



Synthesis and Characterization of Polylactic Acid

TAUHEEDA RIAZ¹, MUHAMMAD IKRAM AUJLA^{1,*}, MUHAMMAD AKRAM KASHMIRI²,
TAYYABA SHAHZADI¹, AMINA ASGHAR¹ and TARIQ ISMAIL¹

¹Department of Chemistry, GC University, Lahore, Pakistan

²Board of Intermediate and Secondary Education, Lahore, Pakistan

*Corresponding author: Tel: +92 42 99231581-8; E-mail: ikramaujla@hotmail.com

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Poly(lactic acid) is among the most important biodegradable polymers. To explore the feasibility of making poly(lactic acid) through cheap and easy to use methods, the direct polycondensation of lactic acid at 200 °C under vacuum was investigated. Five samples of lactic acid were heated under vacuum. In three samples stannous chloride, glycerin and polyacrylamide gel were used as catalyst. Two samples were without the catalyst and heated at pressure 100 mm Hg with different time duration. The effects of catalysts and reaction time on the molecular weight and yield were studied. The polymer was characterized by infrared spectroscopy. The viscosity of the polymer was determined by Brookfield viscometer. The results showed that polymer which was heated under vacuum at 200 °C without the use of catalyst, had highest yield, highest viscosity and highest molecular weight.

Key Words: Poly(lactic acid), Biodegradable, Polycondensation, Polyacrylamide.

INTRODUCTION

The synthesis and application of biocompatible and biodegradable polymers have recently emerged as areas of great interest. These materials are rapidly becoming viable alternatives to biologically intractable polymers for industrial uses such as packaging. They are uniquely suited to specialist biomedical applications, such as the encapsulation and controlled release of bioactive molecules and as scaffolds for tissue engineering¹.

Poly(lactic acid) (PLA) is a biodegradable polymer derived from lactic acid. It is a highly versatile material and is made from 100 % renewable resources like corn, sugar beets, wheat and other starch-rich products. Lactic acid can be produced in chiral and racemic forms by fermentation of above resources. Lactic acid is catalytically dimerized to form lactide. Ring-opening polymerization of lactide forms poly(lactic acid). Poly(lactic acid) exhibits many properties that are equivalent to or better than many petroleum-based plastics²⁻⁸.

Poly(lactic acid) can be formulated to be either rigid or flexible and can be co-polymerized with other materials⁹. Poly(lactic acid) can be made with different mechanical properties suitable for specific manufacturing processes, such as injection molding, sheet extrusion, blow molding, thermoforming, film forming and fiber spinning using most conventional techniques and equipment¹⁰. Poly(lactic acid) is a nonvolatile,

odorless polymer and is classified as GRAS (generally recognized as safe) by the Food and Drug Administration in the United States⁹. When D,L-lactide was polymerized it forms D,L-PLA which is amorphous. L-Lactide and D-lactide form L-PLA and D-PLA, respectively. Chiral L-PLA and D-PLA polymers form a crystalline polymer upon mixing.

Russell¹¹ described the structural flexibility and efficacy of thiourea amine catalyst for the supramolecular activation and ring opening polymerization of lactide. Kim¹² used dipentaerythritol as a chain branching agent in order to synthesize the higher molecular weight poly(lactic acid) by direct condensation polymerization of lactic acid. Poly(lactic acid) of high molecular weight 76000 was obtained by using antimony dioxide with good colour. Its cold crystallization temperature 115 °C and T_g was found to be 54.8 °C and T_n 147 °C. Isobe¹³ prepared polymers useful as plasticizer *etc.*, with good compatibility with other polymers efficiently by ring opening polymerization of lactones in the presence of hydroxy acid initiator.

EXPERIMENTAL

In this research, hot plate of model BIBBY HB502 was used, reflux condenser of pyrex glass, vacuum pump model ULVAC SINKU KIKO, Japan, electrical balance model Sartorius p 324s, IR spectrophotometer model MIDAC corporation, Brookfield viscometer model RVT and vacuum oven model IMRECO. Reagents used were lactic acid and stannous

chloride manufactured by MERCK, polyacrylamide by BIO-RAD, glycerin by MERCK, acetone by BIO-Med, diethyl ether by MERCK, chloroform by FISHER scientific, sodium hydroxide by MERCK, phenolphthalein by MERCK and sodium bicarbonate by PANREAC.

Preparation of polylactic acid: Polylactic acid was prepared by following different experiments with and without the use of catalysts. 50 g of lactic acid was taken in round bottom flask. Round bottom flask was fitted with a reflux condenser. A magnetic stirrer was added into the flask for the purpose of stirring the contents in the flask. Round bottom flask was placed on sand bath. The sand bath was placed on the hot plate to heat the contents in the flask. The sand bath was used to provide maximum heat to the round bottom flask. The contents were heated to 130 °C and this temperature was maintained for 2 h. Then vacuum pump was attached with flask and vacuum was created into it. The temperature was raised to 180 °C and this temperature was maintained throughout the experiment. The contents were stirred throughout the experiment by means of magnetic stirrer.

The vacuum pump was turned on for 1 h and then it was turned off. After 15 min it was again turned on. It was kept on for 1 h and then again turned off for 15 min. This process was repeated for 4 h. After this whole the apparatus was turned off. A pale yellow coloured semisolid was obtained which solidified after cooling. This was called as sample No. 1.

In the same way as above another experiment was done and time duration of heating was increased. The sample obtained was called as sample No. 2. In another 3 experiments, all process was same as above but in each one catalyst was added. The catalysts used were polyacrylamide gel stannous chloride and glycerin. The samples were called as sample No. 3, sample No. 4 and sample No. 5, respectively.

Determination of yield of polylactic acid: 10 mL of filtrate was taken in the conical flask. Standard solution of sodium hydroxide was taken in the burette. One drop of phenolphthalein, used as indicator, was added to the conical flask. Sodium hydroxide was added dropwise to the conical flask from the burette until the solution in the conical flask becomes pink coloured. The volume of the sodium hydroxide used to neutralize the acid was noted and amount of lactic acid was calculated.

The same process was repeated for all the samples and amount of lactic acid present in them was calculated.

Precipitation of the polymer: The impure polymer was precipitated in order to purify it. 500 mL distilled water was added to the polymer. As the polymer was insoluble in water it will be precipitated and the oligomer with low molecular weight and dissolve in water at pH 4. The precipitated polymer was separated by filtration.

Then the precipitated polymer was added to 500 mL distilled water and pH of the aqueous solution was adjusted to 6-8 by adding sodium bicarbonate portion-wise. The precipitated polymer was dissolved in water and some insoluble polymer and impurities were separated. The insoluble polymer and impurities were removed by centrifugation.

The pH of the aqueous solution was adjusted to 2 by the addition of 1 N hydrochloric acid drop-wise. Now at this pH the dissolved polymer was again precipitated.

The precipitated polymer was washed three times with distilled water and then isolated. The pure polymer was dried in vacuum oven at pressure 100 mm Hg. A non-crystalline polymer was obtained.

Determination of viscosity of the polymer: The viscosity of the polymer was determined on Brookfield viscometer. Chloroform was used as a solvent for making solution of the polymer. Viscosity is an important physical property of polymers for the determination of molecular weight of the polymer.

RESULTS AND DISCUSSION

The polymer was formed by various experiments using various catalysts and without catalysts. For the confirmation of the catalyst infrared spectra of the samples were taken.

Infrared spectrum of sample No. 1: The peaks in the region 2950-2850 cm^{-1} are for C-H stretching, therefore, the peak at 2950 cm^{-1} is for C-H stretching and indicates presence of $-\text{CH}_3$ group. The peaks in the region 1750-1735 cm^{-1} are for ester group, so the peak at 1750 cm^{-1} indicates the presence of ester group. The range of C-H bending is 1465-1300 cm^{-1} so peaks at 1454 and 1376 cm^{-1} are for C-H bending and indicate the presence of $-\text{CH}_3$ group. The appearance of strong bands due to C-O stretching at 1300-1050 cm^{-1} indicates the ester group provided C=O stretching is observed in the region 1750-1735 cm^{-1} . As we have a peak at 1750 cm^{-1} for ester group so the peaks at 1050, 1140 and 1200 cm^{-1} are for C-O stretching and confirms presence of ester group. Peaks in finger print region at 750, 855 and 867 cm^{-1} are for C-H bending.

Infrared spectrum of sample No. 2: The peak at 1751 cm^{-1} indicates the presence of ester group. The bands 1453 and 1381 cm^{-1} are for C-H bending and indicate the presence of $-\text{CH}_3$ group. The appearance of strong bands due to C-O stretching at 1300-1050 cm^{-1} indicates the ester group provided C=O stretching is observed in the region 1750-1735 cm^{-1} . As we have a peak at 1750 cm^{-1} for ester group so the peaks at 1186 and 1091 cm^{-1} are for C-O stretching and confirms presence of ester group. Peaks in finger print region *i.e.*, at 869 and 754 cm^{-1} are for C-H bending.

Infrared spectrum of sample No. 3: The peak at 1750 cm^{-1} indicates the presence of ester group. The bands at 1460 and 1380 cm^{-1} are for C-H bending and indicate the presence of $-\text{CH}_3$ group. The appearance of strong bands due to C-O stretching at 1300-1050 cm^{-1} indicates the ester group provided C=O stretching is observed in the region 1750-1735 cm^{-1} . As we have a peak at 1750 cm^{-1} for ester group so the peaks present in this range are for C-O stretching and confirms presence of ester group. Peaks in finger print region *i.e.*, at 860, 830 and 760 cm^{-1} are for C-H bending.

Infrared spectrum of sample No. 4: The peak at 2957 cm^{-1} is due to C-H stretching. The peak at 1743 cm^{-1} indicates the presence of ester group. The range of C-H bending is 1465-1300 cm^{-1} so the peaks at 1449 and 1383 cm^{-1} are assigned for C-H bending and indicate the presence of $-\text{CH}_3$ group. The appearance of strong bands due to C-O stretching at 1300-1050 cm^{-1} indicates the ester group provided C=O stretching is observed in the region 1750-1735 cm^{-1} . As we have a peak at 1750 cm^{-1} for ester group so the peaks at 1050, 1186 and 1129 cm^{-1} are for C-O stretching and confirms presence of

TABLE-1

Sample No.	Concentration C (%)	Viscosity of solution (η)	Viscosity of solvent (η_0)	Intrinsic viscosity $[\eta] = 1/C \times \ln(\eta/\eta_0)$	m.w. $M = a \sqrt{\frac{[\eta]}{K}}$
S1	1	10 cps	0.54 cps	1.268	6341
S2	1	26 cps	0.54 cps	1.683	8416
S3	1	14.4 cps	0.54 cps	1.426	7133
S4	1	12.8 cps	0.54 cps	1.375	6877
S5	1	13.6 cps	0.54 cps	1.402	7009

$a = 0.76$, $K = 0.0002$, $T = 25^\circ\text{C}$.

ester group. Peaks in finger print region *i.e.*, in the range of $1000\text{-}600\text{ cm}^{-1}$ are for C-H bending. Therefore peaks at 920 , 868 , 824 , 754 and 689 cm^{-1} are for -CH bending and indicate presence of -CH₃ group.

Infrared spectrum of sample No. 5: The band at 1750 cm^{-1} indicates the presence of ester group. The adsorption at 1453 cm^{-1} is for C-H bending and indicate the presence of -CH₃ group. The appearance of strong bands due to C-O stretching at $1300\text{-}1050\text{ cm}^{-1}$ indicates the ester group provided C=O stretching is observed in the region $1750\text{-}1735\text{ cm}^{-1}$. As we have a peak at 1750 cm^{-1} for ester group so the peaks present in this range are for C-O stretching and confirms presence of ester group. Peaks in finger print region *i.e.*, at 943 , 866 , 755 and 861 cm^{-1} are for C-H bending.

The molecular weight of the polymer is determined by relating with viscosity. The molecular mass of non-volatile solute can be determined by measuring the viscosity of solution by dissolving a known mass of solute in a known mass of solvent. Molecular weight was calculated from viscosity of polymer by following formula:

$$[\eta] = KM^a$$

where, $[\eta]$ = intrinsic viscosity, M = molecular weight K and a are constants.

It is found empirically that the intrinsic viscosity of a solution depends on the molecular weight of the solute: where a falls between 1 and 2 and is a parameter that is related to the shape of the molecule. When the solute molecule is nearly spherical, a is about 0.5, but when the solute molecule is long, extended or rod shaped, its value may reach 1.7-1.8.

The values of K and a were taken after consulting Mark-Houwink parameters for various polymers and solvents. Using the viscosity data, the molecular weights of polymer samples can be calculated (Table-1).

Conclusion

Polylactic acid was prepared by five different experiments. In two experiments lactic acid was heated under vacuum at different temperature and time duration. In other three experiments polyacrylamide, stannous chloride and glycerin were used as catalysts and lactic acid was heated under pressure. The polymer in the form of yellow coloured semisolid was

obtained. The presence of polymer was confirmed by infrared spectra of the samples. The results showed that the polymer that was prepared by heating lactic acid under vacuum at 200°C sample No. 2 had the highest yield *i.e.*, 96.38 %.

Then the viscosities of the polymer samples were determined by Brookfield viscometer. The results showed that sample No. 2 has the highest viscosity. The viscosities were measured because it is related to the molecular weight of the polymer. The higher the molecular weight, higher was viscosity of the polymer. From the viscosity data the molecular weights of the polylactic acid samples were calculated as shown in Table-1. From the data it was seen that molecular weight of sample No. 1 is 6341, molecular weight of sample No. 2 is 8416, molecular weight of sample No. 3 is 7133, molecular weight of sample No. 4 is 6877 and molecular weight of sample No. 5 is 7009. From these results it was seen that sample No. 2 has highest molecular weight.

REFERENCES

1. T. Grengross and S. Steven, *Sci. Am.*, **283**, 36 (2000).
2. R. Datta, S. Tsai, P. Bonsignore, S. Moon and J. Frank, *Microbiol. Rev.*, **16**, 221 (1995).
3. C.A. Harper, *Modern Plastics Handbook*, New York: McGraw-Hill (2000).
4. M. Verespej, *Winning Technologies: Polylactic Polymers*, Industry Week, December 11 (2000).
5. R.E. Drumright, P.R. Gruber and D. Henton, *Adv. Mater.*, **12**, 1841 (2000).
6. J. Lunt and A. Shafer, *Polylactic Acid Polymers from Corn: Potential Applications in the Textiles Industry*, April (2002).
7. M. O'Brien and J. Gray, *Federal Trade Commission Announces New Fiber Generic: Cargill Dow's Natureworks™ Fibers Receive First Designation of the Century*, Internet (2002).
8. Cargill Dow, *Company Website*, Internet, Available, April (2002). www.cdply.com
9. M. O'Brien and S. Mojo, *New Food Service Alternative for Annually Renewable Resources Unveiled for Use in Major Venues*, Internet (2001) Available (March 2002). www.biocorpusa.com/html/pla_clear_cup.html
10. R. Stein, *Proceed. Natonal Acad. Sci. (USA)*, **89**, 835 (1992).
11. C. Russell, G.G. Pratt, D.A. Lehmeijer, P.N. Long and Pontus Lundberg, *Polyhydron*, **26**, 3817 (2007).
12. S.H. Kim, Y.H. Kim, A. Ann-Christian, C. Emo, F. Jan, S. GERland and V. Michel, *Eur. Polym. J.*, **87**, 69 (2003).
13. T. Isobe and M. Watanobe, *Japanese Patent* 60, 199, 027, Appl. 84/56, 540 (1984).