

**ICEWEST-2015 [05th - 06th Feb 2015]****International Conference on Energy, Water and
Environmental Science & Technology****PG and Research Department of Chemistry, Presidency College (Autonomous),
Chennai-600 005, India****A Study on the Synthesis, Characterization and Generation of
Composite Polyester Nanofibers Containing Arylidene Moiety****P Sathish¹, M Mayavathi¹, D Reuben Jonathan² and D Roopsingh^{1*}****¹PG and Research Department of Chemistry, Presidency college,
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Abstract: Two new random copolyesters with ethereal linkages were synthesized from a potential mesogenic non-linear dicarboxylic acid namely, 4,4'-azodibenzoic acid by direct polycondensation with a common diol hydroquinone bis(2-hydroxyethyl)ether and a variable diol namely, 2,7-bis(4-hydroxy-3-methoxybenzylidene)cycloheptanone and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone in pyridine medium. Diphenyl chloro phosphate (DPCP) was employed as the condensation agent. These copolyesters were characterized by viscosity measurements, solubility studies, FT-IR, ¹H and ¹³C NMR spectroscopic analysis. The thermal behavior of these copolyesters was investigated by differential scanning calorimetry (DSC). Novel copolyester-nanoclay composite nanofibers were fabricated in tetrahydrofuran (THF) medium by electrospinning method. Polyvinylchloride (PVC) was introduced to facilitate the electrospinning process of copolyester-nanoclay composites. The spun copolyester-PVC-nanoclay composite nanofibers were characterized by scanning electron microscopy (SEM). Photocrosslinking experiment suggests that due to the presence of DB, these composite nanofibers may be potential components for photo-optic applications in photosensor industries.

Key words: Polycondensation, Copolyesters, Electrospinning, Nanofibers, Photocrosslinking.

Introduction

Literature survey indicates that arylidene-cycloalkanone-based polymers facilitated the existence of liquid crystalline property¹. Borden has synthesized a series of photocrosslinkable polymeric materials having arylidene-keto moiety in the main chain and have found that polymers with arylidene-keto moiety had photocrosslinkable property which could be exploited in NLO applications²⁻⁴. Kannan and coworkers have reported the synthesis and characterization of photocrosslinkable phosphoramidate esters. The linear unsaturated polyphosphate esters based on divanillylidene cycloalkanone possessing photocrosslinkable property was studied by Sakhivel and coworkers⁵. Thermotropic liquid crystalline polymeric materials have been considered for the last four decades as potential materials to improve the physical parameters like thermal steadfastness, processability and mechanical properties of high-performance⁵. For the past twenty years, LCPs possessing photocrosslinkable chromophore have fascinated the attention of the research fraternity

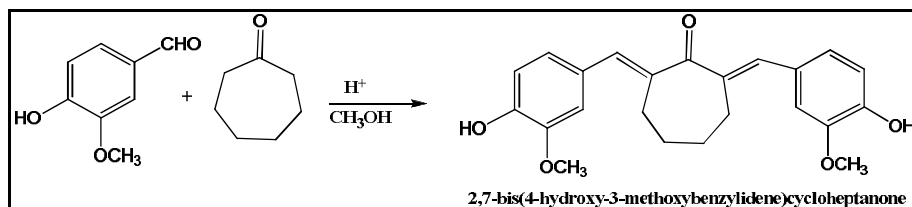
as a result of their special mechanical, electrical and optical properties. These materials are utilized in the manufacture of photoresists, photocurable coatings, photolithographic materials, photosensitizers, LC thermosets and LC elastomers^{7,8}. Even poly(ester-amides) were synthesized by making use of arylidene-ketones. However, there are few reports on the synthesis and characterization of certain copolyester-PVC-nanoclay composites which contain copolyesters possessing arylidene-cycloalkanone moiety in the main chain. Hence, we present herein the preparation and studies on certain copolyester-PVC-nanoclay composites possessing arylidene-cycloalkanone moiety in the main chain of the copolyester.

Experimental Section

Aldrich samples of vanillin and cycloheptanone were used as received. Sulphuric acid (Merck) was used as catalyst for the preparation of the arylidene-diol. Methanol (Merck) was used as a non-solvent for the precipitation of copolyesters and as a solvent for the preparation of the monomer diols. Aldrich samples of diphenylchlorophosphate and hydroquinonebis(2-hydroxyethyl)ether were used as such for the copolymerization process. Merck sample of 4-nitrobenzoic acid and dextrose sugar was utilized in the synthesis of the diacid 4,4'-azodibenzoic acid and lithium chloride was used for the polymerization process. SD Fine AR sample of dimethyl acetamide (DMAc) was used as solvent for determining the inherent viscosity of the copolyester in solution. Spectral grade DMSO-d₆ (Aldrich) was employed as internal standard for recording NMR Spectra. Tetrahydrofuran (THF), a Merck product was used as solvent in the preparation of the copolyester composites.

Preparation of 2,7-bis(4-hydroxy-3-methoxybenzylidene)cycloheptanone (VHCH)

This method was reported by Sidharthan and coworkers⁶. The procedure for the synthesis of the arylidene diol is represented here. About 1 mL of sulphuric acid was added in drops to a well-cooled solution of 4-hydroxy-3-methoxybenzaldehyde (100 mmol) and cycloheptanone (50 mmol) in 100 mL of dry methanol with occasional shaking taken in a 250-mL round-bottomed flask. A yellow-coloured solid of VHCH was precipitated. This precipitate was filtered, washed with distilled water and finally made to dry under room temperature. Finally the crude sample was re-crystallized from hot methanol. Yield: 90%; m.p. >200°C; FT-IR (KBr) 3438 cm⁻¹ (b, O-H) and 1648 cm⁻¹ (s, C=O);

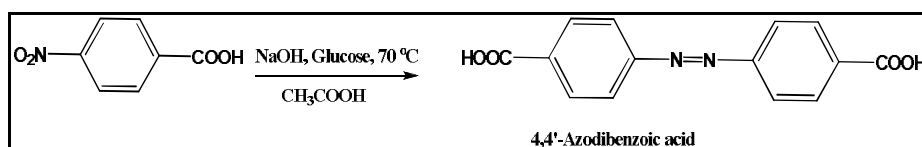


Preparation of 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone (VHCX)

2,6-Bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone was prepared by the method already reported^{11,12}.

Synthesis of 4,4'-azodibenzoic acid

4,4'-Azodibenzoic acid prepared by the method reported by Arulmoli and coworkers¹³.



Synthesis of Copolyester

This method was reported by Arul Moli and coworkers¹³. The procedure for the synthesis of typical copolyester PAHH is represented here.

Diphenyl chlorophosphate (12mmol) in pyridine (10mL) was added to a solution containing LiCl (10mmol) and 4,4'-azodibenzoic acid (5mmol) in pyridine (10mL) taken in a 100mL round-bottomed flask. The reaction mixture was continuously stirred at room temperature for a span of 30 minutes. Then the temperature was raised to 120°C and stirring was carried out at this temperature for about 10 minutes. The solution

containing the VHCH (2.5mmol) and the diol hydroquinonebis(2-hydroxyethyl)ether (2.5mmol) was added over a period of 10 minutes with constant stirring. The reaction mixture was maintained at this temperature for a time frame of 3 hours. Then the reaction mixture was cooled to room temperature and poured into 300mL of methanol when the copolyester was precipitated. It was filtered, washed with dry methanol and dried in vacuum.

Table-1: Monomer diols and diacid used and the copolyester code of the two copolyesters together with percentage of yield and inherent viscosities (η_{inh})

Common Diol: hydroquinonebis(2-hydroxyethyl)ether		Copolyester Code	Yield (%)	η_{inh} (dL/g)
Diacid	Diol-II			
4,4'-azodibenzoic acid	VHCH	PAHH	70.5	1.07
4,4'-azodibenzoic acid	VHCX	PAXH	69.8	1.09

Preparation of Copolyester-PVC-Nanoclay blend fiber by Electrospinning Method

This method was reported by Mayavathi *et al*¹⁰.

Preparation of Blend Solution

About 0.9g of polyvinylchloride, 0.3g of PAHH and 5mL of THF were taken in a 10mL closed container and stirred well for about 2 hours. Then it is taken in an ultrasonicator bath for an hour to ensure that the copolyester and the PVC were well dispersed in THF medium. As a last step stirring for 24 hours was carried out by using a magnetic stirrer.

Similar procedure was adopted to generate the copolyester-PVC-nanoclay composite by taking the PVC, the copolyester and the nanoclay in the ratio of 1:3:1.

Preparation of Blend Fibers

The homogeneous solution was taken in a 2mL syringe and positive voltage was applied to the blended solution through the needle attached to the syringe. The solution jet was formed by electrostatic force, when the electrical potential was increased to 22kV. The flow rate of the solution was set at 0.4mL/h, which was adjusted by means of a computer controlled syringe pump. The distance between the needle tip and the collector was maintained at a distance of 10cm and the drum collector rotation speed of about 1800rpm. The PAHH /PVC nanofibers in a nonwoven form were collected on an aluminum foil.

Results and Discussion

Solubility of all the copolyesters was determined in various solvents qualitatively. The inherent viscosity (η_{inh}) of the polyesters was determined in DMSO solution using Ubbelohde viscometer at 30°C. FT-IR spectra of the two random copolyesters were recorded using Shimadzu FT-IR instrument. The ¹H and ¹³C-NMR spectra were recorded by utilizing BRUKER AV III 500MHz NMR instrument in DMSO-d₆ solvent. DSC thermograms of these two copolyesters were obtained using DSC 200 F3 MAIA instrument. The SEM photomicrographs of the copolyester-PVC and copolyesters-PVC-nanoclay composites were recorded with HitachiS-4800 SEM instrument.

Solubility

The results of the solubility of the copolyesters are presented in table 2. From table 2 it is observed that the copolyesters derived from azodibenzoic acid are soluble in DMSO and is partially soluble in THF, DMF and DMAc solvents which may be due to the rigid azobenzene moiety incorporated in the polymer back bone. All the two copolyesters are insoluble in non-polar solvents. Similar explanation was offered by Arul Moli and coworkers in a series of copolyester¹³.

Table 2: Solubility of the two random copolyesters in some common organic solvents

Copolyester	C ₆ H ₁₄	C ₆ H ₆	CHCl ₃	THF	(CH ₃) ₂ CO	CH ₃ OH	DMAc	DMF	DMSO
PAHH	--	--	+ -	+ -	+ -	--	+ -	+ -	++
PAXH	--	--	+ -	+ -	+ -	--	+ -	+ -	++

Viscosity Measurements

The η_{inh} value of the two copolyesters was determined in DMSO solution at a temperature of 30°C using Ubbelohde viscometer. The inherent viscosity values were found to be in the range of 1.07 – 1.09 dl/g and are presented in table 1. The data shows that these copolyesters are reasonably of high molecular weight.

Spectral Studies

FT-IR spectrum of the two copolyesters was recorded using Shimadzu FT-IR instrument. The FT-IR spectrum of all the two copolyesters showed characteristic absorption in the range of 1731–1739 cm^{-1} due to ester C=O stretching frequency. A typical FT-IR spectrum of the copolyester PAHH is given in figure 1.

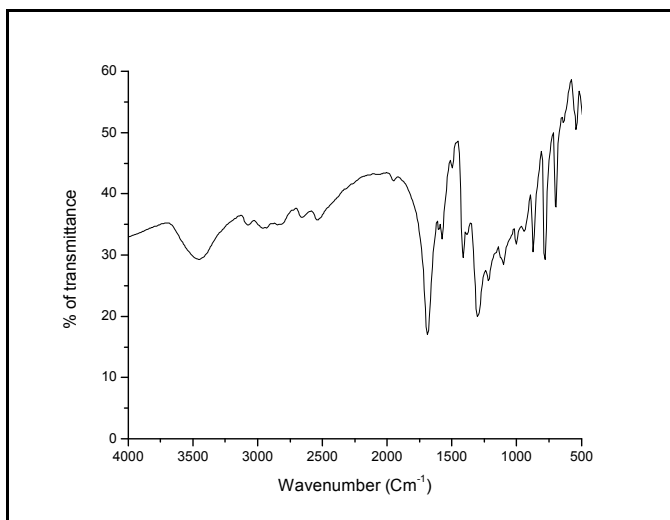


Figure 1: FT-IR Spectrum of the Copolyester PAHH

The NMR spectra were recorded with BRUKER AV III 500MHz NMR instrument in DMSO-d₆ solvent to identify the structural units present in the copolyester chain. The signal at 10.3ppm is due to end phenolic –OH protons. The aromatic protons are observed in the range of 7.3–8.2ppm. The vinylic protons attached to the carbonyl carbon are observed at 6.9ppm. A typical ¹H-NMR spectrum of the copolyester PAHH is given in figure 2.

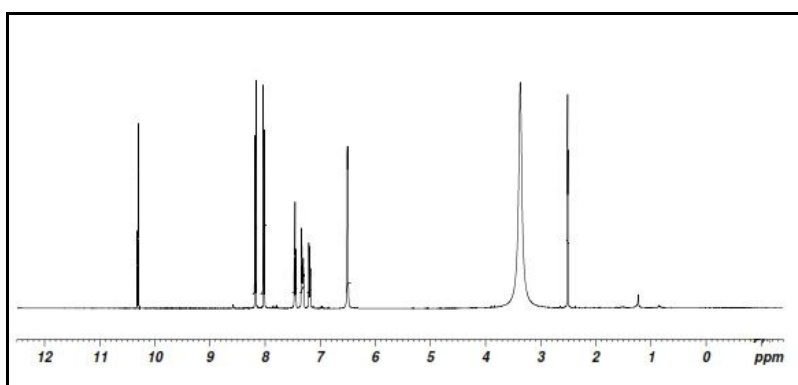


Figure 2: ¹H-NMR Spectrum of the Copolyester PAHH

The signals in the range of 154-167ppm in the ¹³C-NMR spectra of the copolyesters are due to the carbonyl carbon of the ester groups which indicates the formation of copolyester. Aromatic carbon atoms show signals in the range 123-143ppm. The signal due to two methoxy carbons is observed at 39.9ppm. A typical ¹³C-NMR spectrum of the copolyester PAHH is given in figure 3.

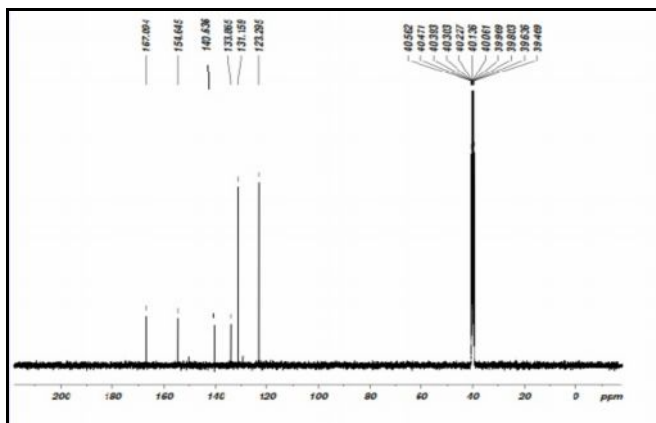


Figure 3: ^{13}C -NMR Spectrum of the Copolyester PAHH

Thermal Characterization

Differential scanning calorimetry was employed to obtain DSC thermograms for the copolyester PAHH. Their phase transition temperatures in the first scan at a heating rate of $10^\circ\text{C}/\text{min}$ are summarized in table 3. From table 3 it is clear that the copolyesters have the T_g values higher than 400°C which may be due to higher molecular weight and also due to the presence of wholly aromatic moieties in the copolyester backbone which is known to create rigidity. This was observed by Sidharthan and coworkers in a series of thermotropic liquid crystalline copolyesters⁹. Figure 4 represents the DSC thermogram of the copolyester PAHH

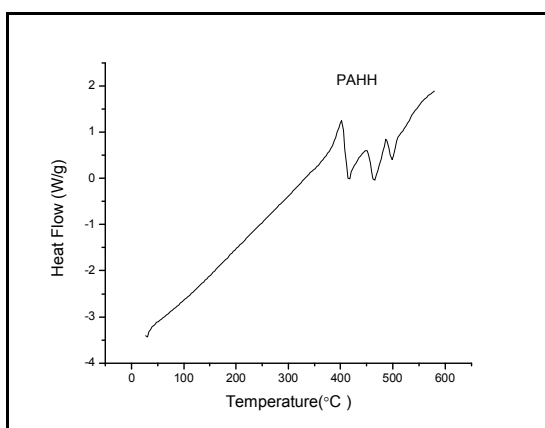


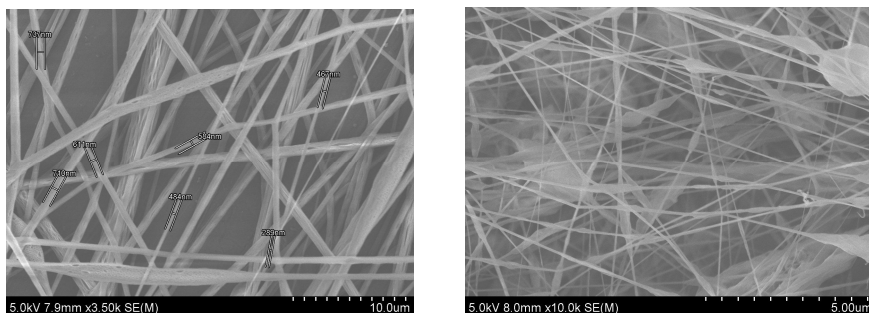
Figure 4: DSC Thermograms of the Copolyester PAHH

Table 3: Phase transition temperatures of the copolyester determined from DSC thermograms

Copolyester Code	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_{cl} ($^\circ\text{C}$)
PAHH	402	460	485

SEM Studies

Scanning electron microscopy (SEM) is applied to picture the morphology of the polymeric material in the form of composite fiber with PVC in which the copolyester is incorporated¹⁴. The electrospinning method was effectively utilized to embed the copolyester in the polyvinylchloride (PVC) matrix, forming composite nanofibers. The polymer composite fibers were characterized by SEM images. The SEM micrographs of the PVC-PAHH, the PVC-PAHH-Nanoclay, the PVC-PAHX and the PVC-PAHX-Nanoclay composites are represented in figures 5(a,b)



a) b)
Figure 5: SEM images of (a) PAHH/PVC (b) PAHH/PVC/Nano clay composites.

The SEM images of the representative copolyesters in PVC matrix indicates that the copolyester/PVC fibers spun by electrospinning method exhibited spherical diameters and found to be smooth surfaced with uniform size. The SEM micrographs also display that the fibers are generally of uniform diameter which ranges between 48nm and 653 nm and are well dispersed without beads on their surface. There is no significant disruption in the fiber structure due to the addition of polyester to PVC. Observation of the SEM micrographs indicates that the composite fibers of copolyester-PVC-nanoclay have higher diameter than the composite fibers of copolyester-PVC. This may be explained by the nature of nanoclay which swells the fiber to higher diameter ranges.

Photocrosslinking Studies

A potential photoactive group such as arylidene-keto moiety undergoes photocrosslinking on UV irradiation. The synthesized copolyesters were tested for their photocrosslinkability by UV irradiation in DMSO solution at regular time intervals successfully. The photocrosslinkability are accounted due to $\pi-\pi^*$ transition of the exocyclic double bond of bis(4-hydroxy-3-methoxybenzylidene)cycloalkanone mesogenic unit in the polymer backbone. A steady rate of photocrosslinking was indicated by the decrease in absorbance with time on UV irradiation. This was predicted to be due to photodimerization of C=C bonds in arylidene unit, which involves $2\pi+2\pi$ cycloaddition reaction leading to the formation of cyclobutane ring^{15,16}. A representative picture of PAXH is shown in Fig 6.

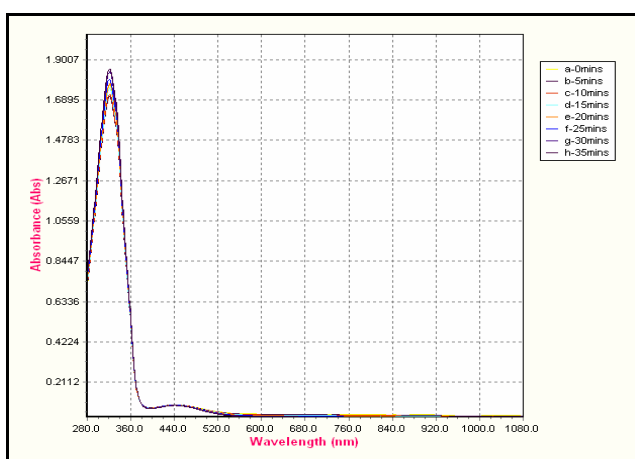


Figure 6: Change of absorbance by UV irradiation during the photocrosslinking of the copolyester PAXH in DMSO at various intervals of time.

Conclusion

A series of two new copolyesters were synthesized by direct polycondensation using diphenyl chlorophosphate and lithium chloride in pyridine medium. The dicarboxylic acid used is 4,4'-azodibenzoic acid. The common diol used is hydroquinonebis(2-hydroxy ethyl)ether and the variable diol used is 2,7-bis(4-hydroxy-3-methoxybenzylidene)cycloheptanone and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone. The synthesized copolyesters was characterized by viscosity measurement data which reveal that these two copolyesters are of high molecular weight. The spectral data supported the structural assignment of the

copolyesters. The presence of azobenzene moiety affected the solubility of the copolyesters in various common organic solvents. As the polyesters exhibit photocrosslinking nature on UV irradiation, they may, after careful designing, emerge as UV absorbing agents in photo-optic shields. The SEM images of all the composites show excellent fiber structure at the nano level. It is a possibility that these fibers may eventually be used in UV absorbing textiles for the prevention of hazards of UV light.

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