Synthesis of polylactic acid using Zn powder under microwave irradiation

Aseel F. Alwan and Hussein I. Khalaf
Polymer research unit, college of science, AL-Mustansiriyah University, Baghdad, Iraq

Corresponding author: aseeloprah83@yahoo.com

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, H1NMR while the molecular weight was calculated using Mark-Hauwink equation, the molecular weight was 12.388 with high purity. This method consumed time compared with traditional methods.

Introduction:
Polylactic acid (PLA) is a biodegradable and biocompatible polymer which have a very promising future in different fields such as environmental and biomedical field\(^{(1,2,3)}\). (PLA) is a biopolymer made from 100% renewable resources, the final products are CO\(_2\) and H\(_2\)O which make it an ideal choice in replacing the fossil fuel\(^{(4,5)}\). 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 depolymeriation reaction at high temperature and the difficulties in removing water and impurities from the reaction\(^{(6,7)}\). In addition, condensation polymerization reaction requires
high vacuum, temperature and time\(^8\). Other disadvantage of this route is the high racemization, coloration in the produced polymer and decreasing in optical purity\(^9\). 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\(^{10}\). 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\(^{11}\). 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\(^{12}\). Among these catalysts tin (II)2-ethyl hexanoate (Sn(Oct)\(_2\)) is the mostly used because of its low toxicity, solubility in molten monomer and the high molecular weight of the resulted polymer\(^{13}\). 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\(^{14-16}\). Microwave irradiation is an electromagnetic radiation used
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\textsuperscript{(17-18)}. 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\textsuperscript{(19-21)}.

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 (CH\textsubscript{2}Cl\textsubscript{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\textdegree C) of temperature for (30) minutes under evacuation (10\textsuperscript{-3}) bar. Then Zn powder (0.5) gm was added to the round bottom flask and the reaction was continued through 150\textdegree C of and 10\textsuperscript{-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 CH₂Cl₂, the precipitated Zn was removed by filtration, CH₂Cl₂ was evaporated and polylactic acid was appeared as a white crystal powder.

**Determination of viscosity average molecular weight (Mᵥ):**  
The molecular weight of the resultant polymer was estimated from Viscosity average molecular weight (Mᵥ) 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 Tg 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 1730cm⁻¹ related to stretching vibration of (C=O) group, peak at 1085cm⁻¹ related to (C-O) group, peaks appears at 2945cm⁻¹ and 2993cm⁻¹ related to CH₂ and CH₃ respectively. The broad band of carboxylic group in lactic acid which appears at 3433cm⁻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)

H¹NMR spectroscopy:

H¹NMR(Avanc 300MHz)spectrum of PLA was shown in Fig.3, illustrated that peaks at 1.56, 4.35, and 5.20 ppm related to CH₃, CH next to terminal group, and CH, respectively
Figure 3: H$^1$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°C/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°C. Only one major decomposition step in discernible from the thermogram occurred at 280°C with maximum rapid weight loss almost 100% within the range of 200-310°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 \((25)\, ^{\circ}\mathrm{C}\)\(^{22}\) \[ \eta = K[Mv] \]

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 |

$\gamma = 3212.6x + 2.4777$

$R^2 = 0.9502$

**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.

References

1 Cheolho LC, Hong S. An overview of the synthesis and synthetic mechanism of poly (lactic acid). Mod. Chem. Appl. 2014;2(4):1-5.

2 Hamad K, Kaseem M, Yang HW, Deri F, Ko YG. Properties and medical applications of polylactic acid: A review. Express Polymer Letters. 2015 May 1;9(5).

3 Lopes MS, Jardini AL. Filho R.M Synthesis and characterizations of poly (lactic acid) by ring-opening polymerization for biomedical applications. Chemical Engineering Transactions. 2014.

4 Sha L, Chen Z, Chen Z, Zhang A, Yang Z. Polylactic acid based nanocomposites: Promising safe and biodegradable materials in biomedical field. International Journal of Polymer Science.;2016.

5 Wee YJ, Kim JN, Ryu HW. Biotechnological production of lactic acid and its recent applications. Food Technology and Biotechnology. 2006 Jun 15;44(2):163-72.

6 Hu Y, Daoud WA, Cheuk KK, Lin CS. Newly developed techniques on polycondensation, ring-opening polymerization and polymer modification: Focus on poly (lactic acid). Materials. 2016 Feb 26;9(3):133.

7 Vink ET, Rabago KR, Glassner DA, Gruber PR. Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. Polymer Degradation and stability. 2003 Jan 1;80(3):403-19.

8 Laonuad P, Chaiyut N, Ksapabutr B. Poly (lactic acid) preparation by polycondensation method. Optoelectronics and
Advanced Materials-Rapid Communications. 2010 Aug 1;4(8):1200-2.

9 Jiang W, Huang W, Cheng N, Qi Y, Zong X, Li H, Zhang Q. Isotactic polycondensation of L-lactic acid with biogenic creatinine. Polymer. 2012 Nov 9;53(24):5476-9.

10 Yoo DK, Kim D, Lee DS. Reaction Kinetics for the Synthesis of Oligomeric Poly (lactic acid). Macromolecular research. 2005 Jan 1;13(1):68-72.

11 Xiao L, Wang B, Yang G, Gauthier M. Poly (lactic acid)-based biomaterials: synthesis, modification and applications. In Biomedical science, engineering and technology 2012. InTech.

12 Chisholm MH. Concerning the ring-opening polymerization of lactide and cyclic esters by coordination metal catalysts. Pure and Applied Chemistry. 2010 Jun 19;82(8):1647-62.

13 Pholharn D, Srithep Y, Morris J. Effect of initiators on synthesis of poly (L-lactide) by ring opening polymerization. InIOP Conference Series: Materials Science and Engineering 2017 Jun (Vol. 213, No. 1, p. 012022). IOP Publishing.

14 Belwal S. Green revolution in chemistry by microwave assisted synthesis: A review. Modern Chemistry. 2013;1(3).

15 Dubey SP, Abhyankar HA, Marchante V, Brighton JL, Bergmann B, Trinh G, David C. Microwave energy assisted synthesis of poly lactic acid via continuous reactive extrusion: modelling of reaction kinetics. RSC Advances. 2017;7(30):18529-38.

16 Gawande MB, Shelke SN, Zboril R, Varma RS. Microwave-assisted chemistry: synthetic applications for rapid assembly of
nanomaterials and organics. Accounts of chemical research. 2014 Mar 25;47(4):1338-48.

17 Gaba M, Dhingra N. Microwave chemistry: general features and applications. Ind J Pharm Edu Res. 2011 Apr 1;45(2):175.

18 Jacob J. Microwave assisted reactions in organic chemistry: A review of recent advances. International Journal of Chemistry. 2012 Nov 20;4(6):29.

19 Veitia MS, Ferroud C. New activation methods used in green chemistry for the synthesis of high added value molecules. International Journal of Energy and Environmental Engineering. 2015 Mar 1;6(1):37-46.

20 Gangrade D, Lad SD, Mehta AL. Overview on microwave synthesis-Important tool for green Chemistry. International Journal of Research in Pharmacy & Science. 2015 Apr 1(2).

21 Ravichandran S, Karthikeyan E. Microwave synthesis-a potential tool for green chemistry. Int J Chem Tech Res. 2011 Mar;3(1):466-70.

22 Cassidy JT, Petty RE, Laxer RM, Lindsley CB. Textbook of pediatric rheumatology E-Book. Elsevier Health Sciences; 2010 Oct 15.