Synthesis, characterization and biodegradable studies of 1,3-propanediol based polyesters

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Abstract

A series of biodegradable polyesters were synthesized from dicarboxylic acids and 1,3-propanediol catalyzed by transestrification polycondensation reaction in the bulk. The structure, average molecular weights and physical properties of the resulting aliphatic polyesters were characterized by ^{1}H NMR, FT-IR, solution viscosity, GPC, DSC and TGA. Homopolyesters show higher degree of crystallinity, melting and thermal stability in comparison to copolyesters. The biodegradability of the polyesters was determined by monitoring the normalized weight loss of polyester films with time in phosphate buffer (pH 7.2) without and with *Rhizopus delemar* lipase at 37 °C. The rate of enzymatic degradation of homopolyesters follows the path PPSu > PPAd > PPSe. PPSe did not show significant weight loss in presence of enzyme which may be due to its highest degree of crystallinity and melting point compared to the PPSu, PPAd and copolyesters. In the soil burial degradation polyester sample showed severe surface degradation by the attack of microorganism.
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1. Introduction

In recent years, biodegradable polymers have received considerable attention because of large number of mass production applications, in packaging, paper coating, fibers, films and other disposable articles, as well as in biomedical applications, such as resorbable surgical sutures, implants, and controlled drug delivery systems [1–5]. Among the biodegradable polymers, aliphatic polyesters have leading position for favorable features that their hydrolytic and/or enzymatic degradation products can be naturally metabolized into non-toxic substances as they are readily susceptible to biological attack [6].

Over the past few years, most of the effort in making aliphatic polyesters has been focused on 1,4-butandiol and very little emphasis has been given to 1,3-propanediol. This is due to the non-availability of sufficient quantity and quality of 1,3-propanediol. In recent years, more attractive processes have been developed [7–10] for the production of commercial high quality 1,3-propanediol derived from renewable resources with low cost. 1,3-Propanediol based polyesters are expected to be different from 1,4-butandiol, because of different interaction between the diol and dibasic acid. Polyesters based on 1,3-propanediol are most promising in terms of biodegradability due to the presence of odd number of methylene units [11]. Thus, we strongly feel the need to explore the possibility of using 1,3-propanediol for synthesis of polyesters. In our earlier communication [12] we reported the synthesis of 1,3-propanediol based polyesters without catalyst. The product obtained shows low molecular weight with low T_m which narrows the field for their practical applications.

In the present article, we describe the synthesis of a series of aliphatic homopolyesters and copolyesters from 1,3-propanediol and some dibasic acids by polycondensation transesterification reaction in the bulk, in presence of

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Ti(OBu)$_4$ as catalyst. The synthesized polyesters were characterized by solubility, spectroscopic, molecular, solution viscosity, and thermal analysis. The biodegradation of polyester films was studied using *Rhizopus delemar* lipase in phosphate buffer and soil burial test.

2. Experimental

2.1. Materials

1,3-Propanediol (98%), adipic acid (99%), succinic acid (99.5%), sebacic acid (99%), tetra-*n*-butyl titanate Ti(OBu)$_4$ (97%), Na$_2$HPO$_4$ (99.9%), phosphate buffer (pH 7.2) and *R. delemar* lipase (Fluka, 0.73 U/mg) were purchased from the Sigma−Aldrich Chemical Co. Methanol, chloroform, acetone, 1-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethylsulphoxide (DMSO), etc., were purchased from E. Merck. All the reagents were used as received without further purification.

2.2. Synthesis of polyesters

Aliphatic polyesters poly(1,3-propylene adipate) PPAd, poly(1,3-propylene succinate) PPSu, poly(1,3-propylene sebacate) PPSe as well as their copolyesters poly(1,3-propylene sebacate-*co*-1,3-propylene adipate)s PPSe-*co*-PPAd, poly(1,3-propylene sebacate-*co*-1,3-propylene succinate)s PPSe-*co*-PPSu, poly(1,3-propylene adipate-*co*-1,3-propylene succinate)s PPAd-*co*-PPSu were synthesized [13−17] in the bulk by transesterification reaction in the presence of the catalyst Ti(OBu)$_4$. The reactor was a three necked flask equipped with a magnetic stirrer, nitrogen inlet, a condenser and thermometer. The copolyester poly(1,3-propylene sebacate-*co*-1,3-propylene succinate) PPSe-*co*-PPSu75, was synthesized by charging sebacic acid (151.5 g, 0.75 mol), succinic acid (29.5 g, 0.25 mol), 1,3-propanediol (76.1 g, 1 mol) + 10% excess, and transesterification catalyst Ti(OBu)$_4$ (0.3 g, 0.882 mmol) into the reactor. The reaction mixture was purged with nitrogen and it was then heated at 170 °C for 5 h. The water formed during the reaction was distilled off. In the second phase of reaction, the reaction mixture was subsequently heated to final temperature 240 °C under reduced pressure (<1 Torr) for 1 h in order to distill off the traces of water. The obtained copolyester was dissolved in minimum amount of chloroform and re-precipitated with a 10-fold amount of ice-cold methanol with vigorous stirring. The reaction mixture was filtered, washed with methanol and the precipitate was then dried at 60 °C in vacuum oven for 24 h. The product obtained was a white solid and the yield is 95%. In a similar manner, the other copolyesters were synthesized by varying the mole percentage of comonomers.

2.3. Characterization of polyesters

The solubility of the polymers were performed by keeping 0.25 g of polyester in 50 ml solvent (water, chloroform, THF, DMSO, NMP, DMF, acetone, *n*-hexane and ethyl ether, ethyl acetate, ethanol, etc.) and the mixture was stirred for 30 min.

It was then kept for 4 h at room temperature (30 °C), the mixture was filtered through pre-weighed sintered-glass crucible (porosity 2 μm) and then the crucible was dried under vacuum to constant weight; from the weight of dissolved polymer the solubility was determined.

^{1}H NMR spectra were recorded by SAIF, IIT, Madras on JEOL GSX 400 NMR spectrometer operated at a frequency of 400 MHz. The polyester samples were dissolved in deuterated chloroform (CDCl$_3$), and tetramethylsilane was used as the reference standard. FT-IR spectra of polymers were recorded from JNARDDC, Nagpur on AVTAR-320, Nicolet instruments by KBr pellet technique. The FT-IR spectra of the degraded polyester samples were measured using a Perkin−Elmer FT-IR spectrophotometer at VNIT, Nagpur.

Average molecular weight and molecular weight distribution were determined by gel permeation chromatographic (GPC) analysis from SAIF, IIT, Powai, Mumbai. The instrument was equipped with a refractive index detector (RI) and PLGel 5 μm mixed-D type column. THF was used as mobile phase at a flow rate of 1 ml/min and polystyrene solution in THF as the calibration standard. Twenty microliters of a 1% polymer solution in THF was injected in all the runs. The number-average (M_n) and weight-average molecular weights (M_w) were calculated from the calibration curve.

Thermal analysis of original and degraded polyesters samples were conducted on a Mettler Toledo Differential scanning calorimetry (DSC)-822 analyzer and Perkin−Elmer, Pyris Diamond TG/DTA at SAIF, Cochin. DSC and TGA scans were recorded in the temperature range −50 to 450 °C and 28 to 600 °C, respectively, at a heating rate of 10 °C/min under nitrogen atmosphere. About 3 mg of polyester sample was taken for analysis. The melting temperature (T_m) was determined from the first scan as the temperature of the main peak in the DSC curves. The glass transition temperatures (T_g) were calculated from the DSC scans as the mid point of the heat capacity change [16].

2.4. Biodegradation studies

2.4.1. Film preparation

2.4.1.1. Hydraulic press method. In order to study the biodegradation of synthesized polyesters, homopolyester and copolyester films (thickness of 0.2 mm) were prepared in a hydraulic press [14] by pressing the polyester samples between two Teflon plates for a minute under a pressure of 1.5 ton/cm^2 below samples melting temperature. The pressed films were stored at 30 °C for one week in order to reach the equilibrium crystallinity.

2.4.1.2. Solution cast method. The homopolyester and copolyester films (thickness of 0.5 mm) were prepared by solution cast method [18,19]. Polyester sample (1.0 g) was dissolved in 10 ml of a chloroform/methanol (9/1) mixture. The solution was cast onto a Petri dish ($d = 8.5$ cm), the solvent was allowed to evaporate under atmospheric condition overnight. The obtained film was dried under vacuum at 30 °C for 2