% PTSA as catalyst, temperature at 170°C and polymerizing time for 7 hr. The number average molecular weight (Mn) and molecular weight (Mw) of the PLA products in fermentative lactic acid were 2,627 and 232 Da, respectively, while for commercial lactic acid were 42,288 and 423 Da.**

***Keywords*—Direct Polycondensation, Lactic Acid, Molecular Weight (Mw), Polylactic Acid**

## I. INTRODUCTION

The synthesis of PLA have three main routes, which are direct polycondensation (DP), azeotrophic dehydrative and ring opening polymerization (ROP). Generally, PLA is synthesized via ring-opening polymerization (ROP) of lactide monomer (Lalita et al., 2013). But this method is lengthy process, expensive and it is difficult to produce PLA because of the several steps involved in this reaction cycle. Therefore, it has been developed that ROP will required low-cost continuous process for the production of lactic acid-based polymers. The process will provides a commercially viable biodegradable commodity polymer made from renewable resources (David E et al., 2005). In contrast, the direct polycondensation (DP) of lactic acid is the simple reaction of PLA production and cheaper than ROP. However, the direct polycondensation is difficult to obtain high molecular weight of PLA polymer due to the resulting depolymerization reaction and the presence of water, impurities and low concentration of reactive end group. But the molecular weight of PLA polymer by this method can be increased by using catalyst. Other than that, on some research, in order to reduce the production cost of polylactic acid (PLA), lactic acid was polymerized by direct polycondensation (DP) under vacuum without using catalysts, solvents and initiators (Feerzet et al., 2009). This process fulfills the conditions of compactness, as well as it is safe and simple operation for an on-site cell plant concept. The efficiency and economics of lactic acid fermentation is still be a problem from many points of view. There have been various attempts to produce lactic acid efficiently from economic resources, such as rice bran, paper sludge, and green microalga (Ying Wang et al., 2015).

Currently, the fermentative production from pure lactic acid has increased because of lactic acid's own features where they are environmental friendliness and cost-effectiveness (Feerzet et al., 2009). As fermentation moves into lower-value and higher-volume chemicals, it becomes necessary to maximize efficiency and minimize costs and waste by-products to compete effectively against traditional options (Rojan et al., 2007). The current process for PLA synthesis is not simple, which using fermentative production of lactic acid followed by chemical process for the chosen methods of lactide and a cyclic dimer derived from the dehydration of lactic acid. Attempts to improve the rather stiff and brittle properties, PLA has been made by copolymerization or blending with other polymers or catalyst (Yu Kyung et al., 2011).

This study is explains on the method of producing polylactic acid from lactic acid where it discuss and compare the molecular weight obtained using different monomer of lactic acid. It also discuss the most suitable method that can give more benefits and can reduce cost of producing PLA.

## II. METHODOLOGY

In present work, the synthesis of PLA from commercial lactic acid and fermentative lactic acid prepared from Lb. rhamnosus TISTR 108 was studied by direct condensation polymerization and using p- toluenesulfonic acid as a catalyst. MRS medium which are the type of bacterial growth medium is so-named by its inventors which are *de Man, Rogosa* and *Sharpe*. It is developed in 1960, this medium was designed to favour the luxuriant growth of Lactobacilli for lab study. Finally, PLA products were increased their value added with forming as PLA film (Lalita Ponmanee et al,. 2013).

## *A. Materials*

The microorganism used was Lactobacillus rhamnosus TISTR 108 that were maintained in MRS medium at 4°C, was used to produce lactic acid. The MRS medium consist of 10g of glucose, 5g of yeast extract, 0.2g of $MgSO_4$, 0.5g of sodium citrate, 0.03g of $MnSO_4$, 0.03g of $FeSO_4$, 2.5g $KH_2PO_4$ and 0.015 ml per liter of $H_2SO_4$. The subjects used in the experiment was 85 wt% of lactic acid as a aqueous solution, p-Toluenesulfonic acid monohydrate (PTSA) catalyst, potassium hydroxide and sodium hydroxide, absolute ethanol, and isopropyl ether.

## *B. Methods*

The methods used in the lactic acid production was performed as fed batch fermentation under strictly anaerobic conditions carried out in a 2 L jar fermenter with an initial medium volume of 0.5 L using 5% (v/v) inoculum, temperature at 37°C, pH 5.7 agitation at 100 rpm for 141 h. After cell removal, lactic acid was recovered from fermentation broth and purified using Amberlite IRA-67 anion exchange resin. For synthesis of PLA by direct condensation polymerization, the polymerization process was optimized using the Taguchi method. Two steps direct condensation polymerization process were developed. The first step was to produce oligomer and then the oligomer of lactic acid was polymerized with p-Toluenesulfonic acid as a catalyst. The aqueous solution of commercial lactic acid in 850 g/L was dehydrated to produce oligo (lactic acid) at 100±5°C without catalysts under a nitrogen atmosphere for 5 hours using 500 mL four-necked flask equipped with a mechanical stirrer.

The second step was to make polymer, the solution of polymerization was carried out a 500 mL four-necked flask equipped with a mechanical stirrer and a reflux condenser with varying the polymerization temperature, concentration of catalyst, and polymerization time. Next, for synthesis of PLA from fermentative lactic acid, the development of the new alternative process for PLA synthesis was investigated by using the fermentative lactic acid prepared from Lb. rhamnosus TISTR 108 as the monomer with lactic acid concentration 180 g/L for PLA synthesis instead of a commercial lactic acid under the appropriate conditions of direct condensation polymerization. Next, in preparation of PLA blend films with mixing PLA synthesized from fermentative and commercial lactic acids, solvent casting method were used.

The weight ratio between both synthesized PLA from fermentative and commercial lactic acids was 50:50. 5g of PLA was dissolved in 100 mL chloroform and were stirred gently at room temperature. The dissolved solution was poured into glass plate and leaved to dry for 24 h at room temperature. Finally, the structure of PLA was characterized by ATR-FTIR for recording transmission spectra in the range of 4000 – 400 $cm^{-1}$. The number average molecular weight (Mn) was measured by titration against a standard alcoholic KOH concentration to obtain terminal functional groups and the number average molecular weight was calculated from equation 1:

$$Mn = \frac{w \times n \times 100}{V \times M}$$

Where w is the mass of the PLA sample, n is the number of reactive functional groups on the monomer (n = 2 for lactic acid), V is the volume of alkali consumed for neutralizing the functional groups and M is the molarity of the potassium hydroxide solution.

# III. RESULTS AND DISCUSSION

## *A. Method of Production*

In the journal (Lalita Ponmanee, 2013), the experiment's result were compared between two samples of PLA which used commercial lactic acid and fermentative lactic acid as the monomer. For the fermentative lactic acid as the monomer, the production of lactic acid by Lactobacillus rhamnosus was performed with the fed batch fermentation under strictly anaerobic conditions that was carried out in a 2 L jar fermenter with an initial medium volume of 0.5 L, using 5 % (v/v) inoculum, at a temperature of 37°C, pH 5.7 for 124 hours. The number average molecular weight (Mn) and molecular weight (Mw) of PLA products were analyzed by end-group analysis and High Performance Liquid Chromatography (HPLC). While the synthesis of PLA from commercial lactic acid as the monomer was performed by direct condensation polymerization and using p-Toluenesulfonic acid (PTSA) as a catalyst with the optimal condition from Taguchi method.

The number average molecular weight (Mn) and molecular weight (Mw) of the synthesized PLA were shown in **Table 1**. The results showed that the molecular weight and number average molecular weight of polymer derived from fermentative lactic acid were 232 and 2,627 Da, respectively. While for PLA derived from commercial lactic acid were 423 and 42,288 Da, respectively

From the result, it is best conclude that synthesis of PLA from commercial lactic acid as the monomer performed by direct condensation polymerization and using p-Toluenesulfonic acid (PTSA) as a catalyst with the optimal condition can obtained higher molecular weight. While fermentative lactic acid as the monomer performed with the fed batch fermentation under strictly anaerobic conditions can obtained lower molecular weight.

**Table 1**: The comparison of molecular weight and number average molecular weight of PLA synthesized from fermentative lactic acid and commercial lactic acid.

| Sample | Monomer | $M_n$ | $M_w$ |
|---|---|---|---|
| $PLA_1$ | Commercial LA | 42,288 | 423 |
| $PLA_2$ | Fermentative LA | 2,627 | 232 |

The method of using lactic acid bacteria are widely used as a cheap method for food maintenance by fermentation and usually no or little heat is required in the fermentation (Boontawan et al., 2011).

The other method for lactic acid fermentations production are using fed-batch, repeated batch, and continuous batch. But the higher concentration of lactic acid has achieved in batch and fed-batch cultures than in others, whereas continuous batch can produce higher productivity and the process can be run for a long period of time (Vijayakumar, Aravindan, and Viruthagiri, 2008).

The detailed of the conditions of PLA synthesis from commercial lactic acid by direct polycondensation performed are as shown in **Table 2**. This result include catalyst concentration, temperature, time, number average molecular weight (Mn) and molecular weight (Mw). From the result obtained, the highest molecular weight is 423 Da, number average molecular weight is 42,288 Da with catalyst concentration of 0.25 wt%, temperature of 170°C and reaction time 7 hour.

**Table 2**: Overall result of molecular weight (Mw) of PLA synthesis from commercial lactic acid by direct polycondensation (DP)

| Exp. | Catalyst concentration (wt% of the oligomer) | Temp. (°C) | Time (hr) | No. average molecular weight, $M_n$ | Molecular weight, $M_w$ |
|---|---|---|---|---|---|
| 1 | 0.25 | 140 | 4 | 16,409 | 259 |
| 2 | 0.25 | 150 | 5 | 17,908 | 317 |
| 3 | 0.25 | 160 | 6 | 26,453 | 350 |
| 4 | 0.25 | 170 | 7 | 42,288 | 423 |
| 5 | 0.50 | 140 | 5 | 16,802 | 285 |
| 6 | 0.50 | 150 | 4 | 17,634 | 323 |
| 7 | 0.50 | 160 | 7 | 32,297 | 286 |
| 8 | 0.50 | 170 | 6 | 25,965 | 333 |
| 9 | 0.75 | 140 | 6 | 18,719 | 270 |
| 10 | 0.75 | 150 | 7 | 18,849 | 277 |
| 11 | 0.75 | 160 | 4 | 20,747 | 307 |
| 12 | 0.75 | 170 | 5 | 30,032 | 344 |
| 13 | 1.00 | 140 | 7 | 19,557 | 270 |
| 14 | 1.00 | 150 | 6 | 23,518 | 307 |
| 15 | 1.00 | 160 | 5 | 25,873 | 323 |
| 16 | 1.00 | 170 | 4 | 25,533 | 317 |

By comparing with fermentative lactic acid, **Fig. 1** shows the result of lactic acid production from glucose for fermentative lactic acid. From **Fig. 1**, it shows that the concentration of lactic acid is much higher compared to the concentration of glucose. After 124 hours of fermentation process, the concentration of lactic acid was obtained to be 117 g/L. The yield was 92.7% and the productivity of lactic acid was 2.10 g/L.hour.

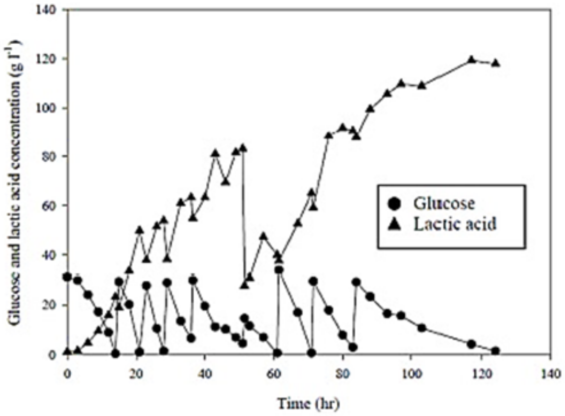

**Fig. 1**: Fed batch fermentation of lactic acid by *Lactobacillus rhamnosus* using glucose as substrate under strictly anaerobic condition (5% v/v inoculum, 37 °C, pH 5.7, 124 hours)

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On the other hand, from journal (Antonija Trontel, 2011), the experiment were conducted to obtain the production of lactic acid by the monoculture of Lactobacillus sp. In the first experiment, glucose and sucrose were fermented by *Lactobacillus* sp. From the first findings, the strain has not been further characterized. But, from the homofermentative strain, it was able to use mono- and disaccharide, grow and produce mainly about 90% L-(+)-lactic acid as shown in **Fig 2** and **Fig 3**.

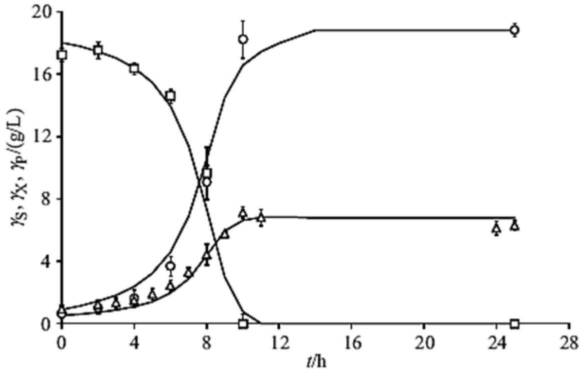

**Fig. 2**: Fermentation of glucose to lactic acid by *Lactobacillus* sp.: substrate concentration ($\gamma_s$, □), dry biomass ($\gamma_x$, Δ), and lactic acid concentration ($\gamma_p$, O)

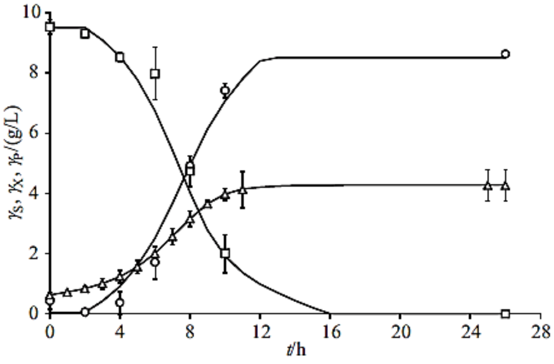

**Fig. 3**: Fermentation of sucrose to lactic acid by *Lactobacillus* sp.: substrate concentration ($\gamma_s$, □), dry biomass ($\gamma_x$, Δ), and lactic acid concentration ($\gamma_p$, O)

From the journal (Antonija Trontel, 2011), it is found that both conversions were rather fast and complete. The concentration of lactic acid in fermentation of glucose (**Fig. 2**) is $\gamma_o = 20$ g/L and was totally fermented in 10 h, while for complete conversion, the fermentation of sucrose to lactic acid (**Fig. 3**) is $\gamma_o = 10$ g/L with approximate 12 h.

From the result, it is best conclude that glucose has higher conversion compared to sucrose. *Lactobacillus* sp. conducts highly efficient homofermentative conversion of glucose to mainly L-(+)-lactic acid and therefore represents a good candidate for the industrial production of lactic acid to be used in the advanced PLA manufacturing.

From method of production of PLA that was stated, there are two monomer of lactic acid that can be use to synthesis PLA. The commercial lactic acid used direct polycondensation method as the synthesis ways and obtained higher molecular weight. While fermentative lactic acid use fed batch fermentation by *Lactobacillus rhamnosus* using glucose as substrate to synthesis PLA.

On the other hand, **Fig. 4** shows the synthesis method of lactic acid into high molecular weight of PLA. Although it shows that ring-opening polymerization (ROP) can yield molecular weight, Mw more than 100,000 of PLA, but it is the most expensive method. Therefore, in the journal (Donald Garlotta, 2001) proposed to use the most economical method which is condensation polymerization or direct polycondensation (DP) method. It is the least expensive route, but it is difficult in a solvent-free system to obtain high molecular weights, and therefore the use of coupling agents or esterification promoting adjuvants is required. There are various methods that can be used to increase the molecular weight of the PLA condensation products by esterification promoting adjuvents and chain extending agents.

Initially, the direct condensation of lactic acid was regarded as a process only to obtain a low molecular weight polymer which was not useful (James L, 1998), but recently the direct polycondensation (DP) of lactic acid can also obtain PLA with a significantly high molecular weight (Miyamoto, 2001). For example, (Moon et al,. 2001) have succeeded in preparing PLA with molecular weight of about $1.0\times10^5$ by conducting melt/solid polycondensation. Furthermore, (Fukushima and co-workers, 2000) also obtained PLA with high molecular weight, $M$w = $2.66\times10^5$ by using a process combining twin screw extrusion and solid-phase polycondensation with the reflux of free lactide.

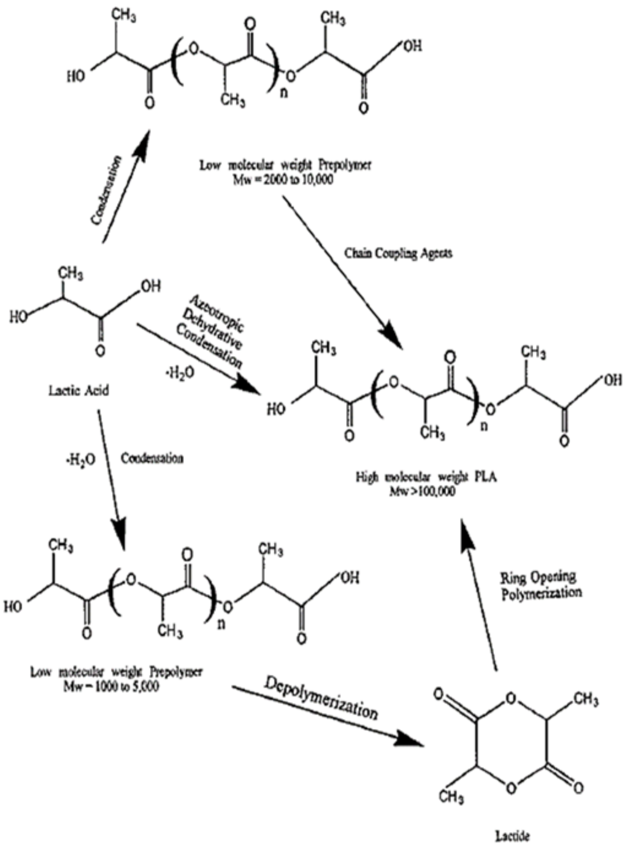

**Fig. 4**: Synthesis method for high molecular weight PLA *(Source: Journal of Polymers and the Environment, Vol. 9, No. 2, April 2001)*

## *B. Effect of Temperature*

From the overall result obtained using commercial lactic acid as a monomer, referring to the journal (Lalita Ponmanee, 2013), the comparison can be discuss more details by collecting all the result with constant temperature and different value of catalyst concentration of the oligomer. The catalyst used is *p*-Toluenesulfonic acid monohydrate (PTSA). As shown in **Table 3** for temperature 140°C, by using catalyst concentration 0.50 wt% of the oligomer, the molecular weight, Mw obtained is the highest which is 285 Da.

**Table 3**: Molecular weight, Mw obtained in temperature 140°C

| Exp. | Catalyst Concentration (wt% of the oligomer) | Temp. (°C) | Mw |
|---|---|---|---|
| 1 | 0.25 | 140 | 259 |
| 5 | 0.50 | 140 | 285 |
| 9 | 0.75 | 140 | 270 |
| 13 | 1.00 | 140 | 270 |

On the other hand, in constant temperature of 150°C, in **Table 4** shows the highest molecular weight, Mw obtained is 323 Da with the catalyst concentration 0.50 wt% of the oligomer.

**Table 4**: Molecular weight obtained in temperature 150°C

| Exp. | Catalyst Concentration | Temp. (°C) | Mw |
|---|---|---|---|

| | **(wt% of the oligomer)** | | |
|---|---|---|---|
| 2 | 0.25 | 150 | 317 |
| 6 | 0.50 | 150 | 323 |
| 10 | 0.75 | 150 | 277 |
| 14 | 1.00 | 150 | 307 |

In constant temperature of 160°C, in **Table 5** shows the highest molecular weight, Mw obtained is 350 Da with the catalyst concentration 0.25 wt% of the oligomer, which the catalyst concentration used was lower than in temperature 140°C and 150°C.

**Table 5**: Molecular weight obtained in temperature 160°C

| **Exp.** | **Catalyst Concentration (wt% of the oligomer)** | **Temp. (°C)** | **Mw** |
|---|---|---|---|
| 3 | 0.25 | 160 | 350 |
| 7 | 0.50 | 160 | 286 |
| 11 | 0.75 | 160 | 307 |
| 15 | 1.00 | 160 | 323 |

In constant temperature of 170°C, in **Table 6** shows the highest molecular weight, Mw obtained is 423 Da with the catalyst concentration 0.25 wt% of the oligomer, which the catalyst concentration used was lower than in temperature 140°C and 150°C.

**Table 6**: Molecular weight obtained in temperature 160°C

| **Exp.** | **Catalyst Concentration (wt% of the oligomer)** | **Temp. (°C)** | **Mw** |
|---|---|---|---|
| 4 | 0.25 | 170 | 423 |
| 8 | 0.50 | 170 | 333 |
| 12 | 0.75 | 170 | 344 |
| 16 | 1.00 | 170 | 317 |

From the result on the effect of the temperature, it can be conclude that the higher molecular weight can be obtained when the temperature is higher and the catalyst concentration is lower. As in this experiment, the highest molecular weight obtained is 423 Da with the highest temperature 170°C and lowest catalyst concentration, 0.25 wt% of the oligomer. Temperature and concentration of catalyst gave more significant influence on molecular weight, Mw and number average molecular weight, Mn values of PLA polymer. An increase of temperature increased the Mw and Mn values of PLA. As a result, the optimal conditions of PLA synthesis were 0.25 wt% *p*-Toluenesulfonic acid monohydrate (PTSA) with temperature 170 °C.

On the other hand, from journal (F. Achmad et al,. 2009), it compares the activation energy (Ea) and deactivation energy (Ed) of direct polycondensation (DP) method between different temperature. From **Table 7**, at temperature between 110 – 170°C, the activation energy (Ea) is the highest which is 56.64 kJ/mol. This result from different experiment can strengthen the previous result that the optimal condition from the earlier experiment which at temperature 170°C, the PLA can produce highest molecular weight with the activation energy (Ea) also higher compared to other temperature.

**Table 7**: A comparison of the activation energy (Ea) and deactivation energy (Ed) for PLA polymerization (*Source: Chemical Engineering Journal 151 (2009) 342–350*)

| **Method** | **Material** | **Catalyst** | **Solvent** | **Temp. (°C)** | **Pressure (Vac/$N_2$)** | **$E_a$ (kJ/mol)** | **$E_a$ (kJ/mol)** | **References** |
|---|---|---|---|---|---|---|---|---|
| DP | L-LA | None | None | 150-250 | Vac. | 50.46 | 38.49 | Present work |
| | D,L-LA | | | 160-200 | $N_2$ | 31.03 | - | Kaitian (1996) |
| | | $SnCl_2$ | | 110-170 | Vac. | 56.64 | - | Harshe (2007) |
| | | $Ti(BuO)_4$ | | 110-180 | Vac. | 31.10 | - | |

Besides, by comparing other journal, which from (Donald Garlotta, 2001), in order for PLA to be processed for application in a large-scale production lines, such as injection molding, thermoforming, extrusion and blow molding, the polymer must possess adequate thermal stability to prevent degradation and to maintain the molecular weight. PLA degradation is dependent on the same parameter that was obtained from the previous experiment, which are time, temperature, molecular weight, and catalyst concentration. Catalysts and oligomers decrease the degradation temperature, but increase the degradation rate of PLA. However, polylactic acid homopolymers have a glass transition and melt temperature of about 55°C and 175°C, respectively. The most widely used method for improving PLA processability is based on melting temperature between 170–180°C. It can be conclude that at melting temperature between 170–180°C, PLA can produce high molecular weight.

As related to all findings from different journal, it can be conclude that the effect of temperature at around 170ºC, the This temperature are slightly the same with previous journal which proposed the best temperature for producing higher molecular weight of PLA at 170°C.

Furthermore, based on the research from (Stawomir Maslanka, 2014), which about the using of milk industry waste in production of biodegradable polymers, it has been observed that the decrease in enantiomer L content is accompanied by the decrease in flow temperature (Tp), glassy temperature (Tg) and crystallinity. The knowledge of Tg values for PLA determines its potential applications on the commercial scale. Glassy temperature (Tg) value for enantiomers D-PLA and L-PLA is between 52 – 65ºC, and at average molecular weight exceeding 25,000 Da, whereas softening point/melting temperature (Tm) value is

highest value of molecular weight, Mw of PLA can be produce.

### C. *Effect of Reaction Time*

Based on journal (Lalita Ponmanee, 2013), the other parameter that can be discuss is reaction time. By collecting all the data from constant reaction time, the highest value of molecular weight can be determine at the best optimal condition of reaction time. This comparison and the method of grouping the constant reaction time can shows more clearly the best result. Table below shows constant reaction time which was use in this experiment, which are 4, 5, 6, and 7 hour with different value of catalyst concentration of the oligomer used and molecular weight obtained.

As shown in **Table 8** for reaction time 4 hour, by using catalyst concentration 0.50 wt% of the oligomer, the molecular weight, Mw obtained is the highest which is 323 Da.

**Table 8**: Molecular weight, Mw obtained in reaction time 4 hour

| Exp. | Catalyst Concentration (wt% of the oligomer) | Time (hr) | Mw |
|---|---|---|---|
| 1 | 0.25 | 4 | 259 |
| 6 | 0.50 | 4 | 323 |
| 11 | 0.75 | 4 | 307 |
| 16 | 1.00 | 4 | 317 |

On the other hand, in constant reaction time of 5 hour, in **Table 9** shows the highest molecular weight, Mw obtained is 344 Da with the catalyst concentration 0.75 wt% of the oligomer.

**Table 9**: Molecular weight, Mw obtained in reaction time 5 hour

| Exp. | Catalyst Concentration (wt% of the oligomer) | Time (hr) | Mw |
|---|---|---|---|
| 2 | 0.25 | 5 | 317 |
| 5 | 0.50 | 5 | 285 |
| 12 | 0.75 | 5 | 344 |
| 15 | 1.00 | 5 | 323 |

In constant reaction time of 6 hour, in **Table 10** shows the highest molecular weight, Mw obtained is 350 Da with the catalyst concentration 0.25 wt% of the oligomer, which the catalyst concentration used was lower than in reaction rate 4 hour and 5 hour.

**Table 10**: Molecular weight, Mw obtained in reaction time 6 hour

| Exp. | Catalyst Concentration (wt% of the oligomer) | Time (hr) | Mw |
|---|---|---|---|
| 3 | 0.25 | 6 | 350 |
| 8 | 0.50 | 6 | 333 |
| 9 | 0.75 | 6 | 270 |
| 14 | 1.00 | 6 | 307 |

In constant reaction time of 7 hour, in **Table 11** shows the highest molecular weight, Mw obtained is 423 Da with the catalyst concentration 0.25 wt% of the oligomer, which the catalyst concentration used was lower than in reaction rate 4 hour and 5 hour.

**Table 11**: Molecular weight, Mw obtained in reaction time 7 hour

| Exp. | Catalyst Concentration (wt% of the oligomer) | Time (hr) | Mw |
|---|---|---|---|
| 4 | 0.25 | 7 | 423 |
| 7 | 0.50 | 7 | 286 |
| 10 | 0.75 | 7 | 277 |
| 13 | 1.00 | 7 | 270 |

From the result by grouping the constant reaction time, the highest molecular weight can be obtained when the reaction time is higher and the catalyst concentration is lower. As in this experiment (Lalita Ponmanee, 2013), the higher molecular weight, Mw obtained is 423 Da with the highest reaction rate 7 hour and lowest catalyst concentration, 0.25 wt% of the oligomer.

However, the use of catalyst concentration that higher than 0.25 wt% decreased the reaction time and molecular weight of PLA, because an excess catalyst was not only accelerated the polycondensation, but also affected depolymerization of PLA.

As a result, the optimal conditions of PLA synthesis were 0.25 wt% *p*-Toluenesulfonic acid monohydrate (PTSA) with polymerization time of 7 hour.

### D. *Effect of Catalyst*

(Donald Garlotta, 2001), in the journal stated that high molecular weight of PLA is easily polymerized in the presence of tin, zinc, aluminium, and other heavy metal catalysts, with tin(II) and zinc yielding the purest polymers. These catalysts are favored because of their covalent metal oxygen bonds and free *p* or *d* orbitals. From the catalysts used, it is strongly said that the best catalyst used is tin(II), same as in journal (Lalita Ponmanee, 2013), which used tin dichloride hydrate or *p*-Toluenesulfonic acid monohydrate (PTSA) as a catalyst in melt polycondensation method, at temperature of 170°C.

On the other studies, which presented the effect of variety of catalysts used to conditions of direct polycondensation (DP) of lactic acid, (Lei and Moon, 2014) used in their research a binary system of catalyst-activator to produce L-PLA isomer. The catalyst used was a tin chloride dihydrate and succinic anhydride, or metallic/half-metallic alkoxides, such as aluminium, titanium, yttrium, silicon and germanium or p-toluenesulfonic acid constituting the activator of tin catalyst. Addition of the latter that allowed to produce L-PLA with efficiency reaching 80% and Mw = 40,000 – 500,000 Da after 5 – 15 hour of reaction, in vacuum, at temperature 180°C. This research result are almost similar with the result from the first findings in this research project where the molecular weight obtained for commercial lactic acid is 42,288 Da with 7 hour reaction rate and 170°C.

(Lei and Moon, 2014) stated that for the effect of catalyst on the melt/solid polycondensation on the basis of catalyst screening tests, the catalyst used which are $SnCl_2\cdot 2H_2O$/PTSA, $SnCl_2\cdot 2H_2O$/succinic anhydride, or $SnCl_2\cdot 2H_2O$/maleic anhydride binary catalysts are the most effective catalysts to obtain PLA with high molecular weight. It was also noted that the polarity of the reaction system were greatly altered with the progress of the melt polycondensation, resulting in a great deterioration of catalyst activity.

It can be conclude that p-toluenesulfonic acid (PTSA), $SnCl_2\cdot 2H_2O$/TSA, $SnCl_2\cdot 2H_2O$/succinic anhydride, and $SnCl2\cdot 2H_2O$/maleic anhydride binary catalysts should be effective binary catalysts to obtain high molecular weight of PLA.

## I. CONCLUSION

In conclusion, direct polycondensation (DP) method has been chosen as the best method to synthesis polylactic acid. As this method are the most simplest and cheaper method compared to ring opening polymerization (ROP) method and azeotrophic dehydrative method. PLA obtained by ring opening polymerization is unavoidably at high cost because exhaustive monomer purification is needed to attain high molecular weight of the resultant polymers (Kim, 2002). Direct polycondensation (DP) method fulfills the conditions of compactness, as well as it is safe and simple operation for an onsite cell plant concept. From the production of lactic acid by Lactobacillus rhamnosus, the commercial lactic acid and fermentative lactic acid that was prepared from Lactobacillus rhamnosus TISTR 108 could be used as monomer for PLA synthesis. The result from commercial lactic acid can be conclude as the highest molecular weight, Mw and number average molecular weight, Mn of PLA obtained which are 423 Da and 42,288 Da, respectively, with using 0.25 wt% catalyst concentration of the oligomer, temperature at 170 °C and the reaction time of 7 hour by using PTSA catalysts. While for fermentative lactic acid obtained molecular weight, Mw and number average molecular weight, Mn of PLA are 232 Da and 2627 Da respectively. From fermentative lactic acid, it can enhances value added for renewable resource and develops an environmental friendly bio-plastic material.

A next step towards the improvement of PLA production, it is founds that new ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process. The new idea can include the usage of crop residue such as stems, straw, husks, and leaves that comes from corn or, potentially, other crops, and use of unfermentable residues as a heat source as well as substituting some part of electricity energy by wind power energy. These approaches can decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment (Vink et al,. 2003).

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