International Journal of Chemistry and Pharmaceutical Sciences

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Research Article **Open Access**

High molecular weight polylactic acid synthesized by applying different binary catalyst

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A B S T R A C T

With the extensive growth of polymers in the modern times and its use almost inevitable, problem of environment pollution has emerged owing to the waste produced from petroleum based non degradable plastics. To overcome this problem researchers all over the world are working to minimize the pollution from polymeric waste, they have concentrated their efforts in mainly two directions viz. to either make the polymer they are using biodegradable to some extent or to use the biopolymer which in turn are biodegradable to replace the petroleum based polymer. One of such polymers which has caught the eyes of researchers is polylactic acid (PLA) it is one of the most useful biopolymers produced by molasses of sugar cane. It has good mechanical properties, physical properties, compatibility with most polymers and biodegradability. Therefore it has managed to find use almost in all the prominent fields of applications like in medicine, packaging and several other areas. It was observed that The properties of PLA changed with the change of molecular weight. The high molecular weight PLA has better properties as compared to low molecular weight PLA. However difficulty is observed in synthesis of high molecular weight PLA, due to high demand and short supply in the market, the researchers are working to developed new and better ways for synthesis of high molecular weight PLA. This present paper addresses the issue; we have tried to synthesize high molecular weight of PLA by applying various binary catalysts such as tin chloride/maleic anhydride, tin chloride / phthalic anhydride and tin chloride/p-toluene sulfonic acid combinations in direct polycondensation synthesis reaction. The product obtained was characterized by several methods mainly molecular weight of synthesized polylactic acid was determined by Gel Permeation Chromatography (GPC). According to given data of GPC analysis the molecular weight of PLA was changed with the change of binary catalyst. The results obtained were supported by FTIR spectral analysis. The structure of synthesized PLA was determined by employing FTIR and H^{-1} NMR spectral analysis.

Keywords: Synthesis of polylactic acid, Uses of different catalysis, characterization by GPC, FTIR and H^{1} NMR

A R T I C L E I N F O

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Article History: Received 19 August 2016, **Accepted** 29 September 2016, **Available Online** 27 October 2016

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Manuscript ID: IJCPS3127

PAPER-QR CODE

Citation: Prashant Anthony. High molecular weight polylactic acid synthesized by applying different binary catalyst. *Int. J. Chem, Pharm, Sci.*, 2016, 4(10): 517-521.

1. Introduction

Since the last few decades, plastic materials made up of non- biodegradable petroleum based polymers are widely used. Most of the petrochemical plastics have resistance against the long-lasting action of the drastic weather and microbial activity. As a result, a large volume of plastic waste material is generated and it has raised many serious environmental issues like the lack of landfill space, soil and air pollution [1]. Only a small percentage of the plastic waste is recycled and recovered by other means whereas rest of the plastic material increases the waste materials. It paves the way for the discovery of biodegradable polymers, its synthesis and application in different fields. There are various types of biodegradable polymers-natural biodegradable polymers such as cellulose, starch, protein and natural rubber and some synthetic biodegradable polymers such as polylactic acid (PLA), poly hydroxyl butanoate (PHB), poly hydroxyl alkanoate (PHA) and blend of starch and poly(vinyl alcohol) that have been reported [2, 3, 4, 5]. Nowadays many researchers have shown interest in the manufacture and application of biodegradable aliphatic polyester generated from lactic acid such as polylactic acid (PLA).

Polylactic acid (PLA) is ecofriendly biodegradable synthetic polyester. It is a linear thermoplastic polymer having high strength, high modulus, high melting point, good barrier properties (gas, water and oxygen), good transparency, good mechanical strength, high elongation, environmental degradability and compatibility [6, 7, 8, 9]. Lactic acid is prepared from 100% renewable resources like corn, sugar beets and rice [10, 11]. It is used in various fields like medicine, packaging and agriculture. Polylactic acid (PLA) has a number of advantages but it has one limitation as well and that is to get high molecular weight polymer at a reasonable cost. Many researchers have tried two different methods to synthesize PLA at a reasonable cost. PLA has been synthesized by ring opening polymerization [12,13] as well as by direct polycondensation reaction [14,15,16]. The ring opening polymerization process is a multistep process and in this method many reagents such as catalysts, solvents and initiators are utilized for the synthesis of PLA. The products obtained by this method require purification which is a complicated and difficult process, thereby increasing the cost of high molecular weight polylactic acid. The direct polycondensation reaction is a reversible reaction and equilibrium is achieved between the reactant and the product because of that it is not easy to synthesize high molecular weight PLA by direct polycondensation reaction. In this paper, we have tried to use different binary catalysts such as tin chloride/phthalic anhydride, tin chloride/ maleic anhydride and tin chloride p-toluene sulfonic acid for the synthesis of high molecular weight of polylactic acid (PLA) in bulk by direct polycondensation reaction.

2. Materials and Methods

Materials

The pure lactic acid was purchased from Merck, India. Tin chloride, phthalic anhydride (PAH), methanol, p-xylene, p-Toluene sulfonic acid (TSA), maleic anhydrate (MAH) and ethanol were purchased from Central Drug Houses (CDH), India.

Method

The polycondensation reaction was accomplished in 500 ml three necked flask equipped with a dean-stark condenser, by varying catalyst at fixed temperature, solvent and time period in nitrogen atmosphere. The lactic acid and p-xylene was taken into a 500 ml three necked flask. The reaction mixture was dehydrated for 5 hours at 140 ^{0}C temperature under nitrogen atmosphere. After that calculated amount of $SnCl_2.2H_2O$ corresponding to 0.5% of the lactic acid was mixed with a reaction mixture in three necked flask. The reaction temperature was gradually increased to 160 ^{0}C and the reaction was allowed to run for 15 hours. After 20 hours, maleic anhydride (MAH)/ phthalic anhydride/ p-toluene sulfonic acid corresponding to 0.5% of the lactic acid was added to reaction mixture and the reaction was allowed to run for 10 hours at the same temperature. At the end, it was cooled to 100 ^{0}C under nitrogen atmosphere. The obtained product was precipitated into methanol. The resulting precipitate was washed 4-5 times with methanol, filtered and dried at 70 ^{0}C. The synthesized polymer was characterized by GPC, FTIR, H^1-NMR.

Spectroscopic analysis

H^1- NMR spectra of the synthesized polylactic acid samples were scanned on a Bruker Avance II spectrometer working at 400 MHz at 293 K in $CDCl_3$. Chemical shifts (δ) were expressed in ppm. The FTIR spectrum was used to determine the functional groups and structure of polymer using Parken Elmer FT-IR spectrum 100 (USA). The absorption peaks in between 4000 cm^{-1} to 500 cm^{-1} were studied.

Gel Permeation Chromatography

The number-average molecular weight (M_n) and weight average molecular weight (M_w) were determined by Younglin ACME 9000 Gel Permeation Chromatography in DMF at 40 ^{o}C with flow rate 0.5 mL/ min on two polystyrene gel columns [PL gel 5μm 10E 4 Å columns (300 × 7.5 mm)] connected in series to a Younglin ACME 9000 Gradient Pump and a Younglin ACME 9000 RI detector. The columns were calibrated against seven poly (methyl methacrylate) (PMMA) standard samples (Polymer Lab, PMMA Calibration Kit, M-M-10).

3. Results and Discussion

Different samples of PLA were synthesized by direct polycondensation by using different binary catalytic composition such as tin chloride/phthalic anhydride, tin

chloride/maleic anhydride and tin chloride/p-toluene sulfonic acid. The molecular weights were ascertained by GPC method and this result was also supported by spectral analysis and the structure of PLA was analyzed by FTIR and H^1 NMR.

The FTIR spectrum of polylactic acid (PLA) is shown in figure 2a. The polymers have an absorption band showing at 1753.59 cm^{-1}, representing the carbonyl group (C=O) of the polyester. The C-O-C stretching modes of ester group of polylactic acid observing at 1360.34 cm^{-1} and The C-O asymmetric mode shown in between 1043.43 cm^{-1} to 1184.97 cm^{-1}. The absorption Bands showing at 753.81 and 869.79 cm^{-1} ascribed to the crystalline and amorphous phases of polylactic acid. The bands at 2996.54 cm^{-1} are assigned to C-H stretching of the asymmetric CH_3 group. The bending vibrations band of CH_3 were observed at 1453.61cm^{-1} [17, 18]. The H^1-NMR spectrum of polylactic acid (PLA) is shown in figure 1. The spectrum peak at 5.173 was represented CH in lactic acid repeat units and the peak at 1.56 ppm was assigned to the methyl (CH_3) protons. In the low molecular weight of PLA peaks absorbed around 10.5-12 ppm indicate -COOH terminal group present in polymeric chain. Whereas in high molecular weight PLA peaks around 10.5-12ppm disappeared [19].

Gel permeation chromatography:

According to obtained data (Table 1) the molecular weight of PLA changed with change of catalyst in polymerization reaction. The molecular weight of PLA was dependent on catalyst used during polymerization reaction. When tin chloride/phthalic anhydride was used as a catalyst in polymerization reaction and the reaction was allowed to run for 35 hours, (sample C1) 22,100 weight-average molecular weight and 6,900 number average molecular weight of the PLA was obtained. Whereas when tin chloride/maleic anhydride was used as a catalyst and the reaction was allowed to run for the same time, (sample C2) molecular weight of PLA was obtained up to 61,700 weight-average molecular weight and 13,400 number average molecular weight. And when tin chloride/p-TSA was used as a catalyst and the reaction time was same, (sample C3) 81,500 weight-average molecular weight and 18,300 number average molecular weight of the PLA was obtained.

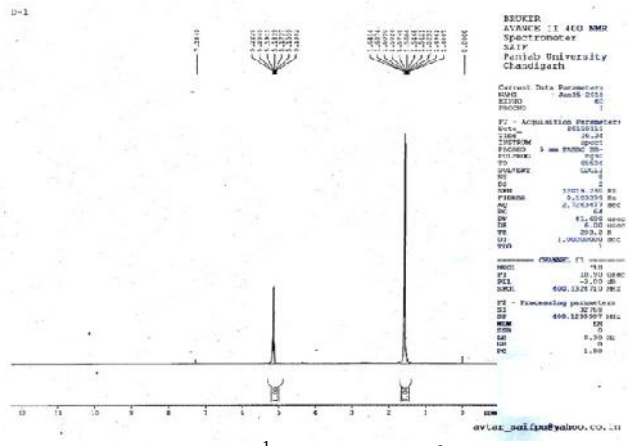

Figure 1: H^{-1}NMR spectra of PLA

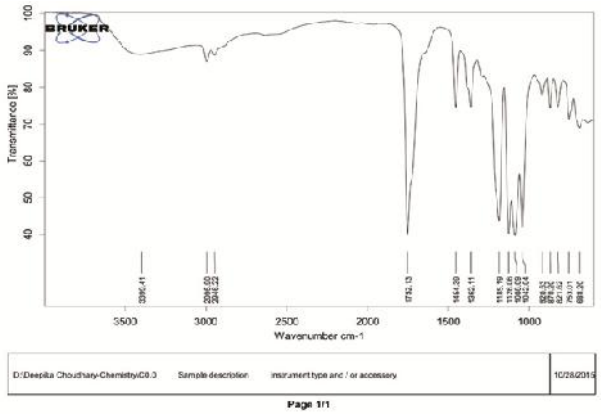

Figure 2a: FTIR spectra of synthesized PLA by using tin chloride /phthalic anhydride

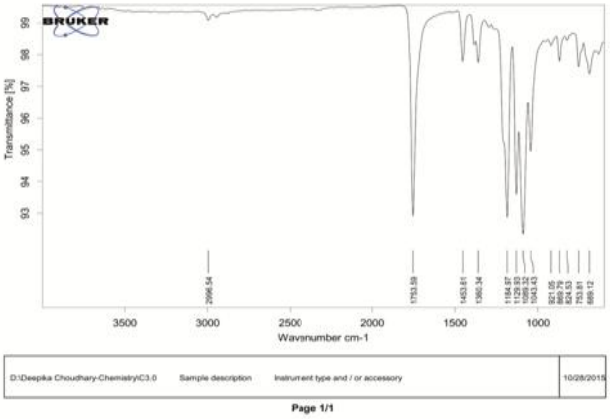

Figure 2b: FTIR spectra of synthesized PLA by using tin chloride/p-toluene sulfonic acid

The data obtained is supported by FTIR spectroscopic analysis. With the change in binary catalyst the molecular weight of polylactic acid should be also changed. In high molecular weight PLA hydroxyl group present in polymeric chain decreases, therefore the intensity of peak at 3507.5 cm^{-1} shown in figure 2a, has decreased in 2b. The decreasing intensity of peak at 3565.5cm^{-1} indicates the increase of molecular weight of polylactic acid [20, 21].

In present study, we synthesized high molecular weight of PLA by using tin chloride dihydrate with various binary catalysts such as phthalic anhydride, maleic anhydride and p-TSA for a longer time period i.e. up to 35 hours. Out of these above binary catalytic combination tin chloride dihydrate with p-TSA is a more effective binary catalyst for the synthesis of high molecular weight of PLA [18, 22, 23]. The catalytic activity gradually changed when reaction was allowed to run for longer time, then the decreasing terminal groups of catalysts behave as the ligands of catalyst coordination sites. With the decreasing terminal groups on catalyst the vacant coordination site of catalyst increased. Because of this change the catalytic behaviour at high temperature and side reaction was started, namely depolymerization gets started and as a result, several byproducts are formed (pyruvic acid, paraldehyde, lactide and acetic acid etc) and causing serious discoloration of

product. The binary catalyst like p-TSA, MAH and PAH added at the later stage fulfilled the vacant sites of catalyst, increased the catalytic activity and reduced side reaction [23, 24]. As a result, we were able to obtain approximately 81,700 molecular weight of PLA without discoloration of product in direct polymerization. Among all these binary catalyst p-TSA is more effective to increase molecular weight of PLA without discoloration of products.

Table 1: Effect of binary catalyst on the direct polycondensation

Sample No.	Different binary catalyst	T (^{0}C)	Mn	Mw	PDI
C1	Tin chloride/phthalic anhydride	160 ^{0}C	6,900	22,100	3.19
C2	Tin chloride/maleic anhydride	160 ^{0}C	13,400	61,700	4.49
C3	Tin chloride/p-toluene sulfonic acid	160 ^{0}C	18,300	81,500	4.45

4. Conclusion

Polylactic acid is one of the most useful ecofriendly biodegradable synthetic thermoplastic polyester polymers. It finds several applications in different fields such as packaging, medicine and industries. But due to high cost and less availability of high molecular weight of polylactic acid, it is used only in a few areas. In this paper we have discussed the effect of various binary catalysts on molecular weight of PLA synthesized by direct polycondensation reaction. We used three different binary catalysts such as tin chloride/phthalic anhydride, tin chloride/maleic anhydride and tin chloride/ p-toluene sulfonic acid. According to GPC results, out of three binary catalysts tin chloride/ p-toluene sulfonic acid is the most effective catalyst for synthesis of high molecular weight of PLA. The results are also supported by FTIR spectral analysis.

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