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## Synthesis of polylactic acid using Zn powder under microwave irradiation

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Key word: poly lactic acid, microwave techniques, green chemistry.

### Abstract:

The research involves synthesis of polylactic acid using an available and low cost catalyst (Zn) using microwave irradiation, the synthesized polymer was characterized using FTIR, <sup>1</sup>H NMR while the molecular weight was calculated using Mark-Houwink equation, the molecular weight was 12.388 with high purity. This method consumed time compared with traditional methods.

### Introduction:

Poly(lactic acid) (PLA) is a biodegradable and biocompatible polymer which have a very promising future in different fields such as environmental and biomedical field<sup>(1,2,3)</sup>. (PLA) is a biopolymer made from 100% renewable resources, the final products are CO<sub>2</sub> and H<sub>2</sub>O which make it an ideal choice in replacing the fossil fuel<sup>(4,5)</sup>. There are two major routes for the synthesis the first is condensation polymerization which involving the reaction of hydroxyl group with carboxyl group in lactic acid and eliminate a water molecule as a byproduct. The produced polymer is always with low molecular weight due to the depolymerization reaction at high temperature and the difficulties in removing water and impurities from the reaction<sup>(6,7)</sup>. In addition, condensation polymerization reaction requires



high vacuum, temperature and time <sup>(8)</sup>. Other disadvantage of this route is the high racemization, coloration in the produced polymer and decreasing in optical purity <sup>(9)</sup>. The second route is known as ring opening polymerization (ROP) of the cyclic dimer (lactide) which it is very successful route in producing a high molecular weight PLA, this route involves Three steps: condensation of lactic acid monomer to low molecular weight polylactic acid (oligomer), depolymerization of the oligomer into the cyclic dimer (Lactide) and catalytic ring opening polymerization of the lactide<sup>(10)</sup>. In spite of the high molecular weight produced in this route, the high cost of purification for the cyclic dimer present a disadvantage for this procedure <sup>(11)</sup>. A wide range of non toxic catalysts derived from, Sn, Ca and Al have been used in ring opening polymerization, these metals are biocompatible and they can be used in biomedical applications <sup>(12)</sup>. Among these catalysts tin (II)2-ethyl hexanoate ( $\text{Sn}(\text{Oct})_2$ ) is the mostly used because of its low toxicity, solubility in molten monomer and the high molecular weight of the resulted polymer<sup>(13)</sup>. Most of the difficulties found in the classical synthetic roles of PLA can be overcome by using microwave irradiation like reducing time of reaction, reducing the power and guarantee an equal distribution of the power to the whole reaction mixture. So microwave irradiation can provide not only a quick route of synthesis, but also a product with high purity<sup>(14-</sup>  
<sup>16)</sup>. Microwave irradiation is an electromagnetic radiation used

as a source of heating in organic compound synthesis. Microwave energy is a non- ionizing energy and thus it isn't change the structure of the molecules for the compound being heated but provides only thermal activation to the molecules<sup>(17-18)</sup>. In today's world of "green chemistry", microwave technique is considered as one of the important method in the chemical synthesis because this technique is environmentally friendly and generate less toxic residue like mineral acids and organic solvents<sup>(19-21)</sup>.

In this study we aim to use Zn powder as a cheap and available catalyst with microwave technique to produce moderate molecular weight polylactic acid with high purity.

#### **Materials and Methods:**

Lactic acid (85%) and Zn powder were purchased from Aldrich Chemicals Company. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), Methanol were purchased from BDH company. All chemicals were used without further purification.

#### **Synthesis of polylactic acid:**

Lactic acid LA (20ml, 0.005mole) was irradiated in microwave oven (MAS-II sineo) using (300) watt of power, with ( $80^0\text{C}$ ) of temperature for (30) minutes under evacuation ( $10^{-3}$ ) bar. Then Zn powder (0.5) gm was added to the round bottom flask and the reaction was continued through  $150\text{C}^0$  of and  $10^{-3}$  bar for 10 minutes. Through this step the color was changed to blue and

small clots began to appear. The temperature was raised to 170 °C for 30 minutes under constant power (300W) the round bottom flask was left to cool under vacuum. The product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, the precipitated Zn was removed by filtration, CH<sub>2</sub>Cl<sub>2</sub> was evaporated and polylactic acid was appeared as a white crystal powder.

**Determination of viscosity average molecular weight ( $\overline{M}_v$ ):**

The molecular weight of the resultant polymer was estimated from Viscosity average molecular weight ( $\overline{M}_v$ ) techniques using Ostwald viscometer, solutions with different concentrations of PLA/Chloroform was prepared and placed in a temperature controlled water bath and the viscosity was measured periodically at 25°C.

**Glass Transition Temperature:**

The T<sub>g</sub> analysis was performed at a heating rate 10°C/min under air condition.

**Results and Discussion:**

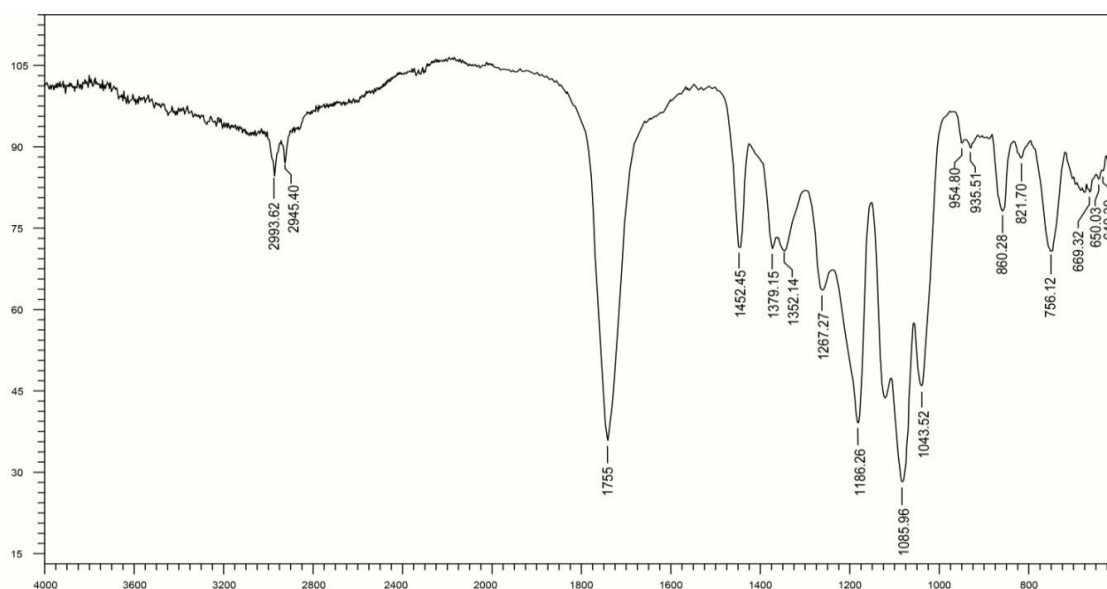
In this study, the reaction proceeds with a programmed temperature with a constant irradiation (300W) the resulted polymer was with moderate molecular weight and high purity.

Microwave assisted polymerization was very useful and has a very good benefit compared with the classical routes (polycondensation and ring opening polymerization) which included heating to temperature between 170-200°C and require time from 16 to 24 hour using oil or sand bath with different catalysts, while

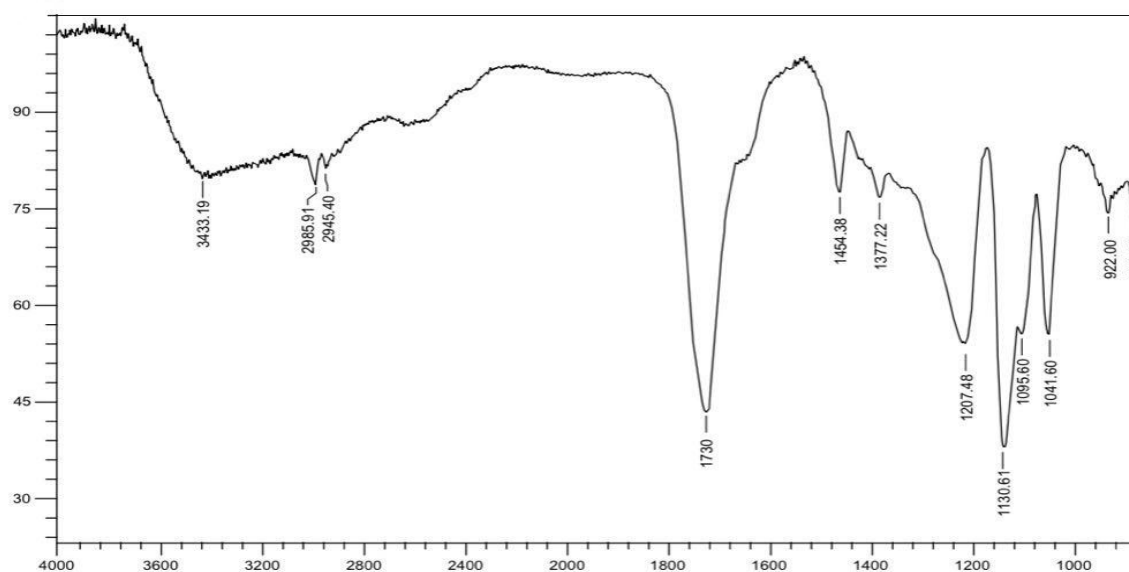
microwave technique provide a direct one step polymerization with less consumed energy and time.

### FTIR spectroscopy:

FTIR spectrum of the produced poly lactic acid in Fig.1 which measured by shimadzu FTIR 3800S, shows a characteristic peak appears at  $1730\text{cm}^{-1}$  related to stretching vibration of (C=O) group, peak at  $1085\text{cm}^{-1}$  related to (C-O) group, peaks appears at  $2945\text{cm}^{-1}$  and  $2993\text{cm}^{-1}$  related to  $\text{CH}_2$  and  $\text{CH}_3$  respectively. The broad band of carboxylic group in lactic acid which appears at  $3433\text{cm}^{-1}$  as shown in Fig. 2 was disappeared in Fig1. Due to the reaction of the Hydroxyl group of one molecule of lactic acid with the carboxylic group of another molecule.



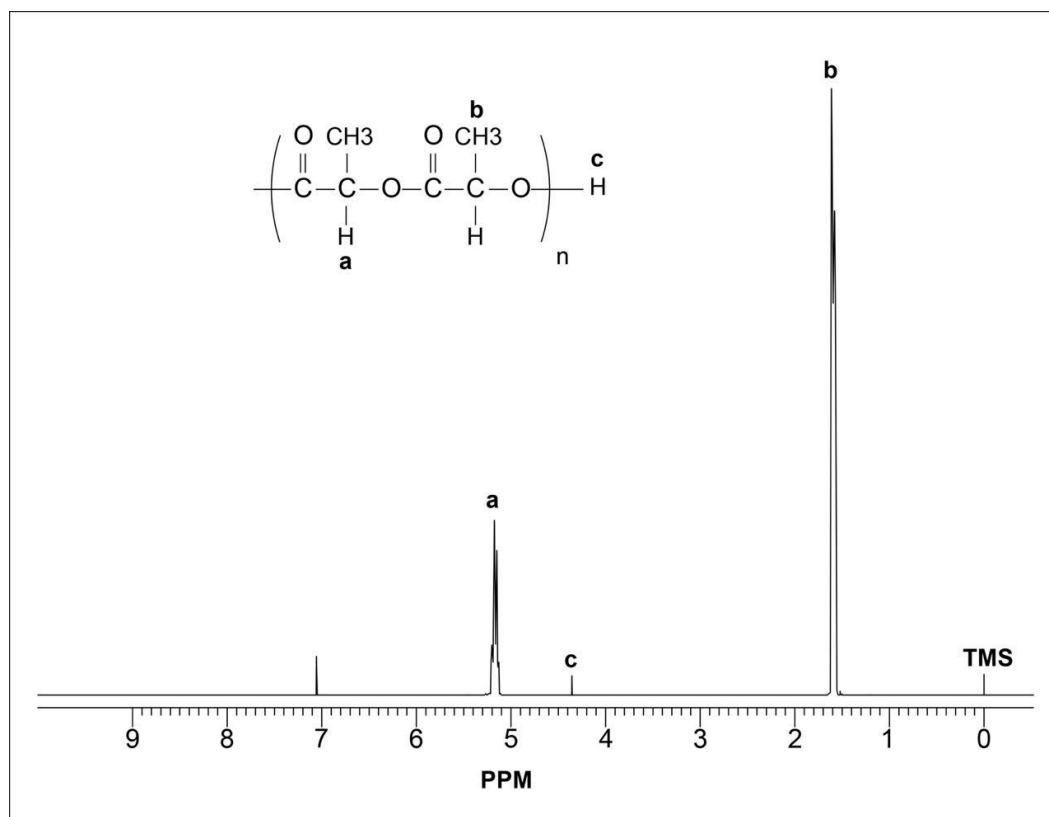
**Figure1. FTIR spectrum of PLA**



**Figure.2 FTIR spectrum of Lactic acid 85% (monomer)**

### **H<sup>1</sup>NMR spectroscopy:**

H<sup>1</sup>NMR(Avanc 300MHz)spectrum of PLA was shown in Fig.3, illustrated that peaks at 1.56, 4.35, and 5.20 ppm related to CH<sub>3</sub>, CH next to terminal group, and CH, respectively

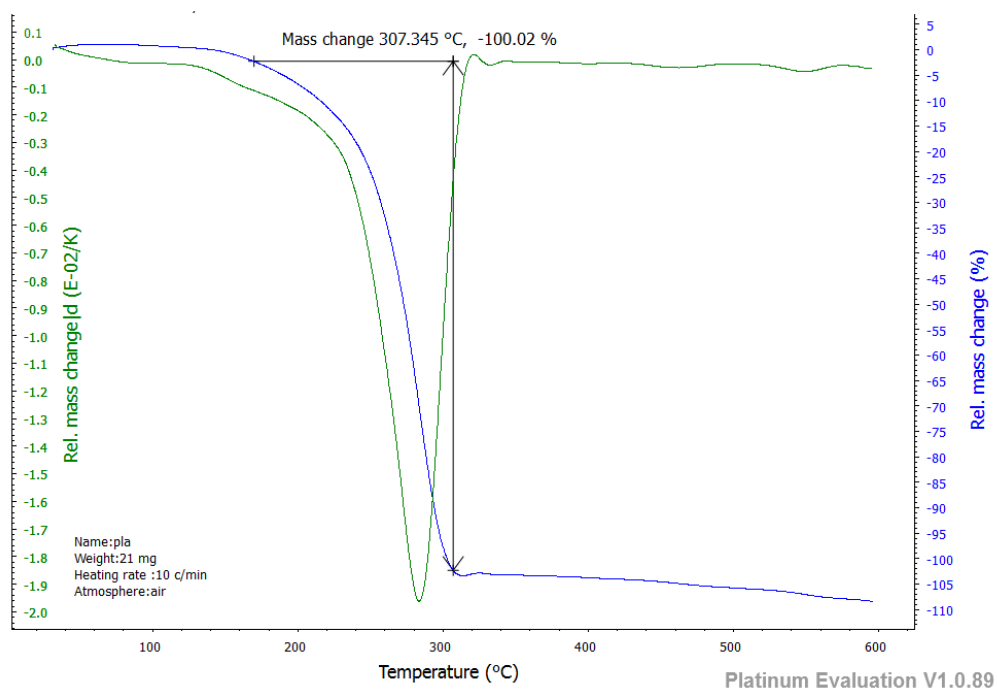


**Figure.3  $^1\text{H}$  NMR spectrum of PLA**

### **Thermal analysis:**

The thermal stability of the synthesized PLA was examined by measuring the sample weight loss at a programmed rate of heating  $10^\circ\text{C}/\text{min}$  under stream of air depicted in Fig. 4, shows a good thermal stability as there was no significant losing of the weight up to  $175^\circ\text{C}$ . Only one major decomposition step is discernible from the thermogram occurred at  $280^\circ\text{C}$  with maximum rapid weight loss almost 100% within the range of  $200\text{--}310^\circ\text{C}$ . This stage may be due to the cleavage and total volatilization of the polymer chain.





**Figure 4. glass transition temperature**

### **Determination of Molecular weight:**

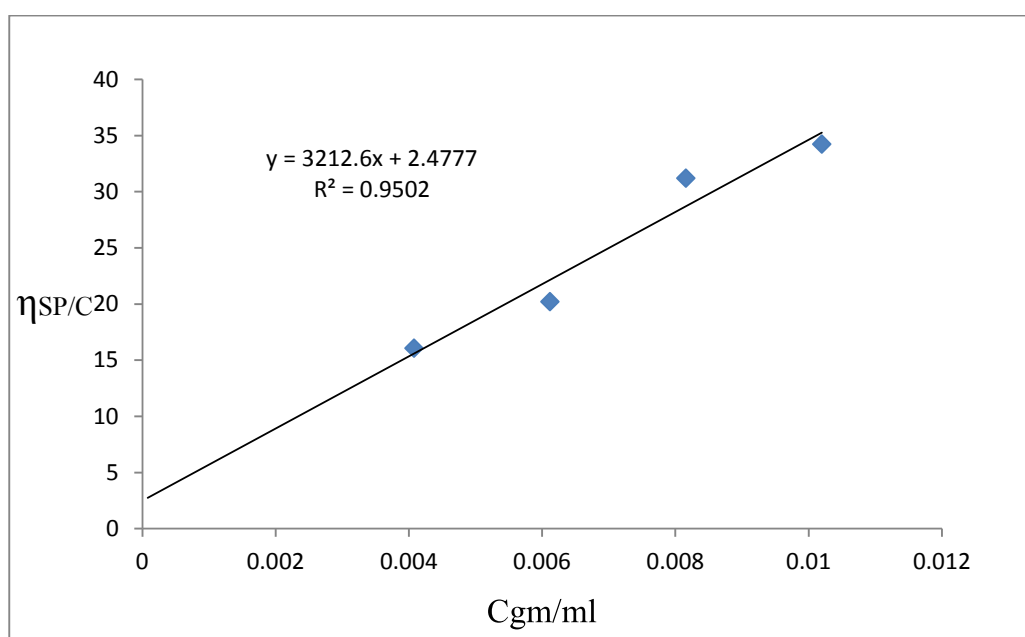
Mark-Hauwink equation was used to calculate the viscosity average molecular weight  $\alpha$  and K constants which values are 0.79 and  $1.33 \times 10^{-3}$  respectively obtained from the literature at  $(25)^\circ\text{C}^{(22)}$

$$[\eta] = K[M_v]$$

The intrinsic viscosity  $[\eta]$  was 2.284 and the viscosity average molecular weight was 12.388 and the number of repeating unit was 154.85 unit.

**Table.1 shows the concentrations of the solutions used in determination of  $\eta_r$  the relative viscosity and  $\eta_{sp}$  specific viscosity respectively.**

C (gm/ml)	Time (solutions)	Time s(solvent)	$\eta_r$	$\eta_{sp}$	$\ln\eta_r$	$(\ln\eta_r)/C$	$\eta_{sp}/C$
0.0102	37.1	27.5	1.34909091	0.3490909	0.299431	29.35598	34.2246
0.00816	34.5	27.5	1.25454545	0.2545455	0.226773	27.79085	31.1943
0.00612	30.9	27.5	1.12363636	0.1236364	0.11657	19.04741	20.20202
0.00408	29.3	27.5	1.06545455	0.0654545	0.063402	15.53959	16.04278



**Fig.5: Higgin's equation**

### Conclusion:

In this work, we produced PLA with high purity and moderate molecular weight using microwave irradiation with Zn as an available low cost catalyst, this process reduce both time and temperature. FTIR analysis of the sample confirmed the presence of characteristic bonds of the PLA. This study proved that the

microwave can be used as one of the best routes in chemical synthesis.

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