



**RESEARCH ARTICLE**

**SYNTHESIS AND CHARACTERIZATION OF CERTAIN PHOTO CROSSLINKABLE RANDOM COPOLYESTERS AND STUDY OF THEIR BLEND NANOFIBERS**

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**ABSTRACT**

Novel random photocrosslinkable copolyesters with Oxygen Bridge were prepared from 4, 4'-oxybis and 1, 6-hexanediol with 1, 8-dihydroxyanthraquinone/1, 4-cyclohexanediol/4, 4'-dihydroxydiphenyl by direct polycondensation in pyridine/LiCl solution (DPCP) was employed as the condensation agent. The glass transition temperature of these polymers was determined by differential scanning calorimetry (DSC). Spectral studies such as <sup>1</sup>H, <sup>13</sup>C NMR and FTIR gave an insight about the microstructure and monomer composition. Resulting polyesters were blended with polyvinylchloride (PVC)/ tetrahydrofuran (THF) in 10% (w/w) ratio. Nanofibers obtained by electrospinning process were subjected to UV irradiation to investigate on the photocrosslinkability by observing the changes in morphology of the fibers by scanning electron microscopy (SEM). The photocrosslinkability of these polymer solutions was established with UV irradiation / UV spectroscopy. These polyesters and their blend nanofibers could be used in photolithographic devices and photosensitizers.

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**INTRODUCTION**

The development of a new polymer blend is generally driven by the need to design a substance with properties not exhibited by a simple material. Blending of common polymers to produce new substances has become very common and often effective and beneficial in many aspects (Paul, *et. al.*, 1999, Utracti, 1989, Paul, *et. al.*, 1979). Recent uptrend in polymer blend research leading to synthesis, characterization and applications of nanosystems such as nanoparticles, nanofibers and nanoplates (Cynthia, *et. al.*, 2011) is astounding. Polymer blend nanofibers are potential candidates for a number of applications in medicine, biotechnology and engineering because of their unique features apart from large surface area to volume ratio and unique nanometerscale architecture.

Photocrosslinkable polymers have attracted considerable attention in the research field because of their interesting mechanical, electrical and optical properties. These polymers contain photocrosslinkable moieties either in the main chain or as a pendant group in the polymer backbone. The photocrosslinkability of the polymers is due to the presence of photocrosslinkable / photosensitive moieties like azopolyesters (Acinerno, *et. al.*, 2000), arylidene esters (Kannan and Murugavel, 1999), arylidene ketones, siloxanes (Racles, *et. al.*, 2003), cinnamate esters (Kawatsuki, *et. al.*, 1998), and acrylate esters (Hageman, 1999) in the polymer backbone. Photocrosslinkable polymers find potential applications in the preparation of photocurable coating, photocrosslinked hydrogels, optical lithographic materials, photosensitizers, photoresists, photorefractive materials (Gangadhara and Kishore, 1993) and information storage devices. Photolinked polymethyl

(methacrylate) surface coatings based on poly (ethyleneglycol) have been commercially used as contact lens materials. Polymers having photodimerizable groups find applications in immobilization of enzymes (Koch, *et. al.*, 1989, Wong, 1993, Chang and Nam, 2001, O' Neill and Kelly, 2000, Hanemann, *et. al.*, 1995, Saminathan and Pillai, 2000).

The primary concern in this work involves synthesis and characterisation of novel random photocrosslinkable polyesters containing oxygen bridge moiety in the main chain and study of PVC/polyester blend nanofibers. The polyesters were synthesized by polycondensing diacid 4, 4'-oxybis (benzoic acid) with 1,6-hexanediol and three different diols using diphenylchlorophosphate (DPCP) as the condensation agent in pyridine medium. The advantage of this method was the mild experimental conditions for synthesis with the temperature of 120<sup>o</sup> C. The photoreactivity of the fibers and polymer solutions were studied by UV irradiation experiments followed by UV/SEM analysis.

**MATERIALS AND METHODS**

**Materials**

Pyridine (Merck, 99% pure) was refluxed over potassiumhydroxide and distilled (b.p: 115<sup>o</sup>C). Lithium chloride anhydrous (Aldrich, Analar) was dried in vacuum. Methanol (b.p. 65<sup>o</sup>C) was purified by refluxing over quicklime and distilled before use. 4,4'-oxybis(benzoic acid), 1,6-hexanediol, 1,8-dihydroxyanthraquinone, 1,4-cyclohexanediol, 4,4'-dihydroxydiphenyl, THF, diphenylchlorophosphate (DPCP) and PVC were purchased from Aldrich Chemicals and used without further purification.

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### Synthesis of copolyesters

The polymers (Table1) were prepared by direct polycondensation of two diols and one dicarboxylic acid in the respective mole ratio 1:1:2 using DPCP in pyridine (Chen, *et. al.*, 1995, Sun, *et. al.*, 2000, Higashi, *et. al.*, 1983).

#### A typical procedure for the synthesis of random copolyester OHDA

The polymers (Table.1) were prepared by direct polycondensation by the procedure similar to the one given below. To a four necked 250 ml round bottomed flask fitted with a condenser, thermometer, mechanical stirrer and an oil bath, 1.2911g (5mmol) of OBBA, 10 ml pyridine and 2.5ml (12mmol) DPCP were added. After stirring for 20 min, 0.4250 g (10 mmol) of LiCl in 10 ml pyridine was added and stirring was continued at room temperature for 30 min. The reaction mixture was slowly heated and maintained at 120°C for 20 min. To this mixture, 0.295g (2.5 mmol) of diol HD in 5 ml pyridine and 0.6005g (2.5 mmol) of diol DHA in 5 ml pyridine were added drop wise simultaneously at 120 °C for a period of 20 min and the whole solution was further stirred under the same condition for 3hr. The solution was cooled to room temperature and poured into 500 ml water. The product was filtered, washed with hot methanol and dried in vacuum oven at 50° C.

#### Preparation of polymer blend and nanofiber by electrospinning

Blending the synthesized copolyester with PVC was carried out by taking 5 ml of THF in 10 ml closed container with pellet in which 0.6g of polyvinylchloride was added and stirred for 15 min and then 0.2 g of polyester was added and stirring continued for 20 min. The solution was removed and placed in an ultrasonicator. The ultrasonicator was run to get homogeneous mixture of sample solution. A positive voltage was applied to the polymer blend solution through the needle attached to the syringe containing the solution. The solution jet was formed by electrostatic force, when the electrical potential increased to 22 KV. The flow rate of the solution was set at 0.4 ml/h, which was adjusted by computer controlled syringe pump. The distance between the needle tip and the collector was maintained at 10cm and the drum collector rotation speed around 1800 rpm. The copolyester/PVC nanofibers in a nonwoven form were collected on an aluminium foil.

#### Characterization of random copolyesters and polymer blend nanofibers

Infrared spectra were recorded by Perkin Elmer FT-IR 240-c Spectrophotometer using KBr pellet from 450 cm<sup>-1</sup> to 4500 cm<sup>-1</sup>. The solubility of the polymers was determined using 0.005 g of the polymer in 1 ml of the solvent. DSC thermograms were recorded at the scan rate of 10°C/min on a DSC Q200 V23.10 Build 79 (Universal V4.4A TA Instruments) under nitrogen atmosphere. High resolution <sup>1</sup>H NMR spectra were recorded on a Jeol FT-NMR AL 300MHz spectrometer operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C nucleus in DMSO-d<sub>6</sub> solvent and with TMS as internal reference. UV spectra were recorded using UV-VIS Spectrophotometer (Elico SL 159). The morphology of the polymer blend nanofibers was investigated by scanning electron microscopy (SEM) using Hitachi S-3400 SEM instrument. Photocrosslinking studies were carried out by UV irradiation on polymer blend nanofibers and changes in

morphology were investigated by SEM analysis. Further investigation of this study was established by recording UV-Visible spectra of the copolymer solution in THF at regular time intervals.

## RESULTS AND DISCUSSION

All the polyesters synthesized had common monomers, namely 4,4'-oxybis (benzoic-acid) and 1,6-hexanediol. The other monomer diol was varied. The diacid was an ethereal one possessing an oxygen bridge in the middle which inculcates a bent structure to the polymer chain. The presence of ether group in the main chain of the polyester enhances the solubility in organic solvents and hence eases processing (Bhowmik, *et. al.*, 1996). 1, 6-Hexanediol is one of the most important chain extender which enhances flexural and chemical resistance properties of the polymer (Gum, *et. al.*, 1992).

This method of solution polymerization using DPCP required lesser time duration under mild conditions. This method also avoided the preparation of acid chloride. The yield was also observed to be quite high. The successful synthesis of novel oxygen bridging copolyesters demonstrated the wide applicability of this method.

#### Spectral characterization

##### FT-IR spectral analysis

The FT-IR spectra of the random copolyesters OHDA, OHCH and OHDP were taken and a representative spectrum is exposed in Fig. 1. For OHDA: 2934(aliphatic), 1717(ester

**Table 1** Polymer codes and monomers used in the synthesis of random copolyesters

OHDA (63%)	4,4'-oxybis(benzoic acid)(OBBA)	1,6-hexanediol(HD)	1,8-dihydroxy anthraquinone (DHA)
OHCH (99%)	4,4'-oxybis(benzoic acid)(OBBA)	1,6-hexanediol(HD)	1,4-cyclohexanedio l(CHD)
OHDP (74%)	4,4'-oxybis(benzoic acid)(OBBA)	1,6-hexanediol(HD)	4,4'-dihydroxydiphenyl(DHD)

carbonyl), 1238 (C—O—C of ester), 763 (aromatic) and 3469 (C-H bending) cm<sup>-1</sup>. For OHCH: 2925(aliphatic), 1715 (ester carbonyl), 1686 (C-C of cyclohexanone ring), 1610(C=C aromatic), 1241(C—O—C of ester) and 765cm<sup>-1</sup>(aromatic). For OHDP: 2920.84(aliphatic), 1714.64(ester carbonyl), 1247.60 (C—O—C of ester), 762.86 (aromatic) and 3434.17 (C-H bending)cm<sup>-1</sup>. The absorptions at 1238, 1241 and 1248 cm<sup>-1</sup> indicated C—O—C stretching of the ester group. The ester carbonyl showed its characteristic frequency at 1717, 1715 and 1715 cm<sup>-1</sup> in these copolyesters.



**Photocrosslinking studies**

Photocrosslinkability was established by recording UV-Visible spectra of the co-polymer [0.01gdL<sup>-1</sup>] in THF solution successfully after UV irradiation at regular time intervals. The UV irradiation was carried out under 160 W medium pressure mercury lamp. The results demonstrated clearly that OHDA and OHCH polymers had photocrosslinkability which was attributed to the flexible nature of oxybis benzoyl unit that had enhanced the movement of adjacent layers for photocrosslinking. Obviously OHDA had the highest photocrosslinking nature than OHCH due to the lack of symmetry in OHDA polymer because of the presence of anthraquinone moiety which was responsible for easy photocrosslinking. These observations are shown in Fig. 6 and 7.

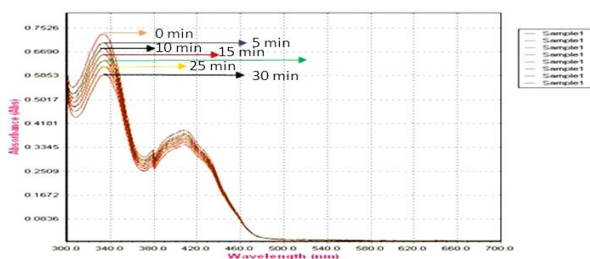


Fig. 6 UV-Visible spectra of OHDA at irradiation time of 0 to 30 min.

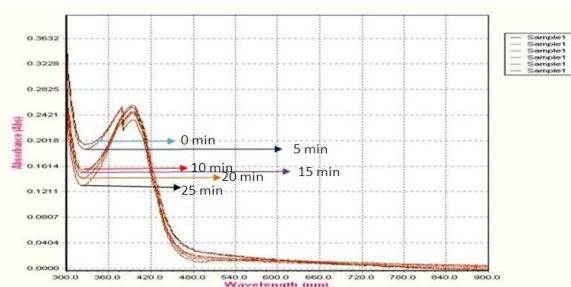


Fig. 7 UV-Visible spectra of OHDA at irradiation time of 0 to 25 min.

The photocrosslinkability was also recognized by the UV irradiation of polyester/PVC blend nanofibers and was observed that the morphology of the nanofiber changes if it has the photocrosslinkability. The SEM micrographs obtained from the unirradiated/irradiated electrospun nanofibers of polyester blends of OHDA/PVC, OHCH/PVC and OHDP/PVC are shown in Fig. 8,9,10,11,12&13. The fibers were found to be smooth, well dispersed and submicron range. SEM micrographs of OHDA/PVC and OHCH/PVC blend nanofibers had shown marked changes on UV irradiation which are obviously complementary to former studies.

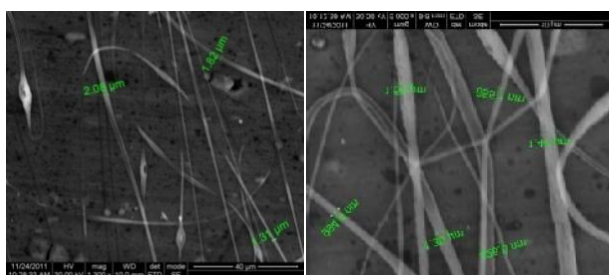


Fig.8 Fig.9 Scanning Electron Micrograph of OHDA/PVC before UV irradiation after UV irradiation

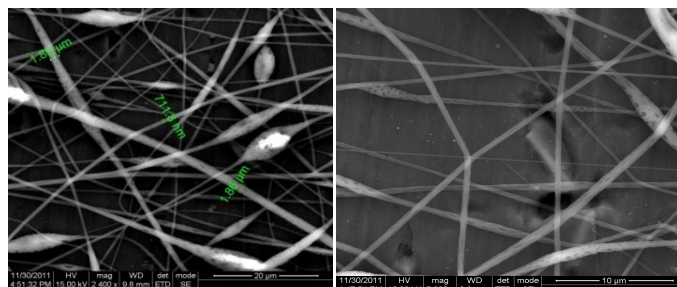


Fig.10 Fig.11 Scanning Electron Micrograph of OHCH/PVC before UV irradiation after UV irradiation

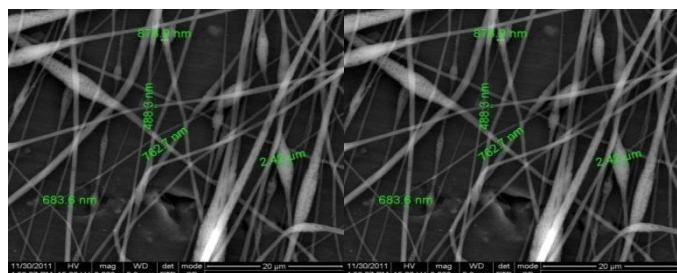


Fig.12 Fig.13 Scanning Electron Micrograph of OHDP/PVC before UV irradiation after UV irradiation

**CONCLUSION**

Three novel random copolyesters OHDA, OHCH and OHDP were synthesized from 4, 4'-oxybis (benzoic acid) with a common diol namely 1, 6-hexanediol. The other varying diols are so chosen that two were aromatic mesogen (1, 8-dihydroxyanthraquinone and 4, 4'-dihydroxydiphenyl) and another one was alicyclic (1,4-cyclohexanediol). The polymerization was carried out by solution polycondensation with DPCP/LiCl in pyridine medium. As expected the yield percentage of OHCH was found to be higher than that of OHDA due to effective copolymerization of the linear structure of OHCH. In OHDA, the 1,8-dihydroxyanthraquinone suspends like a pendent in the backbone of the main chain. The synthesized polymers were characterized by FTIR, <sup>1</sup>H NMR, <sup>13</sup>CNMR. The polyesters were homogeneously blended with polyvinylchloride to enhance the properties such as tensile strength and processability of the polymers. From the spectral studies, it is inferred that all three monomers are well incorporated into the polymer chain. The texture and photocrosslinkability of thenanofibers formed by blending copolyesters with PVC were investigated by SEM studies. It was observed that the nanofibers from OHDA/PVC and OHCH/PVC blend possessed photocrosslinkable nature as there were changes in the morphology after UV irradiation. But such changes could not be found in the nanofibers from OHDP/PVC. This indicates that the OHDA/PVC and OHCH/PVC blend nanofibers could be useful in photoactive sensors. Further the photocrosslinkability was established by recording UV-Visible spectra of the copolymer solution [0.01gdL<sup>-1</sup>] in THF successfully after UV irradiation at regular time intervals.

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