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Preparation and Studies on Certain Random Copolyesters and their Composite Nanofibres

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Abstract*— Three new random copolyesters containing arylidene moiety were prepared from two dicarboxylic acids, namely 2,6-napthalenedicarboxylic acid, 4,4'-oxybis(benzoic acid) and a variable arylidene diol in the ratio of 1:1:2 by direct polycondensation with diphenylchlorophosphate (DPCP) as the condensation agent. The variable diols used are 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone, 2,5-bis(4-hydroxy-3-methoxy benzylidene)cyclohexanone and 2,5-bis(4-hydroxy 3-methoxy benzylidene)cycloheptanone. They were prepared by acid catalyzed Claisen-Schmidt reaction. These copolyesters were characterized by qualitative solubility tests, viscosity measurements and their microstructure in the copolyester main chain is determined by FT-IR, ^{1}H and ^{13}C NMR spectroscopic studies. The phase transition temperatures of these copolyesters were investigated by DSC thermograms. Composite nanofibres of copolyesters were prepared with polyvinylchloride (PVC) and nanoclay in tetrahydrofuran medium in 10% (w/w) ratio and they were obtained by electrospinning method. The morphology of the copolyester composite nanofibres was investigated by scanning electron microscopy (SEM). These nanofibres are expected to be useful fungicidal agents in textile industry.

Keywords- arylidenecyclopentanone, arylidenecyclohexanone, arylidenecycloheptanone polycondensation, diphenylchlorophosphate, copolyesters-nanocomposites, nanofibres

I. INTRODUCTION

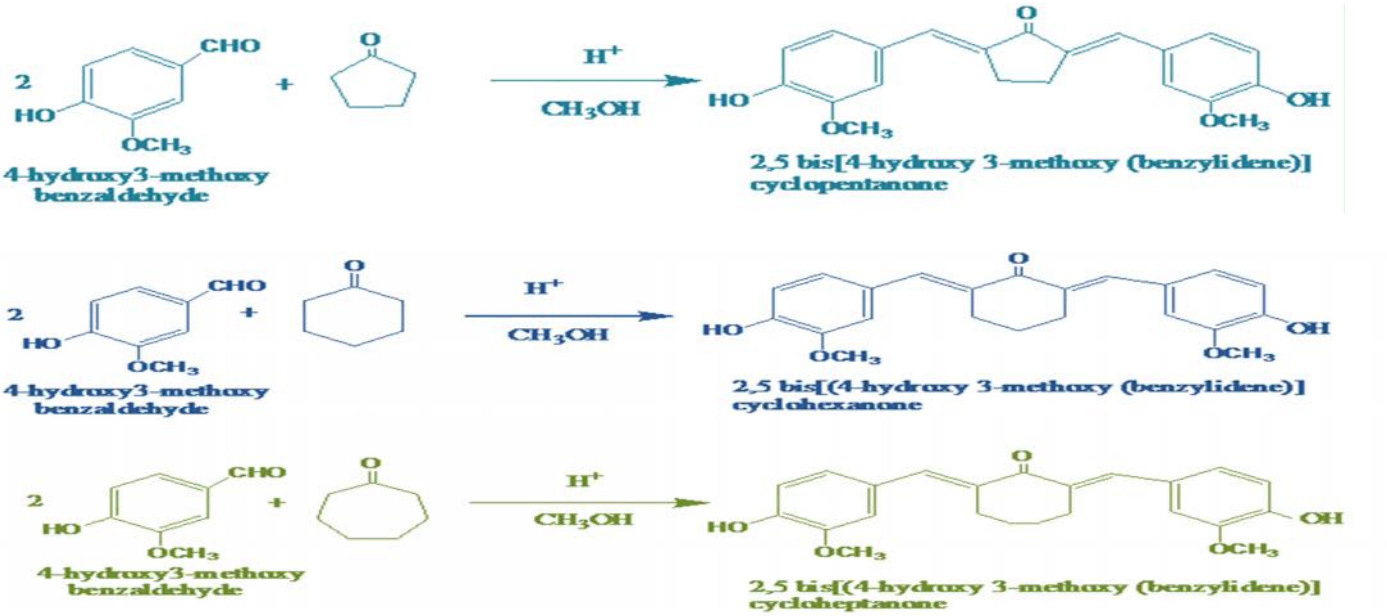
Literature survey indicates that arylidene-cycloalkanone-based polymers facilitated the existence of liquid crystalline property. Borden [1] has synthesized a series of photocrosslinkable polymeric materials having arylidene-keto moiety in the main chain. Kishore *et al* [2, 3] have found that polymers with arylidene-keto moiety had photocrosslinkable property which could be exploited in NLO applications. Kannan and coworkers [4-6] have reported the synthesis and characterization of photocrosslinkable phosphoramide esters. The linear unsaturated polyphosphate esters based on divanillyidine cycloalkanone possessing photocrosslinkable properties were studied by Sakthivel and coworkers [7, 8]. Arumugasamy [9] has synthesized a number of random copolyesters containing 4,4´-dihydroxybis(arylidene)cycloalkanones using aliphatic diacid chlorides and found that they exhibited thermotropic liquid crystalline (TLC) behaviour by optical polarizing microscopic studies. Kannappan *et al.* [10] investigated the rate of photocrosslinking of the random copolyesters with arylideneketo moiety by UV spectral studies. Even poly(ester-amides) were synthesized by making use of arylidene-ketones. [11]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.

II. EXPERIMENTAL METHODS

Aldrich samples of 4-hydroxy-3-methoxy benzaldehyde (vanillin), cyclopentanone, cyclohexanone and cycloheptanone were used as received. Sulphuric acid (Merck) was used as catalyst for the preparation of the arylidenediol. 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 2,6-napthalenedicarboxylic acid and 4,4'-oxybis(benzoic acid) were purchased and used for the copolymerization process. SD Fine AR sample of dimethyl acetamide (DMAc) was used as such as solvent for finding out the inherent viscosity of the copolyester in solution. Merck sample of spectral grade DMSO-d6 (Aldrich) containing as internal standard was used for recording NMR Spectra. Tetrahydrofuran (THF) was used as solvent in the preparation of the copolyester composites.

A. Preparation of arylidene diols

The arylidene diols namely2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone, 2,5-bis(4-hydroxy 3-methoxy benzylidene)cyclohexanone and 2,5-bis(4-hydroxy 3-methoxy benzylidene)cycloheptanone was prepared by the method reported by Sidharthan and coworkers [10] given in the following scheme.



B. Synthesis of Copolyester

The three copolyesters namely NOCPN, NOCHX and NOCHP were prepared by the method reported by Arulmoli and coworkers [12]. Table 1 gives the monomers used in the synthesis, their codes, yield percentage and inherent viscosity.

Table-1

S.No	**Common diacid-I**	**Common diacid-II**	**Varying Diols**	**Polymer Code**	**Yield %**	**η_{inh}dL/g**
1	2,6-NDCA	4,4’-OBBA	2,5-BCPN	NOCPN	73	0.95
2	2,6-NDCA	4,4’-OBBA	2,5-BCHX	NOCHX	75	1.29
3	2,6-NDCA	4,4’-OBBA	2,5-BCHP	NOCHP	69	1.03

C. Preparation of Copolyester-PVC-Nanoclay Composite Nanofibre by Elecrospinning Method

This method was reported by Mayavathi *et al* [13].

(i) Preparation of Blend Solution

About 0.6 g of polyvinylchloride, 0.2 g of NOCHX 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 20 minutes to ensure that the copolyester and the PVC were well dispersed in THF medium. Finally by using a magnetic stirrer solution was stirred for 24 hours.

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.

(ii) *Blend Fibres Preparation*

The homogeneous solution was taken in a 2 mL 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 22 kV. The flow rate of the solution was set at 0.5 mL/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 10 cm and the drum collector rotation speed of about 1800 rpm. The NOCHX/PVC nanofibres in a nonwoven form were collected on an aluminum foil.

III. 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 DMAc solution using Ubbelohde viscometer at 30°C. FT-IR spectra of the entire random copolyesters were recorded using Shimadzu FT-IR instrument. The ^{1}H and ^{13}C-NMR spectra were recorded with PATBO BBPULPROG zgpg3-600 MHZ NMR instrument in DMSO-d6 solvent. DSC thermograms of all the three copolyesters were obtained using DSC 200 F3 MAIA instrument. Copolyester-PVC-nanoclay composites were prepared by making use of ESPIN-NANO instrument and SEM micrographs were taken by utilizing S-3000N instrument.

D. Solubility

The three copolyesters reported here are found to be soluble in highly polar solvents such as DMAc, DMSO, THF, acetone and dimethyl formamide, partially soluble in moderately polar solvents like chloroform but thoroughly insoluble in least polar solvents like benzene and hexane. Similar explanation was offered by Samuel and coworkers [14] in a series of copolyesters.

E. Viscosity Measurements

The η_{inh} value of all the four copolyesters was determined in DMAc solution at 30 °C using Ubbelohde viscometer. In each case 25mg of pure dry copolyester sample was dissolved in 25ml of DMAc, kept aside for some time with occasional shaking. The η_{inh} was calculated from the flow time measurements. The inherent viscosity values were found to be in the range of 0.95-1.29dL/g and are presented in table 1. The data shows that these copolyesters are reasonably of high molecular weight.

F. Spectral Studies

FT-IR spectrum of the three copolyesters was recorded using Shimadzu FT-IR instrument. The FT-IR spectrum of all the three copolyesters showed characteristic absorption in the range of 1738-1740cm^{-1} due to ester C=O stretching frequency. Similar observations were made by Arul Moli and coworkers [15] in a series of copolyesters. A typical FT-IR spectrum of the copolyester NOCHX is given in figure 1.

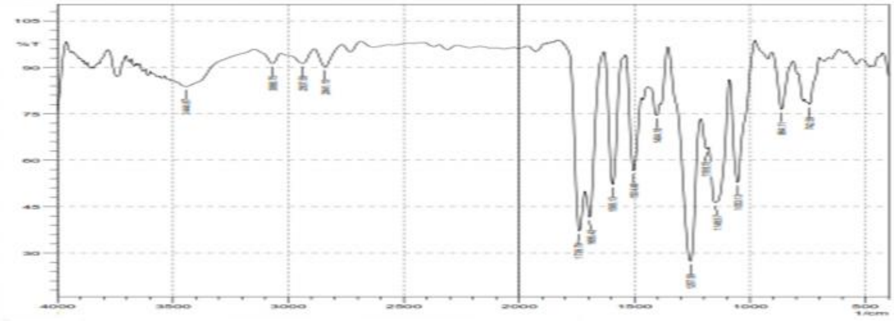


Figure 1: FT-IR Specrum of the Copolyester NOCHX

The NMR spectra were recorded with BRUKER AV III 500 MHz NMR instrument in DMSO-d6 solvent to identify the structural units present in the copolyester chain. The aromatic protons are observed in the range of 7.2-8.4ppm. The vinyllic protons attached to the carbonyl carbon are observed in the range of 6.8-7.0ppm. The methylene protons of the cyclohexanone ring are observed in the range of 2.4-3.3ppm. A typical ^{1}H-NMR spectrum of the copolyester NOCHX is given in figure 2.

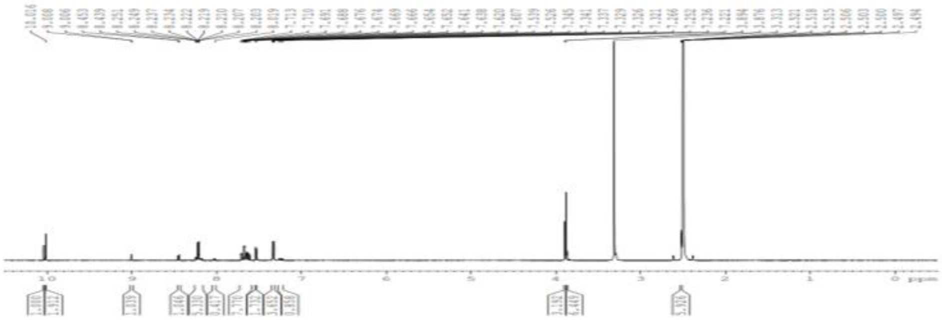


Figure 2: ^{1}H-NMR Spectrum of the Copolyester NOCHX

The signals in the range of 190-193ppm and 151-163ppm in the ^{13}C-NMR spectra of the copolyesters are owing to the carbonyl carbon of the ester groups, respectively, which indicates the formation of copolyester. A typical C^{13}-NMR spectrum of the copolyester NOCHX is given in figure 3.

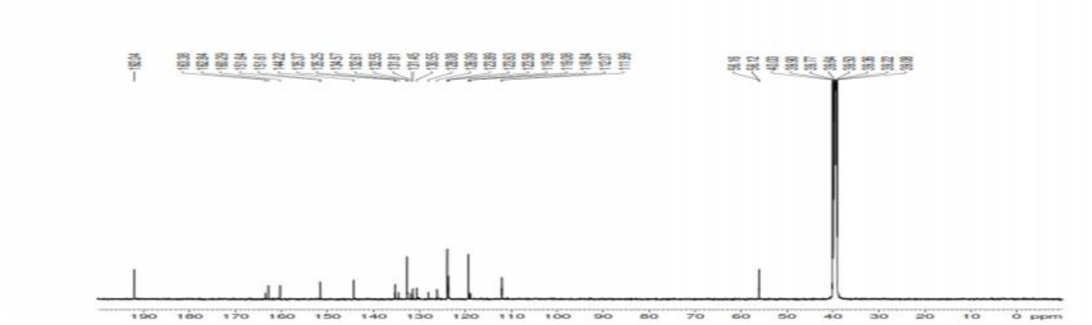


Figure 3: C^{13}-NMR Spectrum of the Copolyester NOCHX

G. Thermal Characterization

Differential scanning calorimetry was employed to obtain DSC thermograms for the copolyesters NOCPN, NOCHX and NOCHP. Their phase transition temperatures in the first scan with the heating rate of 10°C/min are summarized in Table 3.

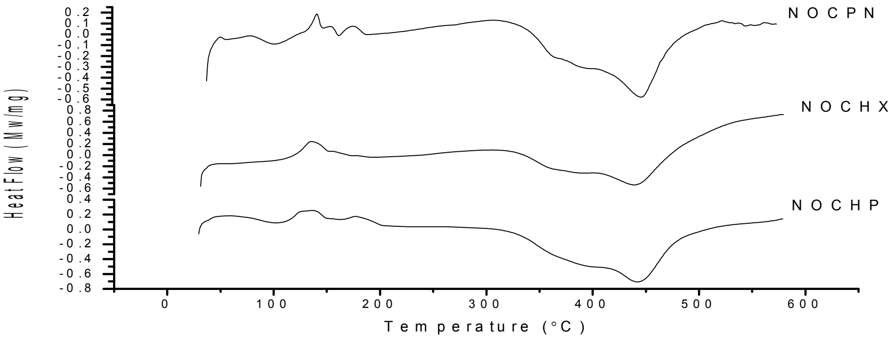


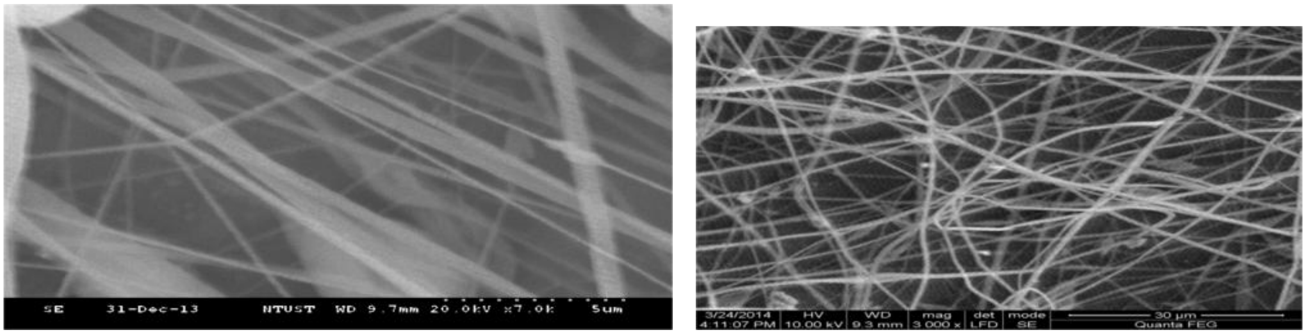
Figure 4: DSC Thermograms of the Copolyester NOCPN, NOCHX and NOCHP

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

Copolyester Code	**T_g (°C)**	**T_m (°C)**	**T_{cl} (°C)**
NOCPN	142	176	442
NOCHX	134	-	439
NOCHP	134	177	442

H. SEM Studies

Scanning electron microscopy (SEM) is applied to picture the topography of the polymeric material in the form of the composite film of PVC in which the copolyester is incorporated [16, 17]. The electrospinning method was effectively utilized to embed copolyester in a polyvinylchloride (PVC) matrix, forming blend nanofibres. The polymer blend fibres were characterized by SEM Images. The SEM micrographs of the PVC-NOCHX Composite, the PVC-NOCHX-Nanoclay Composite, the PVC-NOCHP Composite and that of the PVC-NOCHP-nanoclay Composite are represented in figures5(a),(b),(c) and (d) respectively.



(a) **(b)**

Figure 5: SEM images of (a) NOCHX/PVC (b) NOCHX/PVC/Nanoclay

The SEM images of the representative copolyesters in PVC matrix indicates that the copolyester/PVC fibers spun by electro spinning method exhibited spherical diameters and smooth surfaces in a uniform fashion. The SEM micrographs display that the fibers are uniform, well dispersed and without beads on their surface. There is no significant disruption in the fibre structure due to the addition of polyester to PVC. Parallel observations were made by Mayavathi *et al* [13] in a series of certain random copolyester/PVC composites.

CONCLUSION

A series of three new copolyesters were synthesized by direct polycondensation using diphenylchlorophosphate and lithium chloride in pyridine. The common dicarboxylic acid used is 2,6-naphthalene dicarboxylicacid and 4,4'-oxybis benzoicacid with the varying arylidene diols used is 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone, 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone, 2,5-bis(4-hydroxy-3-methoxybenzylidene)cycloheptanone. The inherent viscosity data reveals that the synthesized copolyesters are high molecular weight materials. These copolyesters were characterized by viscosity measurements, FT-IR, ^{1}H-NMR, and ^{13}C-NMR. Thermal transition temperatures of copolyesters were determined from DSC thermograms. Nanofibres of the copolyesters could be conveniently fabricated by electrospinning with spinnable PVC matrix polymer solution and nanoclay. Blending of the copolyesters derived from 2,6-napthalenedicarboxlic acid with PVC/nanoclay produced neat fibres with diameter in the nano range. The SEM images of copolyester blend fibres show excellent fibrous structure at the nano level which may be utilized for fungicidal applications as reported earlier due to the presence of arylidene diols[18].

ACKNOWLEDGMENT

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