SYNTHESIS AND STUDIES ON AROMATIC COPOLYESTER WITH ANTICANCER ACTIVITY DERIVED FROM 4,4'-DIHYDROXYBIPHENYL AND 3,5-DIHYDROXYTOLUENE

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ABSTRACT

In this investigation, a new wholly aromatic random copolyester containing 4,4'-dihydroxybiphenyl, 3,5-dihydroxytoluene and Isophthaloyl chloride was synthesized using the solution polycondensation methodology in the mole ratio 2:1:3 and its solubility along with inherent viscosity were determined. The chemical structure of the copolyester was established by traditional spectroscopic techniques. The physical parameters of the polyester were studied employing WAXD studies and the thermal stability along with phase transitions were investigated employing TGA and DSC data. The morphological features in the polyester were probed using Scanning Electron Microscopy. The anticancer activity of copolyester was verified using HeLa (Cervical carcinoma) cell line employing MTT assay. **Keywords:** 3,5-dihydroxytoluene, 4,4'-dihydroxybiphenyl, MTT, Scanning Electron Microscopy, Copolyester, Polycondensation

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INTRODUCTION

Aromatic polyesters are renowned for their notable thermal performance and good processability.¹⁻³ They possess exceptional thermal and mechanical properties and are widely exploited as engineering plastics. Lately, numerous research articles have focused on creating high-performance macromolecules involving Isophthaloyl group in the polymer backbone with a wide variety of aromatic diols as they possess phenomenal properties providing a wide scope of utilizations.^{4,5} In the last few decades, it has drawn much attention from researchers to produce new copolyesters containing isophthalate and terephthalate units which have been described to become less likely to crystallizable perfectly coupled with dropping melting temperatures due to the association with isophthalate units.⁶ Modification in tensile strength, thermal and mechanical properties due to induction of isophthalate portions into the backbone of terephthalate polyesters has been reported by Karayannidis, G.P. *et al.*⁷ Exceedingly sluggish crystallizing behavior leading to the development of lamellar crystals owing to lower nuclei density has been observed in entirely bio-based butylene isophthalate polyester.⁸ Recently, an ester-ester exchange reaction between poly (1,12-dodecamethylene isophthalate) and poly(ε-caprolactone) leading to the formation of a copolymer at elevated temperature has been documented.⁹ The incorporation of dimethyl isophthalate units caused improvement in glass transition temperature and augmented the thermal stability, optical characteristics and the gas barrier property in high molar mass butylene carbonate-co-isophthalate polyesters.¹⁰ The thermal changes and melt birefringence property in thermotropic copolyesters prepared by melt polycondensation based on 4,4'-biphenol and bisphenol A has been explored by Tsai, H. B. *et al.*¹¹ Effects of flexible and rigid spacers in the formation of mesophases among polyesters based on 4,4'-dihydroxy biphenyl have been extensively studied by Wale, A. *et al.*¹² Kim, K. H. *et al* successfully studied the effects of attached quaternary salt structure and the effect of polymer catalysts on aromatic polyesters containing Isophthaloyl chloride and Diphenolic acid in the polycondensation reaction in aqueous and organic phases.¹³ Interfacial polymerization involving phase-transfer reaction of biphenyl derivative and Isophthaloyl chloride resulted in amorphous aromatic polyesters connected to biphenyl units in the side chain whose early degradation

temperatures were observed around 450°C.¹⁴ Innovative polyesters have been obtained from monomers containing substituted benzylidene cyclopentanone units with Isophthaloyl and Terephthaloyl dichlorides using interfacial polycondensation technique by Abd-Alla, M. A. *et al.*¹⁵ High-temperature solution methodology has been utilized to obtain novel polyarylates, which are thermally stable up to 350°C derived from hydroxy diphenylethylene derivatives along with aryl dicarboxylic acid chlorides by Watanabe, S. *et al.*¹⁶ Series of aromatic polyesters have been synthesized exploiting the solution polycondensation route involving Isophthalic acid with monomers containing dicyanovinyl substituents.¹⁷ Relatively new aromatic copolyesters synthesized from 5-(propargyloxy) isophthaloyl chloride and bisphenol A have displayed 10% weight loss around 400°C validating their superior thermal stability.¹⁸ Analogy between polyesters derived from Terephthaloyl dichloride and Isophthaloyl dichloride along with hindered Biphenols and bulky substituent bearing Hydroquinones has revealed that polyesters obtained from Isophthaloyl dichloride exhibit better solubility and lower glass transition temperatures.¹⁹ High molecular weight crystalline aromatic copolyesters obtained from bisphenols containing pendant, Quinoxaline moiety by polymerization with Isophthaloyl chloride are reported to be thermally stable.²⁰ With this knowledge in mind, in this paper, we synthesized a novel copolyester containing 4,4'-dihydroxybiphenyl and 3,5-dihydroxytoluene in the main chain along with Isophthalate units and analyzed the polymer highlighting the thermal stability with the aid of Thermogravimetric analysis and also its anticancer activity via MTT assay.

EXPERIMENTAL

Material and Methods

Merck samples of Isophthaloyl chloride, 3,5-dihydroxytoluene and 4,4'-dihydroxybiphenyl (Avra synthesis Private Limited) were used. AnalaR grade chemicals and solvents were employed in work. A viscosity study was done using Ubbelohde viscometer. Electronic spectrum was recorded in Shimadzu-UV-160A spectrophotometer utilizing propanone as solvent and FTIR spectrum of the polyester was obtained (Bruker FTIR Spectrometer) using KBr pellets. Jeol 500 spectrometer employing CDCl₃ as solvent was utilized to record ¹H NMR spectrum. Thermogravimetric analysis was performed in Nitrogen environment employing SDT Q600 thermal analyzer and DSC thermogram of the polyester was recorded using NETZSCH STA449F3 Jupiter instrument. Wide Angle X-ray Diffraction studies were done by means of X'Pert Pro PW 3050 diffractometer (Cu Kα, λ= 1.5406 Å), 2θ ranging from 10° to 80°. SEM Micrographs were obtained using Tescan Vega 3 (30 kV - accelerating voltage). Anti-proliferative studies of the copolyester was investigated using HeLa cell line (MTT method).

Procedure for Synthesis of Copolyester (PTBI)

Poly(3-oxy-5-methylphenyl(4'-oxy-[1,1'-biphenyl]-4-yl)isophthalate was prepared by reacting 4,4'-dihydroxy biphenyl (3.724g, 0.02 mol) with 3,5-dihydroxy toluene (1.241g, 0.01 mol) using about 150mL of 1,2-dichlorobenzene as solvent in to which Isophthaloyl chloride (6.09g, 0.03 mol) was added for solution polycondensation process. The detailed procedure of preparation of polyesters has been reported previously.²¹ The contents were agitated for about 50h at 150°C in Nitrogen atmosphere and cooled, poured into about 300 mL of petroleum ether and kept overnight in a refrigerator followed by filtration; this procedure adopted is similar to earlier report.²² The crude polyester was primarily rinsed with double distilled water, then in Propanone before finally pouring into distilled water. The resultant mixture was ultimately vaporized and dried in a vacuum over Phosphorous pentoxide to obtain the pure polyester with a yield of around 70%. This polyester was prepared in appropriate yield under the reaction conditions, which was better than the other polymers prepared under various experimental conditions, which are not discussed here. The molecular structures and the scheme of preparation are illustrated (Scheme- 1).

RESULTS AND DISCUSSION

Inherent Viscosity and Solubility of the Copolyester

The copolyester was found to be freely soluble in Propanone and also soluble in Chloroform, DMF and o-Chloro Phenol. This may be due to the interactions of the polar solvents with the ester linkages in the polyester. The polymer was found to be almost similar in solubility in DMSO, Methanol and THF which

may be due to secondary bonding interactions between solvent and the polymer. The conformation of biphenyl aromatic units influencing inter chain interactions and disrupting the orderliness of the substituents along the polyester backbone is reported in literature.²³ The viscosity (η_{inh}) of the polymer was assessed using relative viscosity values derived by comparing the flow time of the polyester solution along with solvent (o-Chlorophenol) using Ubbelohde viscometer (concentration = 0.1g/dL at 30°C) was found to be 0.31 dL/g. Ping, Z. *et al* have reported lower viscosity values for aromatic polyesters prepared using Isophthaloyl chloride and esters of diphenolic acid.²⁴

Spectral Studies

UV-Visible Spectrum

The electronic absorption spectroscopy is principally operated to investigate the chromophoric moieties or the extended conjugation present in the aromatic system of polymers.²⁵ The UV-Visible electronic spectrum of PTBI recorded with a concentration of 10^{-5} M in Propanone as solvent depicted in Fig.-1 shows a broadband around 280 nm, which is ascribed to the aromatic chromophores in the polyester.

Fig.-1: UV-Visible Spectrum of PTBI

Fig.-2: FTIR Spectrum of PTBI

FTIR Spectrum

The repeat structure and the functional group present in the polyester were confirmed by FTIR spectral data. Figure 2 shows the characteristic FTIR spectrum of the polyester PTBI. Some characteristic absorptions appeared in the spectrum, such as C-H stretching near 2900 cm^{-1} .²⁶ The copolyester shows distinctive carbonyl stretching absorption bands of the ester group near 1760 cm^{-1} , substantiating the presence of ester linkages in the polyester. The band near 1230 cm^{-1} (ester C-O stretching) also validates the presence of ester moieties in the polymer sample, as reported by Kandaswamy, N.²⁷ The broad detectable band around 3469 cm^{-1} , due to hydroxyl group stretching vibration, is also observed.²⁸ Bands occurring below 866 cm^{-1} reveal C-H bending vibrations and the aromatic ring stretch is illustrated by absorption at 1608 cm^{-1} and 1496 cm^{-1} in the FTIR spectrum.

¹H NMR Spectrum

The structure of the prepared polyester backbone was confirmed by ¹H-NMR spectrum (Fig.-3) employing CDCl₃ as solvent. The signals of methyl protons of 3,5-dihydroxytoluene units in the polyester sequence were assigned to the resonances in the range 1.1 to 2.6 ppm.²⁹ The resonances ranging from 6.8 to 9.2 ppm were attributed to the aryl protons of all the monomers involved in the polymer structure.³⁰

Fig.-3: ¹H Spectrum of PTBI

Fig.-4: TGA Thermogram of PTBI

Thermogravimetric Analysis (TGA)

It is observed that copolyesters containing aliphatic groups in the main chain are thermally less stable compared to those with aromatic groups in the backbone of the polymer.³¹ Thermal studies on the copolyester were performed via Thermogravimetric analysis (TGA) in N₂ environment when the sample was subjected to heating starting from 60 to 800°C (heating rate of 20°Cmin⁻¹) is depicted in Figure 4. The polymer shows initial decomposition temperature at 350°C and char yield was found to be at 600°C. From this, it was shown that the synthesized polyester was found to be thermally stable at 350°C, which could be due to the aromatic rings present in the polymeric chain as indicated by similar studies reported in the literature for thermal decomposition of polyesters.^{32,33}

Differential Scanning Calorimetry (DSC)

The thermogram (Fig.-5) reveals the commencement of T_g at 80.9°C and also multiple peaks are observed at 269.7°C, 292.7°C and 330.0°C with enthalpy of melting being 18.07 J/g. Aromatic polyesters comprising of suspended carboxyl groups derived from Isophthaloyl chloride have been reported to possess glass transition temperatures in the range 79 to 96°C which is in harmony with the results obtained in the DSC thermogram.³⁴ Simitzis, J. *et al* have observed that the parameters achieved from the results in the DSC scan vary with the nature and proportion of the comonomers in the specific polyesters, presence or absence of catalyst during the polyesterification process.³⁵ Reports on aromatic polyesters derived from Terephthaloyl chloride possessing rigid p-phenylene groups displayed higher values of T_g compared to those resulting from Isophthaloyl chloride containing comparatively less rigid, the symmetric orientation of the m-phenylene groups in the polymer chain are available in literature.²¹

Fig.-5: DSC Thermogram of PTBI

Fig.-6: X-ray Diffraction Pattern of PTBI

Wide-angle X-ray Diffraction (WAXD)

The WAXD powder pattern of copolyester PTBI, presented in Figure 6, indicates the polyester to be semi-crystalline in nature, as reported by Jadhav, S. A. *et al*, among polyesters synthesized from Isophthaloyl chloride.³⁶ This may be due to the occurrence of polar ester moieties influencing the crystalline nature of the copolyester.³⁷ The polyester sample revealed a prominent reflection with maxima at $2\theta=19.2569^\circ$, height (cts) 222.08, corresponding to d value 4.60927 Å. Peaks at 2θ values ranging from 23.7923 to 28.1368 with interplanar spacing in the range 3.73990 to 3.17154 Å were also observed in the copolyester.

Scanning Electron Microscopy (SEM)

In the literature, it has been reported that the SEM pictures can reveal vital information regarding the morphology and crystal formations between the fibers in aromatic polyesters.³⁸ The comparison of the SEM micrographs of the copolyester PTBI (Fig.-7) with the reports on aromatic polyesters by Jasinski, W. *et al* show resemblances in the presence of nodules and holes.³⁹ The fracture texture and cracks which are apparent throughout the surface of the polyester sample are analogous to previous reports in the literature.⁴⁰

Fig.-7: SEM Micrographs of PTBI

Anticancer Study

MTT Assay

Antiproliferative effects and studies on cytotoxicity of aliphatic copolyesters are found in the literature.^{41,42} The MTT analysis on cytotoxicity using HeLa cell viability based on products formed from polyester hydrolysis has been analyzed in detail by Kim, M. N. *et al*.⁴³ In the present study on the aromatic copolyester, PTBI was analyzed employing HeLa (Cervical carcinoma) cell line following MTT assay with the routine procedure, the cells were seeded in 96 wells were cultured at 37°C along with 5% CO₂. The given polyester samples in DMSO solution were diluted to 100 to 50 µg/mL with DMEM and were added to every culture well at a concentration of 50 µM and incubated for 24h. The supernatant was separated and the residues were dissolved in DMSO after the addition of 20 µl of MTT (5 mg/mL) to each culture well. Subsequently, the reduction of MTT was computed by measuring the absorbance at 570 nm. The formula used to estimate the % of viable cells was:

$$\% \text{ Cell Viability} = [\text{Treated Cells Absorbance} / \text{Untreated Cells Absorbance}] \times 100$$

Fig.-8: Cell Viability of PTBI

In HeLa cell line, 50, 60 $\mu\text{g/mL}$ concentrations revealed 75 to 80% cell viability, whereas 70 $\mu\text{g/mL}$ concentration resulted in the percentage of cell viability ranging from 65 to 75% as displayed in Figure 8. The other concentrations of 80, 90 and 100 $\mu\text{g/mL}$ revealed cell viability ranging from 90 to 125%. The polyester exhibited increased cell viability boosted by increment in concentration except for the concentration, 70 $\mu\text{g/mL}$, which may act as a potential drug against the HeLa cell line.

CONCLUSION

The aromatic polyester was synthesized from 4,4'-dihydroxybiphenyl, 3,5-dihydroxytoluene and Isophthaloyl chloride employing a well-established, conventional polycondensation procedure. The copolyester showed better solubility in many well-known organic solvents such as Propanone and Chloroform, which is requisite for its diverse applications. The chemical structure of the recurring units in the synthesized polyester was ratified on the basis of standard spectroscopic techniques, namely UV-Visible, FTIR and Proton Nuclear Magnetic Resonance. The thermal properties were summarized on the basis of TGA, indicating superior thermal stability up to 600°C and DSC thermograms revealing T_g at 80.9°C and T_m around 292.7°C. From the WAXD study, it is disclosed that PTBI is semi-crystalline in nature, as expected based on earlier reports. The SEM micrographs revealed heterogeneous morphology with nodules and holes. The anticancer efficacy studies suggest that the copolyester PTBI displays potent anticancer activity at a concentration of 70 $\mu\text{g/mL}$. The ratio of various diol concentrations in the polymer structure may influence the Anti-cancer activity. The work along this direction is in progress.

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