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To cite this article: Harsh Desai, Tejal Mehta, Ankur Dwivedi, Nimish Shah, Dhaivat Parikh & Mamta Saiyad (2024) Novel catalyst-solvent system for high molecular weight polylactic acid synthesis via azeotropic solution polycondensation method, Materials Research Innovations, 28:7, 589-596, DOI: [10.1080/14328917.2024.2350828](https://doi.org/10.1080/14328917.2024.2350828)

To link to this article: <https://doi.org/10.1080/14328917.2024.2350828>



Published online: 17 May 2024.



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Novel catalyst-solvent system for high molecular weight polylactic acid synthesis via azeotropic solution polycondensation method

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ABSTRACT

Polycondensation for PLA synthesis is widely used due to its cost-effectiveness, but it often leads to low molecular weight PLA. To address this limitation, researchers have explored different catalysts, with the stannous chloride and p-toluene sulfonic acid combination being a popular choice. However, this method typically yields PLA with a MW of no more than 35000 g/mol, which is unsuitable for commercial applications. In contrast, ring-opening polymerization is considered the most effective method for synthesizing high MW PLA, despite its complexity and cost. Industrial-scale production predominantly employs ROP due to its capability to produce high MW PLA. The use of stannous octoate as a catalyst for ROP has shown promise in synthesizing higher MW PLA. However, its sensitivity to water limits its use in polycondensation, where stannous chloride is commonly employed but is not capable of synthesizing high MW PLA. This study explores the use of stannous octoate for the synthesis of high MW PLA with higher yield.

ARTICLE HISTORY

Received 5 March 2024
Accepted 29 April 2024

KEYWORDS

Polylactic acid; solution polycondensation; azeotropic polycondensation; stannous octoate

1. Introduction

Poly(lactic acid) (PLA) is one of the focused biodegradable polymers, widening its applications. Various research groups are working to synthesise PLA. Three methods are known for the polymerisation of lactic acid: direct polycondensation, ring-opening polymerisation (ROP) and enzyme polymerisation. The enzyme polymerisation method is still in the experimental phase among these methods. The first time PLA was synthesised in 1920s by direct polycondensation method [1]. Due to lower MW, the method was not found viable, so industries weren't interested in commercial production. In 1932, DuPont patented ring-opening polymerisation (ROP) as a new technology for the synthesis of PLA [2]. It was claimed that high molecular weight PLA synthesis was possible with this patented method. In 1992, a joint venture of Cargill and Dow Chemicals invented and patented a new method for producing PLA using renewable resources, such as corn starch. This process used the ring-opening polymerisation of lactide, which led to a very high yield. This encouraged industries for large-scale production of PLA.

In ROP method, the Dupont team used stannous octoate (tin alkoxide) as a catalyst to obtain chiral pure and high molecular weight (Mw) products with excellent control of properties [3,4]. That research was adapted and the first commercial PLA resin was marketed under NatureWorks PLA by Cargill Dow LLC in 2002. In 1994 & 1995, Mitsui Toatsu Chemicals, Inc., Tokyo, Japan, patented methods to synthesise PLA using inert solvents in solution polycondensation. This novel method was claimed to manufacture PLA at affordable industrial production cost, but the application of hydrocarbon solvent and possible contamination prevents its sustainability in the market. Applications of PLA widened its span from the packaging industry, biomedical and drug delivery, agricultural industry and, in recent decades, additive

manufacturing and many more. Global production of PLA reached 190,000 tons in 2019, almost 19% of the total biodegradable polymer production [5].

The oldest method for synthesis of PLA, direct polycondensation, is oversight due to the intricacy involved in the process, such as increment in viscosity throughout the polymerisation process, high temperature (180–210°C) required with deep vacuum and low molecular weight product obtained. Many researchers explored considerable modifications in the polycondensation method for synthesising high MW PLA [6]. Researchers studied the diversity of solvent, catalyst and their countless combinations, etc. Mitsui Toatsu Chemicals team used diphenyl ether as a solvent and tin powder as a catalyst, which produced 137,000–210,000 Mw in 10–40 hr with a higher yield. The hydrocarbon inert solvent used in the method tends to form azeotrope with the by-product water and helps to remove it during polymerisation.

When PLA is synthesised by condensation of LA, the by-product is water as reaction mechanism shown in Figure 1. So, while selecting the catalyst, one of the prerequisites is the water sensitivity of the catalyst for polycondensation. The catalyst must be stable in water to achieve desirable catalytic effects. Considering the reported studies, in polycondensation of LA among the catalysts such as GeO₂, Sb₂O₃, ZnO, Fe₂O₃, Al₂O₃, SnO, TiO₂, SiO₂, H₂SO₄, HCl, the most effective were SnO, SnCl₂·2H₂O and SnCl₂ with p-toluene sulfonic acid (p-TSA) as a co-catalyst. SnCl₂/p-TSA catalyst system is pretty stable against water but none of them achieve more than 35,000 gm/mol MW [4].

Direct polycondensation results in a low MW product due to viscosity increment, and the ROP method has a lower overall yield, which is effectively encountered by the solution polymerisation method [7]. Another group of Mitsui Toatsu Chemicals, Inc. researchers explore the method with solvents like Anisole and O-Chlorobenzene and stannous chloride

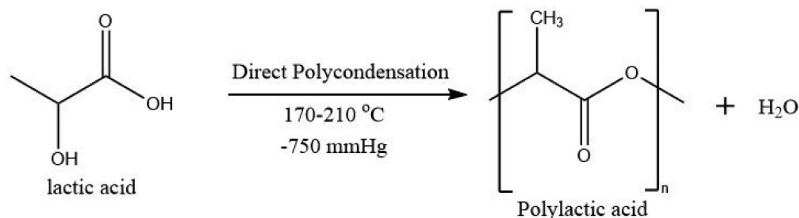


Figure 1. Direct polycondensation reaction of lactic acid to obtain poly(lactic acid) and by-product water.

catalyst [8]. Junzo Otera et al. explored Decalin and Limonene solvent with distannoxane catalyst to effectively synthesise PLA [9]. T. Fukushima et al. reported a polycondensation catalyst combo $\text{SnCl}_2/p\text{-TSA}$ to synthesise PLA in diphenyl ether [10]. Jian Zhang et al., S.K. Singh et al., and Yanty Maryanty used catalyst SnCl_2 in combination with solvent xylene [11–13]. Ki Woong Kim et al. polymerised lactic acid in anisole and xylene with SnO/TiO_2 and SnCl_2 Catalyst [14]. Dina A.S. Marques et al. also used anisole and xylene and compared the effectiveness of SnCl_2 , titanium butoxide and 4-dodecylbenzenesulfonic acid (DBSA) catalysts [15]. Sławomir Dutkiewicz et al. explored solvents like p-xylene, o-chlorotoluene, o-dichlorobenzene and diphenyl ether to study their effects on Mw of PLA with SnCl_2 and tin powder catalyst [16]. Also, S. Shyamroy et al. explored solvents like p-xylene, mesitylene and decalin with the help of self-made catalyst 1,3-Dichloro-1,1,3,3-tetra-n-butyl-distannoxane and tetraphenyl-tin for PLA synthesis [17]. A.K. Pandey investigated the performance of solvents like xylene, decalin, mesitylene, anisole and diphenyl ether with SnCl_2 [18].

Akinori Takasu et al. studied novel catalysts Scandium trifluoro methane sulphonate [$\text{Sc}(\text{OTf})_3$], Scandium trifluoro methane sulfonimide [$\text{Sc}(\text{NTf}_2)_3$] in xylene. Masanobu Ajioka et al. thoroughly investigated the role of catalysts in solution polymerisation. They explored H_2SO_4 , H_3PO_4 , $\text{CH}_3\text{SO}_3\text{H}$, Nafion-H, Sn, SnO, Mg, Al, Ti, Zn, TiO_2 , ZnO, GeO_2 , ZrO_2 , SnO_2 , SnCl_2 , SnCl_4 , Sb_2O_3 , $\text{Mn}(\text{AcO})_2$, $\text{Fe}_3(\text{LA})_3$, $\text{Co}(\text{AcO})_2$, $\text{Ni}(\text{AcO})_2$, $\text{Zn}(\text{LA})_2$, $\text{Al}(\text{i-PrO})_3$, $\text{Ti}(\text{BuO})_4$, (Bu_2SnO) as a catalyst in diphenyl ether solvent. They reported that tin catalysts produce more than 2,00,000 gm/mol MW PLA with an overall 60% yield [11–13,19–21] Shinji Yamada et al. synthesised PLA by microwave irradiation with $\text{Sc}(\text{OTf})_3$, SnCl_2 , and $\text{SnCl}_2/p\text{-TSA}$ in xylene [8].

Exploring catalysts and solvents for the synthesis method is a continuous process for the betterment of the PLA quality. In the ROP method, stannous octoate's performance as a catalyst is remarkable. It is dominantly preferred in ROP but not applied for the polycondensation method for PLA synthesis due to its most significant limitation of water sensitivity. In the ROP method, no water is present, so it performs best. Whereas, in polycondensation, the water formed as a by-product hinders its activity, which prevents its application as a catalyst. Stannous octoate can be protected against produced water, it may perform best like in ROP or it was expected that at least would be better than other reported catalysts. In this work, the biggest challenge of water sensitivity of stannous octoate has been addressed and it is investigated as a catalyst in the synthesis of PLA by solution polymerisation. O-xylene has been used as an inert solvent, forms azeotrope with water. Produced water during the reaction is removed in the form of azeotrope with O-xylene, which effectively controls temperature and viscosity and protects the polymer and catalyst against moisture and oxygen. The results

are compared with the most widely used catalyst $\text{SnCl}_2/p\text{-TSA}$ concerning the resultant polymer product's overall yield, molecular weight and thermal properties.

2. Materials

Lactic acid (88%), O-xylene (99.5%), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and p-TSA, Dichloromethane, and methanol were purchased from SRL India and Stannous Octoate (92.5–100%) was purchased from Sigma Aldrich. All the reagents are used without further purification.

3. Methodology

Solution polycondensation is a two step process [1], azeotropic dehydration and oligomerisation and [2] polymerisation. 25 ml of 88% lactic acid and 25 ml of O-xylene were added into a round-bottom flask mounted with a Dean-Stark trap, as illustrated in Figure 2.

Step 1 The water present and formed during oligomerisation is expelled by azeotropic distillation. So this method can also be named as azeotropic dehydrative solution

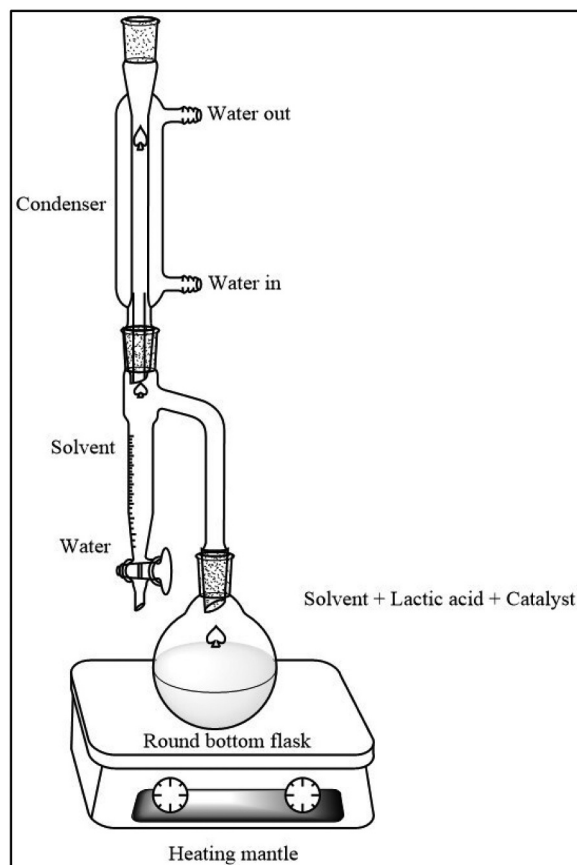


Figure 2. Lab scale solution polymerisation setup for PLA.

polycondensation. The temperature is raised to the reflux of the solvent.

Step 2 After a certain time, the system is cooled to 110°C, and the catalyst is added. Stannous octoate was dissolved in a small quantity of xylene and added into the reactor to prevent oxidation. The polymerisation is carried out for 72 hr. The polymer product is then filtered, and the excess solvent is removed. The dried polymer is then dissolved in Dichloromethane, precipitated in methanol, and dried in a vacuum oven at 50°C. The stannous octoate catalyst can be dissolved in small quantity of toluene rather than xylene and injected into the system to prevent its exposure to moisture and oxygen.

4. Characterisation

4.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is the common and preliminary methods for identifying or confirming material. The method provides spectrum data between 500 and 4000. 'Jasco IRT-3000' integrated with ATR has been used for sample analysis. The polymer sample is simply blended with anhydrous potassium bromide (KBr) in ratio of approximately 1:10 polymer to KBr. The spectras are interpreted with the help of JASCO-IR Software.

4.2. Proton Nuclear Magnetic Resonance (^1H NMR)

A Proton nuclear magnetic resonance (proton NMR, hydrogen-1 NMR, or ^1H NMR) are dominantly preferred for confirmation and cross-referencing of molecular structures and positioning of bonds, as well as material purity. In the case of polymers, it also provides a degree of polymerisation. Synthesised PLA samples analysed in 'Bruker AdvanceCore' model with a 400 MHz two-channel NMR spectrometer by diluting in Deuterated chloroform. The raw NMR data are interpreted with the help of 'MNova' software.

4.3. Differential Scanning Calorimetry (DSC)

In the field of polymers, essential thermal properties like melting point (T_m), glass transition temperature (T_g), and

crystallinity temperature (T_c) can be determined by DSC. 'Hitachi DSC 7020' model is used to determine the thermal properties of synthesised PLA in the range of 30 to 200°C.

4.4. Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography is the most commonly used technique to determine the molecular weight distribution in polymers, resins, oils, oligomers, and organic compounds. A 'Turbo Matrix-40' model made of 'Perkin Elmer' was used to determine the molecular weight and number average molecular weight of the synthesised samples using polystyrene and THF solvent.

5. Results and discussions

5.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is one of the primitive characterisation techniques. In Figure 3, comprising the spectra region, it is evident that both catalysts produce the PLA. C=O sharp stretch at 1758 cm^{-1} in both spectra confirms the presence of ester linkage. O-H stretch at 3648 and 3502 cm^{-1} in upper spectra, and 3652 and 3509 cm^{-1} at lower spectra denote hydroxyl group with quite faded stretch, explaining the considerable reduction of the group due to polymerisation and loss of by-product water. Light peaks at 3000 , 2950 and 2884 cm^{-1} in upper spectra and 2996 , 2954 , and 2881 cm^{-1} in lower spectra justify the presence of C-H and =C-H alkanes group.

5.2. Proton Nuclear Magnetic Resonance (^1H NMR)

NMR analysis is performed for the polymer to understand and validate the predicted chain structure, conversion of monomer and end group analysis. The PLA synthesised from catalyst SnCl_2 and $\text{Sn}(\text{Oct})_2$ was analysed by ^1H NMR, as shown in Figures 4 and 5. Signals located at $\delta\text{H} = 5.12$ to 5.18 in both the spectra and 1.57 ppm were allocated to the methine (CH, 3) and methyl (CH_3 , 7) in the polymer, respectively. Notably, the signal at $\delta\text{H} = 4.33\text{ ppm}$ was accredited to the methine end-group (CH, 8). Analysed integrals are noted with signs, in which it is worth noting

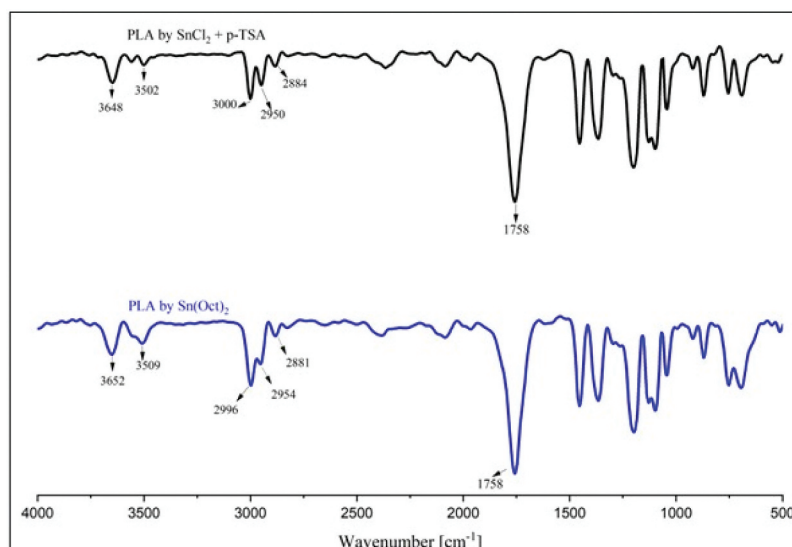


Figure 3. Spectra analysis of PLA synthesised by $\text{SnCl}_2/\text{p-TSA}$ and SnOct_2 .

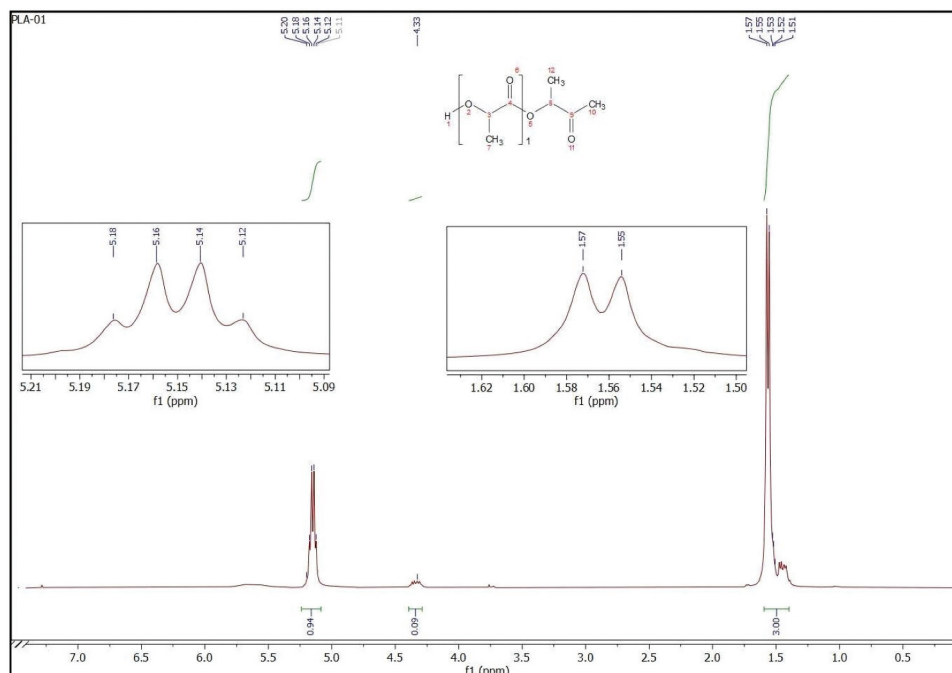


Figure 4. ^1H NMR of PLA synthesised by $\text{SnCl}_2/\text{p-TSA}$.

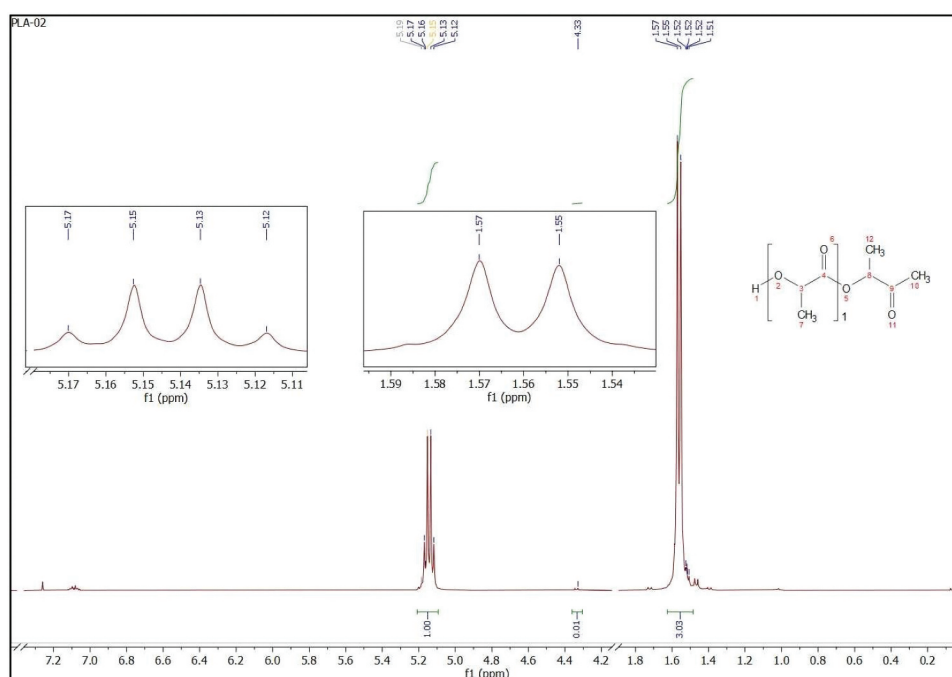


Figure 5. ^1H NMR of PLA synthesised by $\text{Sn}(\text{Oct})_2$.

Table 1. Comparative results of PLA samples.

Sample no.	Catalyst used	Melting point $^{\circ}\text{C}$ (T_m)	Yield %	Mw (gm/mol)	Mn	Mw/Mn (PDI)
PLA-1	SnCl_2 (0.5 wt%)	152	62.4	26,403	13,302	1.98
PLA-2	$\text{Sn}(\text{Oct})_2$ (0.5 wt%)	166.5	76.1	1,46,211.1	1,20,002.3	1.21
PLA-3	$\text{Sn}(\text{Oct})_2$ (0.25 wt%)	155	79.4	74,012.0	38,049.1	1.94
PLA-3	$\text{Sn}(\text{Oct})_2$ (0.1 wt%)	146	83.5	17,401.5	7936.0	2.19
PLA-4	$\text{Sn}(\text{Oct})_2$ (0.05 wt%)	148	84.8	9159.3	4618.1	1.98
PLA-5	$\text{Sn}(\text{Oct})_2$ (0.025 wt%)	150	77.24	6701.0	3484.1	1.92

that the ratio of CH to CH_3 integrals is 3:1 in both cases, which denotes the chain formation of the LA unit repetitively. The degree of polymerisation (DP) can be calculated by integrating a proton signal from the end group versus

a proton signal from the polymer repeating unit. In our case, we selected the peaks of methines (CH) 7 (4.33 ppm) and 3 (5.17/5.18 ppm), which resulted in a DP of 10.14 for SnCl_2 and 100 for $\text{Sn}(\text{Oct})_2$.

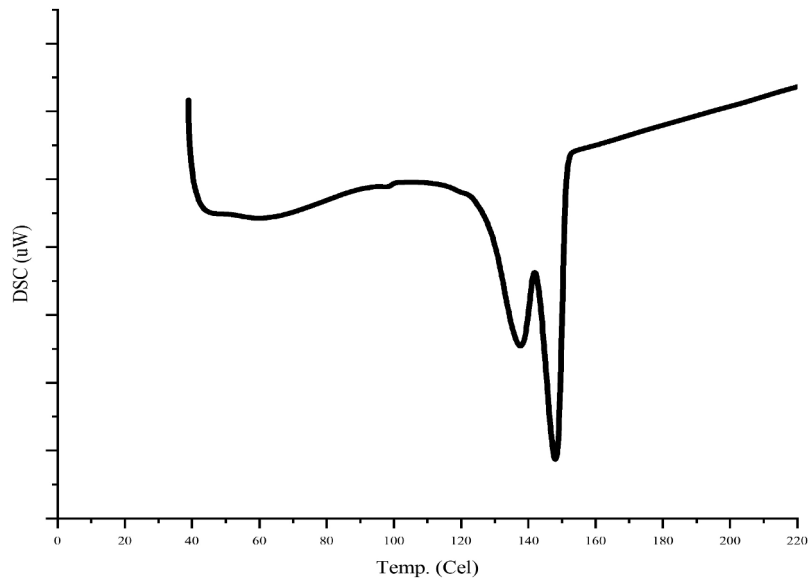


Figure 6. DSC analysis of PLA-1 (synthesised using 0.5 wt% SnCl₂).

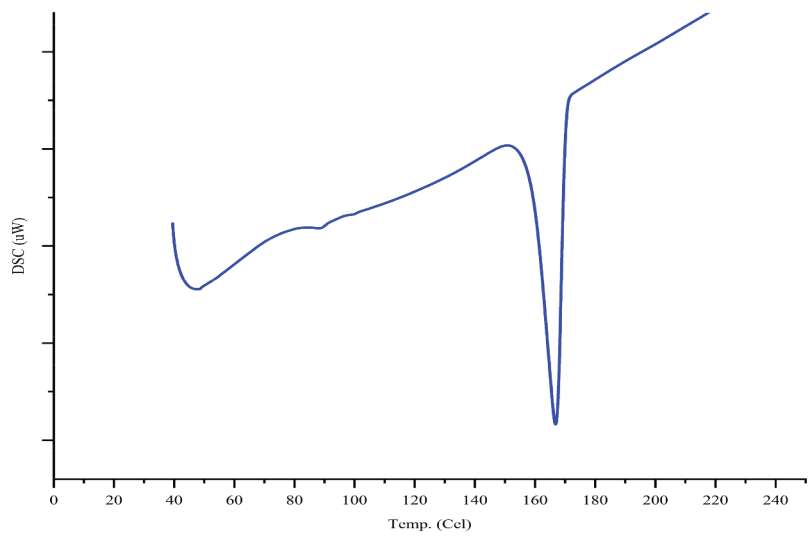


Figure 7. DSC analysis of PLA-2 (0.5 wt%) Sn(Oct)₂.

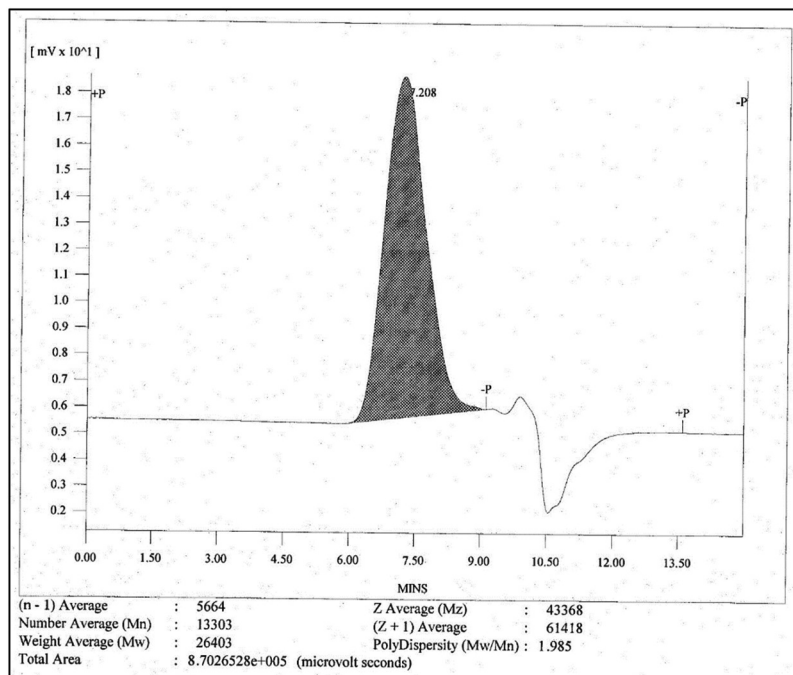
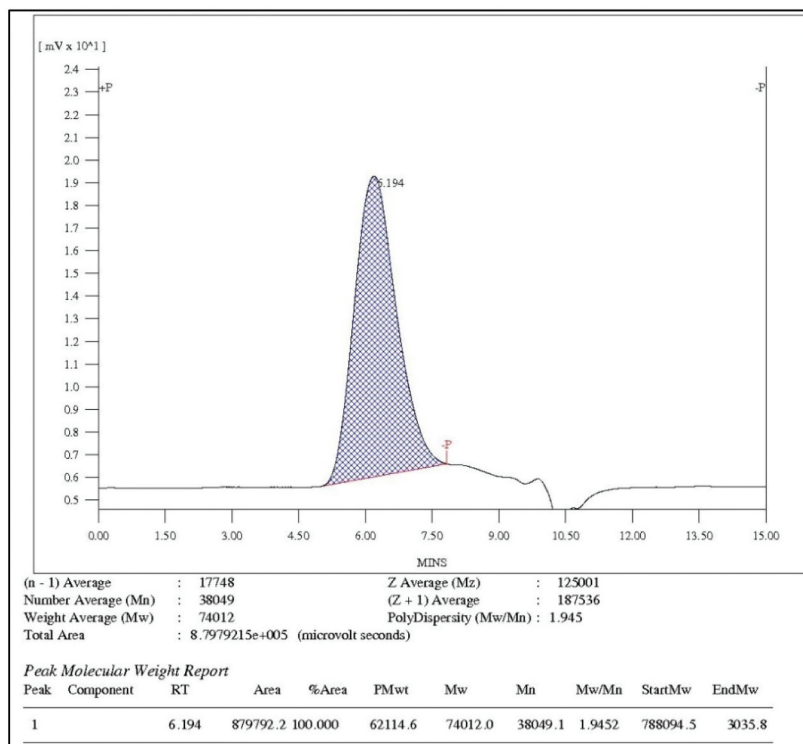
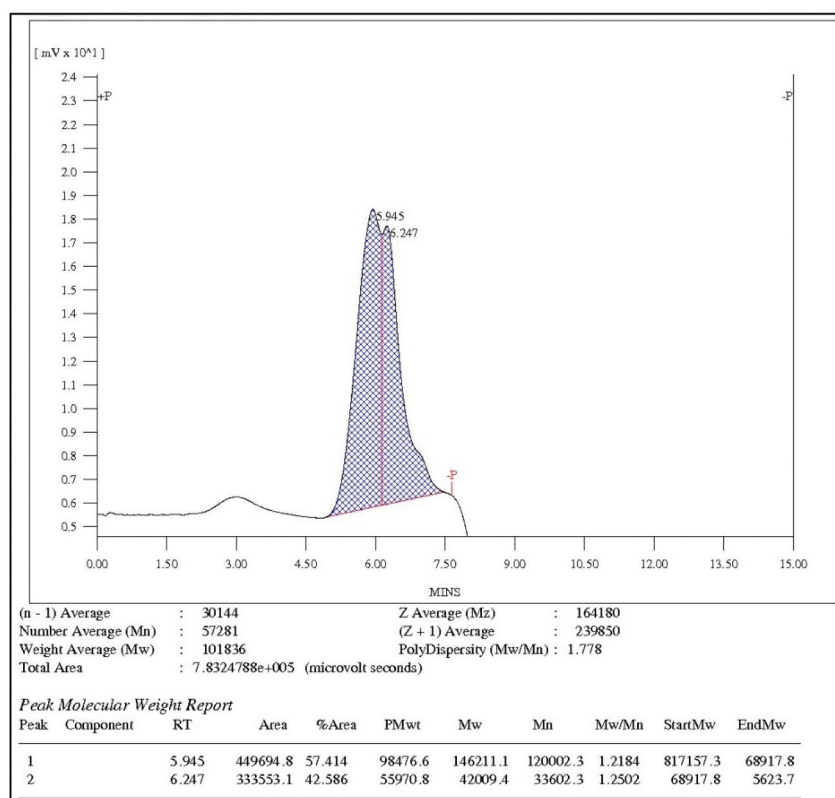


Figure 8. GPC peak analysis of PLA synthesised by SnCl₂.



(a)



(b)

Figure 9. GPC peak analysis of PLA synthesised by Sn(Oct)₂ (a) 0.5 wt% (b) 0.25 wt%.

5.3. Differential Scanning Calorimetry (DSC)

The thermal properties of synthesised PLA samples from Stannous Chloride and Stannous octoate show some remarkable thermal properties ranging from 145 to 165°C melting point, which is quite a spot-on result compared to the polycondensation and solvent polycondensation research

conducted by other researchers. In Table 1 we summarised the analysis results of DSC plots. The table mentions the essential aspects of synthesised polymer melting point. As well as the GPC analysis in form of molecular weight (Mw), number avg. molecular weight (Mn) and total yield of PLA after purification is mentioned.

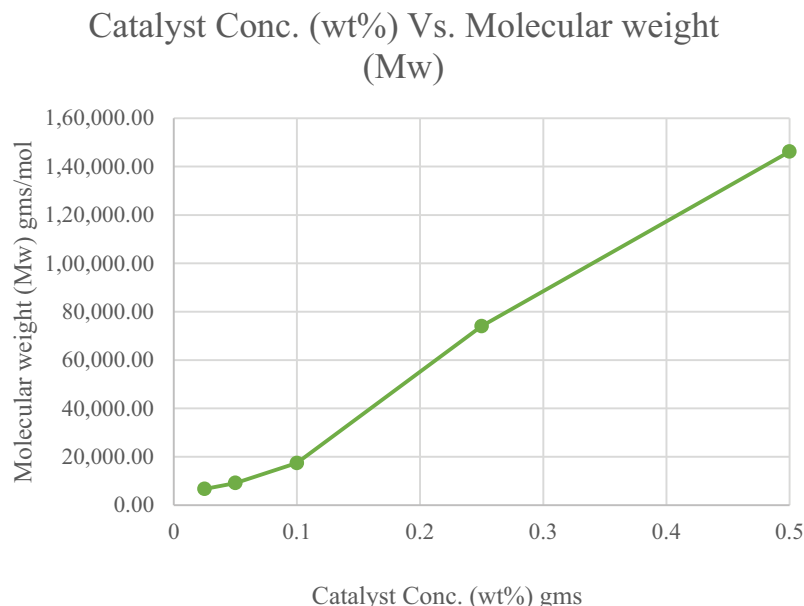


Figure 10. Stannous octoate catalyst concentration (based on dehydrated oligomer) vs. molecular weight (MW) obtain.

The double peak of the melting point of the PLA sample in Figure 6, with the application 0.5 weight% stannous chloride suggests the presence of the α and β crystalline structure in the polymer, which is quite common in unprocessed mid-range molecular weight PLA. Which is missed in stannous octoate catalysed PLA which have comparatively high MW in Figure 7. As both crystalline structures are quite evident in the PLA samples, there is not much difference in the basic morphology of PLA synthesised by both catalysts.

5.4. Gel Permeation Chromatography (GPC)

Gel permeation chromatography is one of the essential studies to determine the quality and potential applicability of synthesised polymer samples. The analysis of molecular weight suggests that the samples synthesised from the stannous chloride shows 26,403 Mw as in graph of Figure 8, which can be consider as a medium range of Mw for PLA, contrary stannous octoate shows outstanding results. Similar amount of stannous octoate boost the Mw upto the 1,46,000 gm/mol and 0.25 weight% shows 74,000 gm/mol indicated in Figures 9(a, b). Which is backed by NMR data, which concludes the DP of stannous octoate more than 100. The amount of stannous octoate in the range of 0.5 to 0.025 weight% is the feasible range to explore the relevance. The effect of catalyst on MW of PLA illustrated graphically in Figure 10.

6. Conclusion

The solution polymerisation method is cheaper and relatively easy to adopt in industry. However, the limitation of lower MW PLA can be synthesised was the biggest hurdle. The highest achieved MW of PLA synthesised by the polycondensation method is now raised to more than 146,000 in this work compared to the reported 26,000 without use of chain extenders. It has been shown that compared to stannous chloride, the proposed pair stannous octoate–O-Xylene can produce multifold MW PLA on the higher side by using the same quantity. The $^1\text{H-NMR}$ suggests stannous octoate

has more reactivity with an accelerated degree of polymerisation almost ten times. The use of stannous octoate in polycondensation was hindered due to its water sensitivity and is now solved with this new method and the results show the MW achieved is almost the same as ROP. Along with high MW, the yield can also be achieved up to 84.8%, making this process competitive with ROP. It has been noted that with a change in the quantity of catalyst stannous octoate, the MW can vary according to our expectations. It is for sure that this new method will certainly open the doors for not only research but also industrial-scale production of high MW PLA synthesis via this cheaper and easier method. As well as the produced PLA is viable for different applications.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Directorate of Research & Innovation (DRI), Nirma University under Grant of Minor Research Project (MRP), [UID no: ITNU/2024-2025/107].

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Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to legal or ethical reasons.

References

- [1] Garlotta D. A literature review of poly (lactic acid). *J Polym Environ.* 2002;9(2):63–84. doi: 10.1023/A:1020200822435
- [2] Hamad K, Kaseem M, Yang HW, et al. Properties and medical applications of polylactic acid: a review. *eXPRESS Polym Lett.* 2015;9(5):435–455. doi: 10.3144/expresspolymlett.2015.42

- [3] Sin LT, Tureen BS. Polylactic Acid and Copolymers for Biomedical Applications. In: *Polylactic Acid: A Practical Guide for the Processing, Manufacturing, and Applications of PLA*. 2nd ed. 2019. p. 50–51.
- [4] Peng Q, Mahmood K, Wu Y, et al. Effective binary catalysts of Brønsted acidic ionic liquids and stannous chloride dihydrate for melt polycondensation of l-lactic acid. *Mol Catal*. 2017;434:140–145. doi: [10.1016/j.mcat.2017.03.008](https://doi.org/10.1016/j.mcat.2017.03.008)
- [5] Mehmood A, Raina N, Phakeenuya V, et al. The current status and market trend of polylactic acid as biopolymer: awareness and needs for sustainable development. *Mater Today Proc*. 2023;72:3049–3055. doi: [10.1016/j.matpr.2022.08.387](https://doi.org/10.1016/j.matpr.2022.08.387)
- [6] Moon S-I, Lee C-W, Taniguchi I, et al. Melt/Solid polycondensation of l-lactic acid: an alternative route to poly(l-lactic acid) with high molecular weight. *Polymer*. 2001;42(11):5059–5062. doi: [10.1016/S0032-3861\(00\)00889-2](https://doi.org/10.1016/S0032-3861(00)00889-2)
- [7] Ichikawa F, Kobayashi M, Ohta M. Process for preparing polyhydroxycarboxylic acid. United States Patent US00544880008A. 1995 Aug.
- [8] Ajioka M, Enomoto K, Suzuki K, et al. Basic properties of polylactic acid produced by the direct condensation polymerization of lactic acid. *Bull Chem Soc Jpn*. 1995;68(8):2125–2131. doi: [10.1246/bcsj.68.2125](https://doi.org/10.1246/bcsj.68.2125)
- [9] Ikeda K, Obuchi S, Ohta M. Preparation process of polyhydroxycarboxylic acid. 1997.
- [10] Fukushima T, Sumihiro Y, Koyanagi K, et al. Development of a direct polycondensation process for poly (L-lactic acid). *Int Polym Proc*. 2000;15(4):380–385. doi: [10.3139/217.1615](https://doi.org/10.3139/217.1615)
- [11] Zhang J, Krishnamachari P, Lou J, et al. Synthesis of poly(L(+)-lactic acid) by polycondensation method in solution. In: *Proceedings of the 2007 National Conference on Environmental Science and Technology*; Springer, New York NY; 2009. p. 3–8.
- [12] Singh SK, Anthony P, Chowdhury A. High molecular weight poly (lactic acid) synthesized with apposite catalytic combination and longer time. *Orient J Chem*. 2018;34:1984–1990. doi: [10.13005/ojc/3404036](https://doi.org/10.13005/ojc/3404036)
- [13] Maryanty Y, Hadianoro S, Widjajanti K, et al. Poly lactic acid (pla) development using lactic acid product from rice straw fermentation with azeotropic polycondensation process. *IOP Conf Ser Mater Sci Eng*. 2021;1053(1):012043. doi: [10.1088/1757-899x/1053/1/012043](https://doi.org/10.1088/1757-899x/1053/1/012043)
- [14] Woong Kim K, Sli W. Synthesis of high-molecular-weight poly (L-lactic acid) by direct polycondensation. *Macromol Chem Phys*. 2002;203:2245–2250. doi: [10.1002/1521-3935\(200211\)203:15<2245:AID-MACP2245>3.0.CO;2-3](https://doi.org/10.1002/1521-3935(200211)203:15<2245:AID-MACP2245>3.0.CO;2-3)
- [15] Marques DAS, Jarmelo S, Baptista CMSG, et al. Poly(lactic acid) synthesis in solution polymerization. *Macromol Symp*. 2010;296:63–71. doi: [10.1002/masy.201051010](https://doi.org/10.1002/masy.201051010)
- [16] Dutkiewicz S, Grochowska-Łapienis D. Synthesis of poly(L(+)-lactic acid) by polycondensation method in solution. *Fibres Text East Eur*. 2003;4:66–70.
- [17] Shyamroy S, Garnaik B, Sivaram S. Structure of poly(L-lactic acid)s prepared by the dehydropolycondensation of L-lactic acid with organotin catalysts. *J Polym Sci A Polym Chem*. 2005;43(10):2164–2177. doi: [10.1002/pola.20679](https://doi.org/10.1002/pola.20679)
- [18] Pandey AK. Oriental. Synthesis of poly (L-Lactic acid) by dehydropolycondensation using various pore sizes of zeolite. *Int J Adv Pharm Biol Chem*. 2013;2:68–83.
- [19] Takasu A, Narukawa Y, Hirabayashi T. Direct dehydration polycondensation of lactic acid catalyzed by water-stable Lewis acids. *J Polym Sci A Polym Chem*. 2006;44(18):5247–5253. doi: [10.1002/pola.21639](https://doi.org/10.1002/pola.21639)
- [20] Yamada S, Takasu A, Takayama S, et al. Microwave-assisted solution polycondensation of l-lactic acid using a Dean-stark apparatus for a non-thermal microwave polymerization effect induced by the electric field. *Polym Chem*. 2014;5(18):5283–5288. doi: [10.1039/c4py00639a](https://doi.org/10.1039/c4py00639a)
- [21] Desai H, Mehta T, Shah N. Azeotropic dehydrative (solution) polycondensation of lactic acid to Polylactic Acid (PLA): a in-depth review of an overlooked method for manufacturing PLA. *Polym Plast Technol Eng*. 2023;62(11):1394–1402. doi: [10.1080/25740881.2023.2209644](https://doi.org/10.1080/25740881.2023.2209644)