SYNTHESIS AND CHARACTERIZATION OF POLYESTERS BASED ON TARTARIC ACID DERIVATIVES

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by

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Dedicated to my Parents

CERTIFICATE

This is to certify that the thesis entitled **'Synthesis and Characterization of Polyesters Based on Tartaric Acid Derivatives'** being submitted by **Mr. Sunil Dhamaniya** to the Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. Sunil Dhamaniya** has worked under my guidance and supervision and has fulfilled the requirements for the submission of his thesis, which to our knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any University or Institute for the award of any degree or diploma.

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ABSTRACT

Aliphatic polyesters, such as poly(lactide) (PLA), poly(glycolide) (PGA), poly(β-hydroxy butyrate) (PHB), poly(butylene succinate) (PBS) and poly(ε-caprolactone) (PCL) are well established biodegradable polymers and used in various biomedical and pharmaceutical applications. However, existing aliphatic polyesters are hydrophobic in nature and do not possess reactive sites, a practical limitation to their use in biomedical applications due to lack of desirable hydrophilicity and reactive pendant functional groups. Therefore, functional aliphatic polyesters with hydrophilic reactive pendant groups like hydroxyl, carboxyl and amino have attracted a great deal of interest as new biomaterials. The present work deals with the synthesis of novel aliphatic polyesters based on tartaric acid derivatives. Tartaric acid is a natural resource and the most striking feature is the presence of functional hydroxy groups, which provides its polyesters enhanced hydrophilicity, high degree of chemical functionality and tunable biodegradability as compared to the existing aliphatic polyesters such as PLA, PGA, and PCL.

In the first section of this work aliphatic polyesters were synthesized from protected L-tartaric acid derivatives with various alkane diols and diacids using step polycondensation method. Two classes of polyesters were synthesized and characterized, the first by polycondensation of dimethyl 2,3-*O*-isopropylidene tartrate with various alkanediols, and the second by reaction of 2,3-*O*-isopropylidene threitol with various diacid chlorides. Acid catalyzed deprotection of isopropylidene groups gave well defined polyesters having pendant hydroxyl functional groups regularly distributed along the polymer chain. The number average molecular weights (M_n) of the polymers were found to vary in the range of 2.3 - 15.7 × 10^3 $gmol^{-1}$. Differential scanning calorimetry (DSC) analysis showed the glass transition temperatures (T_g) of

the polyesters varied from -36.1 °C to 17.9 °C on varying the chain length. Furthermore, the hydrolytic and microbial degradation studies were conducted to evaluate the biodegradability of synthesized polyesters.

In the next section, the syntheses of a series of aliphatic copolyesters based on tartaric acid derivatives are reported. The hydroxyl groups of the tartaric acid were protected and copolyesters were synthesized by taking different feed molar ratio of dimethyl 2,3-*O*-isopropylidene tartarate and dimethyl succinate with 1,6-hexanediol. Then a series of copolyesters were synthesized by taking equal feed molar ratio of dimethyl 2,3-*O*-isopropylidene tartrate and dimethyl succinate or dimethyl adipate with different alkane diols. The acetal protecting groups were then selectively hydrolyzed to prepare a new series of copolyesters with pendant hydroxyl groups along the copolymer chain. The hydrolytic degradation studies of copolyesters were carried out to determine the degradability of synthesized copolyesters.

The polyesters synthesized by step growth polymerization have showed characteristic physical and thermal properties, however they did not possess sufficient molecular weight to examine their mechanical properties. Therefore, in the next section of this work a chain-coupling method was employed to increase the molecular weights of polyesters and a series of chain-coupled polyesters based on tartaric acid were prepared. In the first step tartaric acid based hydroxyl terminated polyesters were prepared and then in the second step hexamethylene diisocyanate was used to synthesize a series of chain-coupled polyesters. The number average molecular weights (M_n) of polyesters were found to vary in the range of $4.8\text{-}28.1\times 10^3$ g/mol. DSC analysis showed the T_g of the polyesters varied from -36.8 °C to -15.0 °C on varying the chain length. The thermo-mechanical properties of the synthesized chain-coupled polyesters were measured by DMA. Moreover, the microbial degradation studies were conducted to evaluate the biodegradability of the synthesized polyesters.

In the last section of this study, the syntheses of a series of ABA type triblock copolymers PLA-*b*-PHIT-*b*-PLA based on renewable monomers L-tartaric acid and L-lactide are described and the chain length of the PLA block has been systematically varied to investigate the effect of the chain length on the properties of the triblock copolymers. In the first step, tartaric acid based hydroxyl terminated PHIT has been prepared by step-growth polymerization and it was used as a macroinitiator in the second step for the tin(II) 2-ethylhexanoate catalyzed ring opening polymerization of L-lactide. Solution cast films of these triblock copolymers turned out to be brittle in nature and to overcome this, ε-caprolactone was copolymerized with lactide to generate a separate series of triblock copolymers [PLA-*ran*-PCL]-*b*-PHIT-*b*-[PLA-*ran*-PCL] and characterized. In addition, the influence of block composition on structural, thermal and mechanical properties was systematically investigated.

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