Synthesis and Studies on Certain Semiconducting Copolyesteramides Containing 2, 5-Pyridine Dicarboxylic Acid and their Photocross linkable Blend Nanofibers

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Abstract— *A series of novel random copolyesteramides from 2, 5-pyridine dicarboxylic acid and 1, 6-hexandiol/ arylidenediol with varying diamine namely, 1, 4-diaminobenzene, 4, 4'- diamino diphenyl methane and 1,6-diaminohexane were synthesized, using diphenylchlorophosphate as the condensation agent. Their structural features were investigated by viscosity measurements, FTIR, ^{1}HNMR and ^{13}CNMR spectral data and thermal behaviour was established by Differential Scanning Calorimetry (DSC). The synthesized copolyesteramides/PVC blend nanofibers drawn by electrospinning process were tested for photocrosslinking efficacy using UV irradiation technique. The changes in morphology of the nanofibers by UV irradiation were studied by Scanning Electron Microscopy (SEM). The frequency dependent dielectric and conductivity behaviour of the synthesized copolyesteramides were studied at different temperatures using LCR meter. The synthesized copolyesteramides with such unique properties are expected to be of use in electrochemical devices and sensors.*

Keywords— Electrospinning, Frequency, Nanofibers, Photocrosslinking, Semi conducting.

I. INTRODUCTION

Study of conducting polymers (CPs) is a challenging exercise from both fundamental point of view and commercial potential. In the application arena, CPs are bringing radical innovations like electromagnetic interference shielding , pixel drivers in displays and electronic alfactometer, drug delivery, artificial muscles, bio affinity sensors and screen displays. The combination of metal-like conductivity and processability of polymers have created wide range of applications. [1-5]

Photocrosslinkable polymers have attracted considerable attention in the research field because of their interesting mechanical, electrical and optical properties. Photocrosslinkable polymers find potential applications in the preparation of photo curable coating, photocrosslinked hydrogels, optical lithographic materials, photo sensitizers, photo resists, photorefractive materials [6] and information storage devices. Polymers having photodimerizable groups find applications in immobilization of enzymes [7-13].

In the present investigation a. c conductivity of some of the synthesized novel random copolyesteramides containing 2, 5-pyridine dicarboxylic acid moiety in their main chain was determined using LCR meter. Photocrosslinkability of copolyesteramides/PVC blend nanofibers were determined by UV irradiation techniques. The polyesteramides were synthesized by the direct polycondensation of 2, 5-pyridine dicarboxylic acid, one diol and one diamine (2:1:1) in LiCl/pyridine using diphenylchlorophosphate as the condensation agent. The advantage of this method is the mild experimental condition for synthesis with the temperature of 120 ^{0}C.

II. EXPERIMENTAL

2.1. Materials

Aldrich samples of Vanillin(99%), 2,5-pyridinedicarboxylic acid (PDCA), 1,4-diaminobenzene(DAB), 4,4'-diaminodiphenyl methane (DADPM), 1,6-diaminohexane(HMDA), 1,6-hexanediol(99%) (HD), diphenylchlorophosphate (99%) (DPCP) and cycloheptanone (99%) (CH) were used as supplied. Pyridine (Merck, 99% pure), Lithium chloride anhydrous (Aldrich, Analar), dimethyl sulphoxide, methanol, N,N-dimethylformamide, N, N-dimethylacetamide and tetrahydrofuran were distilled before use.

2.2. Methods

2.2.1. Synthesis of Monomer- Arylidenediol [14, 15]

A mixture of 18.5 g (0.15 mol) 4-hydroxy 3-methoxy benzaldehyde (vanillin) and 8.4g (0.075 mol) cycloheptanone were dissolved in 75 ml. of dry methanol and maintained in ice cold condition. To this mixture, catalytic amount of concentrated sulphuric acid was added slowly drop by drop and kept as such for 24 hours. The product was filtered, washed several times with distilled water and dried. The crude monomer was recrystallized twice from ethanol to yield pale yellow crystals of 2, 7-bis (4-hydroxy3-methoxybenzylidene) cycloheptanone. Yield was 80%. FTIR (KBr): 1672 cm^{-1} (C=O) of cycloheptanone, 3184 cm^{-1} (OH) and 1591cm^{-1} (C=C).

2.2.2. Synthesis of random copolyesteramides

A typical procedure for the synthesis of random copolyesteramides PADM is as follows.[16, 17]

To a four necked 250 ml. round bottomed flask fitted with a condenser, thermometer, mechanical stirrer and an oil bath, 0.835 g (5mmol) of PDCA, 10 ml pyridine and 2.5 ml (12mol) 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 ^{0}C for 20 min. To this mixture, 0.95 g (2.5 mmol) of diol ADCH in 5 ml pyridine and 0.495 g (2.5 mmol) of diamine DADM in 5 ml pyridine were added drop wise simultaneously at 120 ^{0}C for a period of 20 min and the whole solution was further stirred under the same condition for 3 h. The solution was cooled to room temperature and poured into 500 ml water/methanol (1:1, v/v). The product was filtered, washed with hot methanol and dried in vacuum oven at 50 ^{0}C.

2.2.3. Preparation of Polymer/ PVC Blend Nanofibers by Electro spinning process

Blending the synthesized polymers with PVC was carried out by taking 5 ml of THF in 10 ml closed container with pellet in which 0.6 g of PVC was added and stirred for 15 min and then 0.2 g of polymer 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 was 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 10 cm and the drum collector rotation speed around 1800 rpm. The Polymer/PVC blend nanofibers in a non woven form were collected on an aluminium foil.

2.3. Studies on Electrical property

A.C conductivity has been evaluated from dielectric data by using LCR meter in accordance with the relation

$$\sigma_{ac} = \varepsilon^0 \omega \varepsilon''$$

Where $\varepsilon^0 = 8.854X10^{-24}$ $\omega = 2\pi f$
ε'' = Dielectric loss f = frequency

III. RESULTS AND DISCUSSION

All the copolyesteramides were synthesized by the direct polycondensation of 2, 5-pyridine dicarboxylic acid, one diol and one diamine in the mole ratio 2:1:1, using DPCP as the condensing agent. This method avoided the tedious preparation of acid derivatives. The time required for the polymerization is only 3 h under mild conditions. The shorter time duration and low temperature required for polymerization reduces the risk of degradation of monomers, thereby enhances the molecular weight of polymers. The successful preparation of polymers using monomers demonstrated the wide applicability of Higashi method. Presence of aliphatic and arylidene keto moiety of the polymer enhances the solubility in organic solvents and hence facilitates processing.[18] The inherent viscosities (η_{inh}) were found to be in the range of 1.080- 1.170 dl/g as listed in Table 2. The results indicated that the synthesized polyesteramides have high molecular weight.

3.1. Solubility of copolyesteramides

The solubility of copolyesteramides was tested qualitatively by dissolving 0.005g of it in 1ml of solvent. Solubility of all the synthesized copolyesteramides are listed in Table 1. The copolyesteramides were found to be soluble in polar solvents like DMSO, DMAc, DMF, THF, NMP and pyridine. All the polyesteramides dissolved freely in concentrated sulphuric acid but with degradation. However, they were sparingly soluble in $CHCl_3$, CH_3OH, C_6H_{14} and benzene.

Wholly aromatic polymers have poor solubility in common organic solvents.[19] Borden *et al*.[20,21] synthesized photo- responsive linear bis(benzylidene) polycarbonates and observed that they were poorly soluble. In 1993, Gangadhara and Kishore [6] prepared polybis (benzylidene) esters from tetragolic acid dichloride and bis(4-hydroxy benzylidene) cyclohexanone and reported improved solubility. The present investigation showed appreciable solubility in polar solvents. The incorporation of arylidenediol and 1, 6-hexanediol with 2, 5-pyridine dicarboxylic acid along with other monomer diamine provide structural variants which enhances solubility of these polymers in common polar organic solvents.

Table.1: Solubility of copolyesteramides

S.No	Polymer code	DMSO	DMF	DMAc	NMP	THF	$CHCl_3$	Pyridine	H_2SO_4	C_6H_6	C_6H_{14}	CH_3OH
1	PHDB	++	++	++	++	++	--	++	++	--	--	--
2	PHDM	++	++	++	++	++	--	++	++	--	--	--
3	PHHA	+-	++	++	++	++	--	++	++	--	--	--
4	PADM	++	++	++	++	++	--	++	++	--	--	--
5	PAHA	+-	++	++	++	++	--	++	++	--	--	--

++ = highly soluble +- = less soluble -- = sparingly soluble

3.2. Spectral characterization of Copolyesteramides

3.2.1. Infrared spectroscopy

Formation of copolyesteramides was followed by FTIR spectra, which were recorded for all the synthesized copolyesteramides. A representative FTIR spectrum of PHDB and PADM are presented in Fig. 1 and Fig. 2. Successful esterification and amide formation could be confirmed by substantial reduction in the characteristic O-H stretching absorption frequency in the spectra. In all spectra, copolyesteramides showed the characteristic carbonyl stretching frequency of ester groups in the range of 1706 to1716 cm^{-1}. 2923-2930 cm^{-1} (-CONH-) specified the amide formation. The absorption in the range of 1603-1651 cm^{-1} are characteristic of N-H stretch in amide.[22, 23] The arylidene ketone showed their characteristic carbonyl stretching frequency of 1691-1697 cm^{-1}. It is pointed out that the carbonyl stretching frequency of the keto group in the arylidene keto moiety is slightly less than that of polyesters which may be due to increase in the rigidity of arylidene keto moiety, when present in the polymer chain.[24]

The absorption in the range of 1566 and1592 cm^{-1} indicated C=C of arylidene moiety where as absorption in the range of 1508-1517 cm^{-1} was accounted to be due to aromatic carbon –carbon double bond.

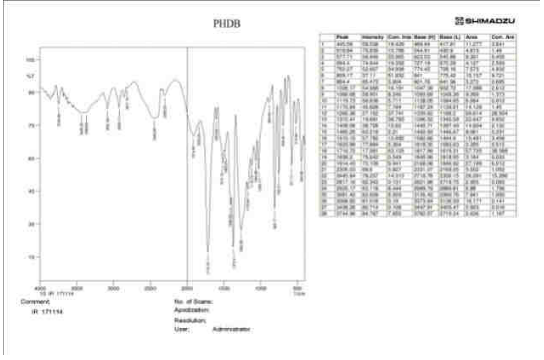


Fig. 1: FTIR spectrum of PHDB

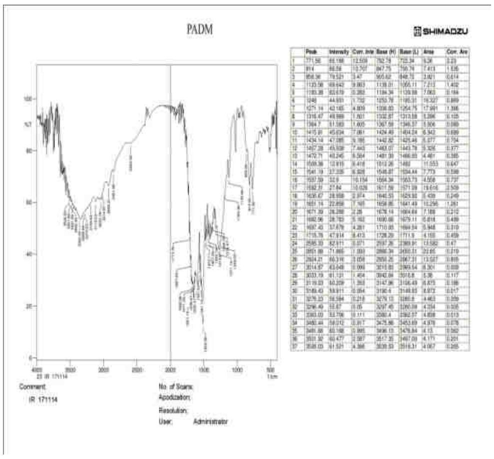


Fig.2: FTIR spectrum of PADM

Structural units of the copolyesteramides were identified by ^{1}HNMR and ^{13}CNMR spectra. The representative ^{1}HNMR spectrum of typical random copolyesteramide PHDM recorded in DMSO-d_6 as solvent and TMS as an internal standard is prescribed inFig.3

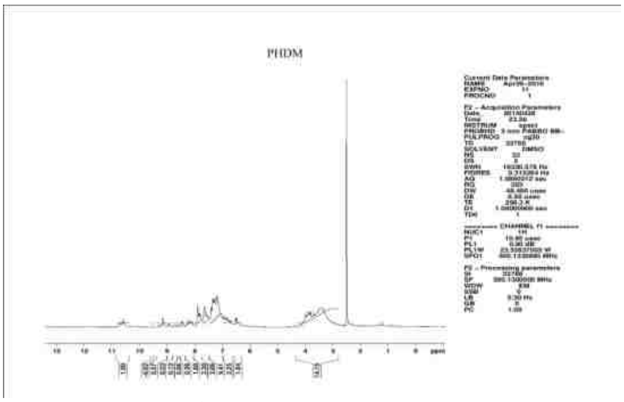


Fig.3: ^{1}HNMR spectrum of PHDM

The aromatic protons of dicarboxylic acid appeared in the region of 8.1- 8.2 δ. The protons of –O-$(CH_2)_6$-O- found in the region of 2.5- 3 δ. A singlet at 10.5- 10.7 δ is attributed to 2^0 amide proton. [25]

A singlet at 2.65 δ is due to the methylenic proton attached to N-atom. 7.1-7.8 δ is due to the aromatic protons of the monomer, diamine. The microstructure of repeat units in the polymer chain can be identified satisfactorily using 13CNMR spectra. A representative 13CNMR spectrum of PHDM recorded in DMSO is shown in Fig. 4.

The signal at 54 ppm was assigned to the methylenic carbon of 4, 4'- diaminodiphenyl methane. The aromatic protons were indicated by the signals from 114- 139 ppm. The ester carbonyl was assigned by the signal around 161-164ppm and amide group at 166 ppm.[26, 27] This shows the incorporation of all the three monomers in the polymer backbone.

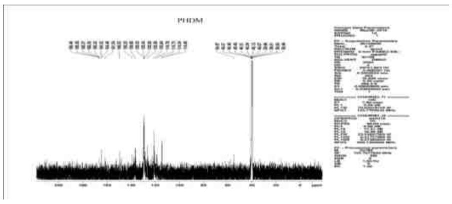


Fig. 4: ^{13}CNMR spectrum of PHDM

Table.2: Physical properties of random copolyesteramides and their IR data

S. No	Polymer code	Monomers	Yield %	Colour	η_{inh} dL/g	C=O	C=C	C=C Aromatic	CONH	N-H	C-OH	C=O Arylidene ketone
1	PHDB	PDCA+HD+DAB	63	Dark Brown	1.110	1716	-	1515	2925	1603	3368	-
2	PHDM	PDCA+HD+DADPM	68	Dark Brown	1.120	1716	-	1508	2923	1647	3336	-
3	PHHA	PDCA+HD+HMDA	52	Dark Brown	1.080	1707	-	1517	2930	1645	3309	-
4	PADM	PDCA+AD+DADPM	70	Dark Brown	1.170	1715	1592	1509	2924	1651	3363	1697
5	PAHA	PDCA+AD+HMDA	54	Dark Brown	1.090	1706	1566	1512	2930	1646	3304	1691

Phase transition of the investigated polyesteramides was found by Differential Scanning Calorimetry (DSC). The influence of random copolymerization on glass transition temperature (T_g) and melting temperature (T_m) is noteworthy and technologically important.[28] T_g is used as a measure of evaluating the flexibility of a polymer molecule and T_g along with the T_m value gives an indication of the temperature region at which a polymeric material transforms from a rigid solid to soft viscous state. This helps in choosing the right processing temperature and the temperature region in which the material can be converted into finished products through different processing techniques such as moulding, calendaring and extrusion.[29] Thermal properties deduced from DSC traces are given in Table 3. DSC thermogram of PHDB as a representative case is depicted in Fig.5.

Table.3: Thermal properties deduced from DSC traces

S.No	Polymer code	T_g ^0C	T_{k-k} ^0C	T_m ^0C	ΔH J/K
1	PHDB	112.2	-	325.1	292.7
2	PHDM	128.8	185.7	>340	-
3	PHHA	92.2	-	328.9	265
4	PADM	56.1	-	>340	-
5	PAHA	84	146.7	>340	-

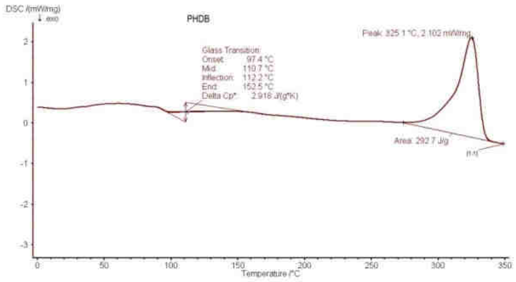


Fig. 5: DSC thermogram of PHDB

The PEAs, containing bis (3-methoxybenzylidene) moieties, have slightly lower glass transition temperatures, which is attributed to (i) The methoxy groups tend to push the neighbouring main chains further apart and thereby increase the chain mobility.[30] (ii) Usually highly crystalline polymers, possessing regular chain geometry have higher glass transition temperature.[31] The PEAs having-(CH_2)-units have comparatively regular chain geometry and show higher glass transition temperatures.

3.3. Electrical properties

A. C conductivity of the synthesized copolyesteramides has been evaluated from dielectric data, using LCR meter in accordance with the relation, [32]

$$\sigma_{ac} = \varepsilon^0 \omega \varepsilon''$$

Where $\varepsilon^0 = 8.854X10^{-24}$ $\omega = 2\pi f$

ε'' = Dielectric loss

Variation of conductance(G) and A. C conductivity(σ_{ac}) of PEA, PADM with frequency at various temperature as a representative case is shown in Fig.6 and Fig.7.

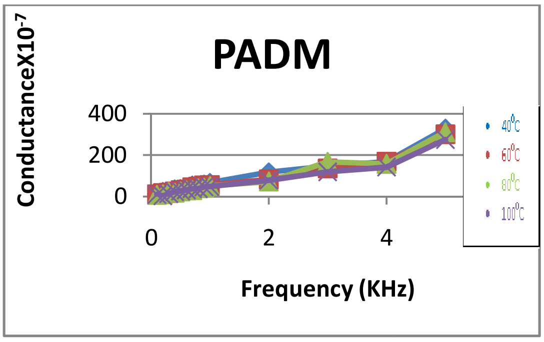


Fig.6: Variation of conductance with frequency of PADM

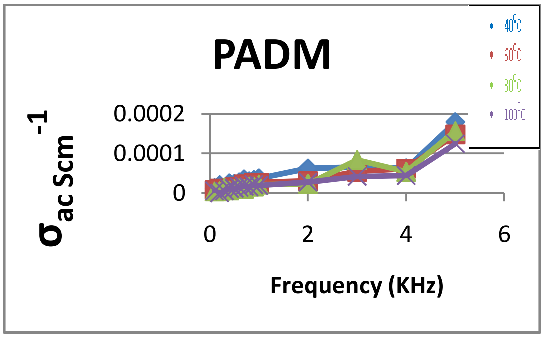


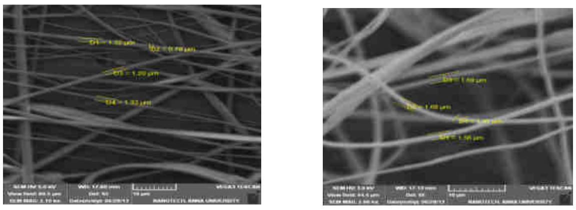
Fig. 7: Variation of A C conductivity with frequency of PADM

In the present investigation, conductivity of copolyesteramides may be attributed to the lone pair of electrons on nitrogen atom of 2, 5-pyridine dicarboxylic acid and amide groups which in turn is conjugated with benzene ring and arylidene moiety. The increase in conductance of the polymers with frequency may be due to increase in speed of mobile electrons throughout the molecule. [33, 34] This may be attributed to the fact that lone pair of electrons on nitrogen atom, which is found to be lacalised on the nitrogen of pyridine ring and also due to the presence of delocalized lone pair of electron on nitrogen atom of amide group. Hence such lone pair of electrons can move freely in the applied electric field with increase of frequency resulting increase in conductivity.

3.4. SEM studies of Polymer/PVC blend Nanofibers and their photocrosslinkability

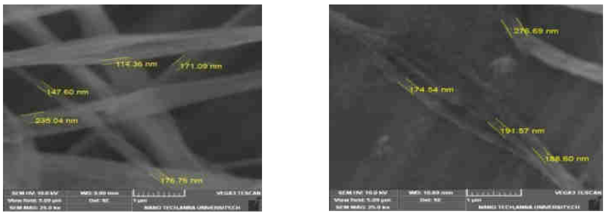
The rigid structure of aromatic polymers reduces solubility of the polymers in most organic solvents that affects the formation of polymer solution and processability, which diminishes its applicability. Such defects were rectified and processability was enhanced by blending the polymers with PVC, PVA etc. Wide range of applications of PVC due to its multi functionality attracted to choose PVC as blending polymer to prepare nanofibers by electrospinning process. Scanning Electron Microscopy was used to study the morphology of the nanofibers. The observations showed that nanofibers were smooth, well dispersed and submicron range. The photocrosslinkability of the synthesized polymers were justified by SEM photographs of Polymers/PVC blend nanofibers before and after UV irradiation. The topographical changes observed in the SEM pictures of nano fibers may be attributed to the photocrosslinking effect of C=C bonds in the arylidene units of adjacent layers. The photo reaction involving 2 +2 addition of the bis[4-hydroxy(3-methoxy benzylidene) cycloheptanone unit in the polyesteramides PADM and

PAHA result in conjoining of the chains.[35-37] The photocrosslinkability is also attributed to the flexible nature of oxybisbenzoyl unit which enhances the movement of adjacent layers for photocrosslinking. The SEM micrographs obtained from the unirradiated and irradiated electrospun PHDB/PVC and PADM/PVC blend nanofibers are shown in Fig. 8 and Fig. 9



Before UV irradiation After UV irradiation

Fig. 8: Scanning Electron Micrograph of PHDB/PVC blend Nanofibers



Before UV irradiation After UV irradiation

Fig.9: Scanning Electron Micrograph of PADM/PVC blend Nanofibers

IV. CONCLUSION

Five new random copolyesteramides PHDB, PHDM, PHHA, PADM and PAHA having photocrosslinkability and semi conducting property were synthesized successfully from 2,5-pyridine dicarboxylic acid and 2,7-bis[4-hydroxy3-methoxy(benzylidene)cycloheptanone]/ 1,6-hexanediol with three different diamines namely 1,4-diamino benzene, 4,4'- diamino diphenyl methane and 1,6-diamino hexane by direct polycondensation with diphenylchlorophosphate and characterized spectroscopically. The spectral data supported the structural assignment of the polymers. The inherent viscosity data reveals that the polymers have high molecular weight. Presence of arylidene moiety and aliphatic linkages has positive effect on solubility of the copolyesteramides. The copolyesteramides were homogeneously blended with PVC to enhance the properties like processability and tensile strength. The photocrosslinkability of the polymer /PVC blend nanofibers were investigated by UV irradiation technique. The topographical changes of the fibers were predicted by Scanning Electron Microscopy. The electrical conductivity of the polymers were predicted by dielectric measurements using LCR meter and increase in conductivity of the polymers with frequency at different temperatures reveal semi conducting property of the polymers and this property can be increased by doping techniques. Thus the synthesized polymers having photocrosslinking and semiconducting property could be useful in electrochemical devices and photoactive sensors.

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