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Synthesis of Chain Extended Lactic Acid/Polypropylene Glycol Co-polymer

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Abstract

The synthesis of high-molecular-weight lactic acid based polymers by chain extension polymerization was investigated. A hydroxyl terminated telechelic prepolymer was synthesized and then it was chain extended to the high molecular weight polymer. All polymerizations were carried out in the melt, using tin octoate as catalyst. The products were characterized by titrametric methods, Dynamic mechanical analysis (DMA), FTIR and Viscometry. An increase in the molecular weight as well as storage modulus along with glass transition temperature (Tg) was observed.

Keywords: Lactic acid, Chain extended polymer, Dynamic mechanical analysis

Introduction

With growing environmental awareness, ecological concerns and new legislations, fully biodegradable materials, biocomposited [1] [2], and nanocomposites[3] of biodegradable materials are of prime interest. However fully biodegradable materials Lactic acid is an attractive monomer in the synthesis of biodegradable polymers, being obtained from renewable resource. In last few decades lactic acid have been studied extensively for a number of applications [4-6]. To have good mechanical strength PLA should possess higher molecular[7]. Direct polycondensation of lactic acid is a low cost process to produce PLA; however it does not give high-molecular-weight polymer because of difficulty of removal of water from the polymerization reaction[8]. Furthermore, during the polycondensation, the molecular weight of poly(lactic acid) is reduced by depolymerization and other side reactions at higher temperature where the lactide is formed. High molecular weight Poly(lactic acid) can also be produced by the ring opening polymerization of lactide, which is the dilactone of lactic acid [9-11] and synthesized from thermal cracking of low molecular weight PLA at higher temperature and low pressure. This process requires high energy and time. Chain coupling of low molecular weight PLA is a better alternative to obtained high molecular weight polymer [12-14]. In the present work, initially the lactic acid was condensation-polymerized to a low-molecular-weight prepolymer, which contains one kind of end group. In the second step, the molecular weight is raised by joining prepolymer chains together using difunctional substances, such as diisocyanates, as the chain extenders [14-16]. Resulting polymer was investigated by using various techniques.

Experimental

Material

Lactic acid was purchased from Merck 90% aqueous solution, ethylene glycol from Thomas Baker, tin octoate from Sigma Aldrich, chloroform from Thomas Baker was distilled over calcium chloride before used and MDI from BASF Chemicals was used as received.

Characterization

Viscosity of the polymers were determined using Ubbelohde viscometer using 2% solution in chloroform on thermostatically controlled water bath with accuracy of ±0.1^{o} C

Dynamic mechanical analysis (DMA) was performed at Perkin Elmer DMA 8000 in single cantilever mode at 1 Hz of frequency and displacement of 0.05 mm at heating rate of 2^{o}K/min.

FTIR was performed on Nicolet 380 Attenuated Total Reflectance-Fourier transform infrared (ATR-FTIR) in reflectance mode using polymer bar.

Synthesis of Hydroxyl terminated poly (lactic acid) (PLAol)

Polymerization was carried out in 150 ml round bottom flask with stirrer and thermostatic controller oil bath. Water was removed from the lactic acid aqueous solution at 100° C under reduced pressure for 2 hrs (Fig. 1). Lactic acid based telechelic prepolymer was synthesized using ethylene glycol as diol and tin octoate as catalyst at 200° C under the continuous flow of nitrogen for 48 hrs. The hydroxyl value of the resulting polymer was determined as 4 by titrimetric method [17, 18].

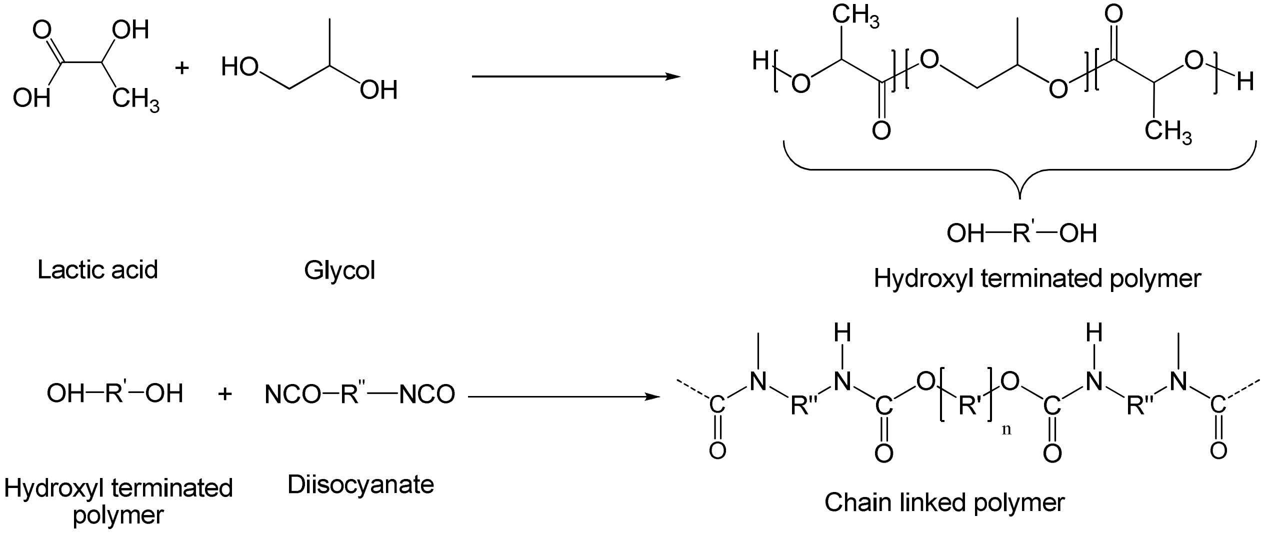

Figure 1 : Synthesis of chain extended poly(lactic acid)

Synthesis of poly (lactic acid) urethane (PLAU)

Polymerization of polyether ester urethane was carried out in 150 ml round bottom flask with stirrer (Fig. 1) and thermostatic controller over oil bath in melt under nitrogen blanket using PLAol with MDI and 20% (w/w of PALol) polypropylene glycol.

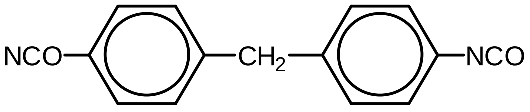

Figure 2: Methylen diphenyldiisocyanate (MDI)

Ratio of PLAol/diisocyanate was kept 1:1 (mole) to get linear thermoplastic polyester ether urethane. The amount of MDI was calculated on theoretical basis of hydroxyl number and isocyante content of MDI determined by titrimetric method (Fig. 2).

Result and Discussion

PLAol obtained was of low molecular weight as it possesses low viscosity, having lower Tg and lower strength. However PLAU obtained have higher Tg, higher strength and was yellowish in color.

Characterization

Viscosity of the PLAol and PLAU was obtained to be 1.188 and 1.582 respectively. The Intrinsic viscosity was evaluated using formula given in equation 1[18-20].

$$[\eta] = \frac{\sqrt{2\left(\frac{t}{t_0} - 1 - \ln\frac{t}{t_0}\right)}}{C}$$

………Equation 1

Where t and t_0 is the flow time taken for polymer solution and solvent respectively and C is the concentration (g/cc) of solution.

Table 1 : Viscosity of PLAol and PLAU

	Relative Viscosity (ηrel)	Specific Viscosity (ηsp)	Reduced Viscosity (ηred)	Intrinsic Viscosity [η]
PLAol	1.188	0.188	0.094	0.088
PLAU	1.582	0.582	0.291	0.259

An increase in the viscosity of polymer, after chain linking, indicates the increase in the molecular weight of resulting polymer (Table 1). Since the [η] is directly proportional to the molecular weight of the polymer [15] by Mark Houwink equation,

$$[\eta] = k\overline{M}_v^a$$

………**Equation 2**

Where k and a are constants depends on solvent, polymer and conditions
Therefore

$$[\eta] \quad \alpha \quad \overline{M}_v$$

………**Equation 3**

FTIR results for PLAol shows characteristic peaks at 3495^{-1} (OH stretching) and 1745 cm^{-1} (C=O stretching), 1089 for -O- , methylene absorption (CH_2, CH_3) at 2971cm^{-1} (Fig. 3). FTIR of PLAU peak at 3495 cm^{-1} for –OH is replaced by Peak at 3350 cm^{-1} for -NH indicates the formation of polyurethane. However no peak was observed at 2300 cm^{-1} this indicates the complete conversion of diisocyante into urethane.

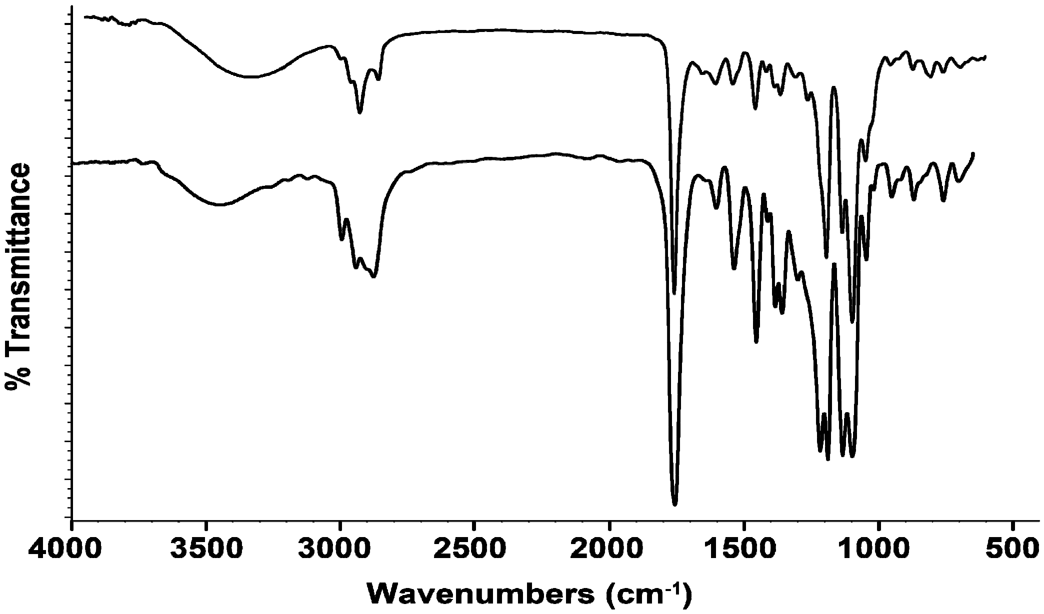

Figure 3 : FTIR spectra of PLAU and PLAol

Dynamic mechanical analysis is a powerful tool for the determination of Tg and thermo mechanical properties of the polymers. Samples for DMA were prepared by compression molding at 120°C.

Table 2: DMA results of PLAol and PLAU

	Tg	**Storage Modulus at -20°C (MPa)**	**Storage Modulus at 0°C (MPa)**
PLAol	34.18	480	417
PLAU	37.77	866	745

DMA results of chain extended polymer showed an increase in the glass transition temperature (Tg) along with the increase in storage modulus (figures 4 and 5). Tg was increased from 34.18 to 37.77° C and storage modulus increased from 480 MPa to 866 MPa at -20°C and 417 MPa to 7451 MPa at 0 °C (Table 2).

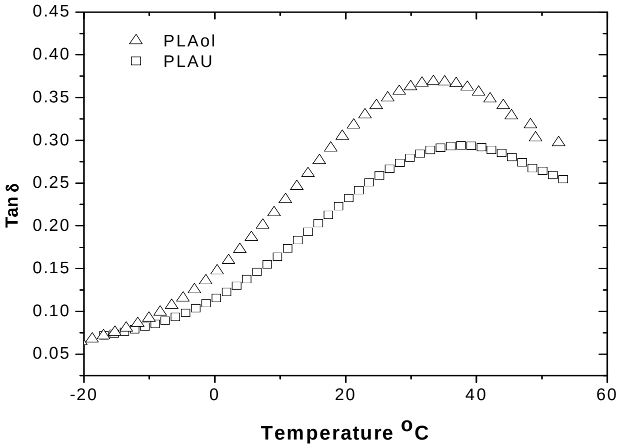

Figure 4 : Tan δ of PLAol and PLAU

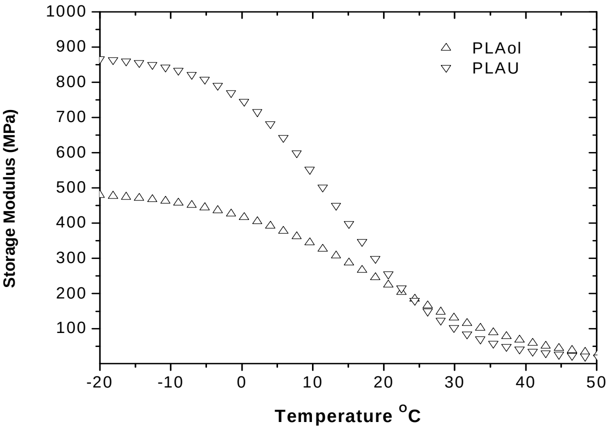

Figure 5 : Storage modulus of PLAol and PLAU

Conclusion

Chain coupling of PLA is an attractive method for the synthesis of high molecular weight PLA over other conventional lengthy methods. Chain coupling also offers the cost effectiveness, since it does not require sophisticated techniques and polymerization is possible a shorter time. Chain coupling of PLA result in increase in molecular weight along with higher glass transition temperature and storage modulus.

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