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Studies On Electrical Conductance Of Novel Random Copolymers And Photocrosslinking Efficacy Of Their Blend Nanofibers

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Abstract

A series of novel random copolymers with oxygen bridges were prepared from4,4'-oxybisbenzoicacid and 1,6-hexandiol/arylidenediol with varying diols namely, 1,8-dihydroxyanthraquinone, 4,4'-dihydroxydiphenyl and 4,4'-diamino diphenyl -methane using diphenylchlorophosphate as the condensation agent. Their structural features were investigated by viscosity measurements, FTIR, ^{1}HNMR and ^{13}CNMR spectral data and thermal behavior was established by Differential Scanning Calorimetry (DSC) and Hot Stage Optical Polarised Microscopy (HOPM). The synthesized polymers/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 polymers were studied at different temperatures using LCR meter. The synthesized polymers with such unique properties are expected to be of use in electrochemical devices and sensors.

Key words: Nanofibers, Semi conducting, Electro spinning, Dielectric, Frequency

1. INTRODUCTION

Polymers are very attractive materials that can be tailored for specific needs and functionalities. Based on their chemical structure, they can for instance be made electrically insulating, semi conducting or conducting with specific mechanical properties. Polymer electrolytes have received considerable attention because of their potential applications in solid-state batteries, chemical sensors and electrochemical devices [1-3]. These polymer electrolytes have to satisfy several requirements, including high ionic conductivity, good mechanical properties and excellent electrochemical stability. Several methods, such as copolymerization, plasticization, blending and addition of ceramic fillers have been used to modulate conductivity of the polymer electrolytes. Among the above, blending of polymers is a useful tool to develop new polymeric materials with improved mechanical stability. Main advantages of the blend system are simplicity of preparation and ease of control of physical properties by compositional change [4-13]. The present investigation is to focus on the synthesis and characterization of novel random copolymers with photocrosslinkability and electrical conductivity containing arylidene/ n-hexane moiety in the main chain and study of their PVC blend nanofibers.

2. EXPERIMENTAL

2.1. Materials and Methods

2.1.1. Materials

Vanillin(99%), 4,4’-oxybisbenzoic acid(99%),cycloheptanone(99%), 1,6-hexanediol(99%),1,8-dihydroxyanthroquinone(99%), 4,4’-dihydroxydiphenyl (99%), hexamethylenediamine(99%), p,p’-diaminodiphenylmethane(99%) and diphenylchlorophosphate(DPCP)(99%) were purchased from Sigma Aldrich and used as supplied. Lithium chloride anhydrous(Merck, India)was dried at 130^0 C under vacuum for 4 hours and at 180^0 C for 10 hrs. Other solvents pyridine, dimethyl sulphoxide, methanol, N, N-dimethylformamide, N,N-dimethylacetamide and tetrahydrofuran were distilled before use.

2.1.2 Synthesis of Monomer-Arylidenediol

Arylidenediol was synthesized by a [14, 15] procedure as reported elsewhere. The scheme of synthesis of bis[4-hydroxy(3-methoxy benzylidene)cycloheptanone(ADCH) is described as a representative case. A mixture of 18.5g (0.15mol) 4-hydroxy 3-methoxy benzaldehyde and 7.36g (.075mol) cycloheptanone were dissolved in 75ml of dry methanol and maintained in ice cold condition. To this mixture, catalytic amount of con.sulphuric acid was added slowly drop by drop and kept as such for 24 hrs. The product is filtered, washed several times with distilled water and dried. The crude monomer was recrystallised twice from methanol to yield yellowish white crystals. Yield was 80%. FT –IR (KBr): 1650(C=O) of cycloheptanone, 3233(OH) and 1592 cm^{-1} (C=C).

2.1.3. Synthesis of polymers

Polymers were synthesized by the direct polycondensation of two differentdiols/one diol andone diamine with one dicarboxylic acid in the respective mole ratio 1:1:2 using diphenylchlorophosphate in pyridine [16-18]. A typical procedure for the synthesis of random copolyester OADA is as follows.

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 120ºC for 20 min. To this mixture, 0.95g (2.5 mmol) of diol ADCH in 5 ml pyridine and 0.27g (2.5 mmol) of diol DHA in 5 ml pyridine were added drop wise simultaneously at 120 ºC 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/methanol (1:1, v/v). The product was filtered, washed with hot methanol and dried in vacuum oven at 50 ºC.

2.1.4. Preparation of Polymer Blend Nanofiber by Electrospinning 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 0.6g 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.

2.2. 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

3. RESULTS AND DISCUSSION

All the Polymers were synthesized by the direct polycondensation of diacid and diol/diamine monomers using DPCP as the condensing agent. This method avoided the tedious preparation of acid derivatives. The time required for the polymerization is only 3hr. 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 ether group in the main chain and arylidene keto moiety of the polymer enhances the solubility in organic solvents and hence facilitates processing [19].The inherent viscosities (η_{inh}) were found to be in the range of 1.005- 1.088 dl/g as listed in Table 1. The results indicated that the synthesized polmers have high molecular weight.

The representative FT-IR spectrum of polyester OHDA and OAHA are shown in Fig.1

Table 1

Physical properties of random co polymers and their IR data

Polymer code	Monomers	Yield %	η_{inh} dl/g	FTIR Data (cm^{-1})				
				-CONH-	-C=O stretch in ester	-C=O stretch in amide	C=C	C-O-C
OHDA	OBBA+HD+DHAQ	63	1.025	-	1717	-	-	1238
OADA	OBBA+AD+DHAQ	75	1.005	-	1741	-	1595	1275
OADP	OBBA+AD+DHDP	70	1.041	-	1740	-	1595	1248
OHDM	OBBA+HD+DADM	74	1.05	2930	1703	1666	-	1252
OAHA	OBBA+AD+HMDA	69	1.088	2934	1741	1632	1596	1248

Note: OBBA-4,4'-oxybisbenzoic acid, AD- 2,7-bis[4-hydroxy 3-methoxy(benzylidene)cycloheptanone, HD- 1,6-hexanediol, DADM- p,p'-diaminodiphenylmethane, DHAQ- 1,8-dihydroxyanthraquinone, DHDP- 4,4'-dihydroxydiphenyl, HMDA- Hexamethylenediamine

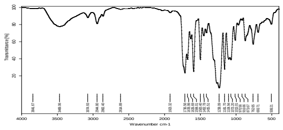
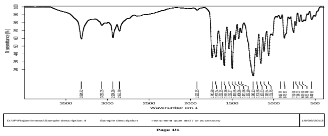


Figure 1 FT-IR spectrum of OHDA



FT-IR spectrum of OAHA

3.1. Solubility

The polymers reported here are found to be soluble in highly polar solvents, partially soluble in moderately polar solvents and insoluble in benzene, hexane and methanol. The results of the solubility of the polymers are presented in Table 2.

Table 2

Solubility of Polymers in common organic solvents

-- = Insoluble; +- = sparingly soluble; ++ = soluble

Polymer	Hexane	Benzene	CH_3OH	$CHCl_3$	THF	DMSO	DMF	DMAc	NMP
OHDA	--	--	--	--	++	++	++	++	++
OADA	--	--	--	--	+-	++	++	++	++
OADP	--	--	--	--	+-	++	++	++	++
OHDM	--	--	--	--	++	+-	++	++	++
OAHA	--	--	--	--	++	++	++	++	++

Structural units of the polymers were identified by ^{1}HNMR and ^{13}CNMR spectra. The representative ^{1}H NMR spectrum of polymers OHDA and OAHA recorded in DMSO-d6 are exposed in Fig.2 and ^{13}CNMR spectrum in Fig.3. The aromatic protons of anthraquinone moiety appeared in the region of 6.85 to 7.42 δ. The aromatic protons of OBBA units appeared in the region of 7.63-8.30 δ. A singlet at 4.668δ is assigned to the OCH_2 protons connected to the aliphatic spacer of the common diol 1,6-hexane diol. The signals at 2.5-3.9 δ show the methylenic protons of cycloheptanone in arylidene keto moiety of OAHA. The signal for the aromatic protons of dicarboxylic acid lie around 7.3-8.7 δ and a singlet at 2.65ppm is due to methylenic proton attached to N-atom. This shows the incorporation of all the three monomers in the polymer backbone.

Figure 2 ^{1}H NMR spectrum of OHDA ^{1}H NMR spectrum of OAHA

The micro structure of repeat units in the polymer chain can be identified satisfactorily using ^{13}CNMR spectra. The signal at 159-166 ppm and 192 ppm indicate the carbonyl carbon of ester and amide groups. The aromatic carbon atoms are indicated by 110-135ppm. The olefinic protons of arylidene moiety appear at 149ppm [20]. The aromatic carbon atoms are indicated by the signals in the range of 116-136 ppm. The methylenic carbon of 1, 6-hexanediol and methylenic carbons of cycloheptanone moiety appeared at 28 ppm and 65 ppm respectively.

Figure 3 ^{13}CNMR spectrum of OHDA ^{13}CNMR spectrum of OAHA

3.2. Thermal properties

The thermal transition temperature of random copolymers was investigated from DSC thermogram and hot stage optical polarized microscopy. The representative DSC thermograms and OPM pictures of OHDA and OAHA are shown in Fig. 4 and Fig. 5.

Figure 4 DSC of OHDA DSC of OAHA

Table 3

Phase transition temperature of the polymer determined by DSC

Polymer code	T_g	T_{k-k}	T_m	T_i
OHDA	95.9	-	332.5	-
OADA	70.9	-	133.3	-
OADP	45.3	139.7	205.9	180.3
OHDM	21.8	278	-	\ -
OAHA	53.4	123.6	191.7	-

The DSC thermograms revealed that the synthesized polymers undergo more than one phase transition processes, when subjected to thermal treatment. The low T_g values indicate that the polymers become soft and flexible even at low temperature which is attributed to the presence of flexible and bent -O- ether linkages causing reduced linearity of the synthesized polymers. The additional exotherm may be attributed to crystal transition which is the characteristic meson phase transition.

Figure 5 OPM micrograph of OHDA OPM micrograph of OAHA

3.3. SEM studies of 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 fibes 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 polymers

OADA, OADP and OAHA result in conjoining of the chains[21-23]. 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 OHDA/PVC and OAHA/PVC blend nanofibers are shown in Fig. 6.

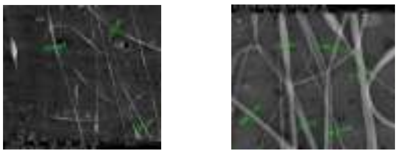
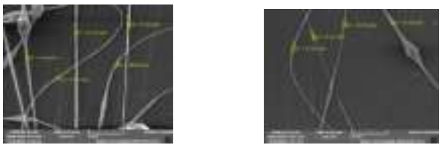

Before UV irradiation After UV irradiation

Figure 6 OHDA/PVC blend nanofibers


Before UV irradiation After UV irradiation

OAHA/PVC blend nanofiber

3.4. Electrical properties

a.c conductivity has been evaluated from dielectric data. The conductivity of the polymers may be attributed to the lone pair of electrons on Oxygen atom of OBBA, 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 [24, 25]. The variation of conductance and a.c conductivity of OADA and OHDA with frequency at different temperatures is shown in Fig.6 and Fig.7.

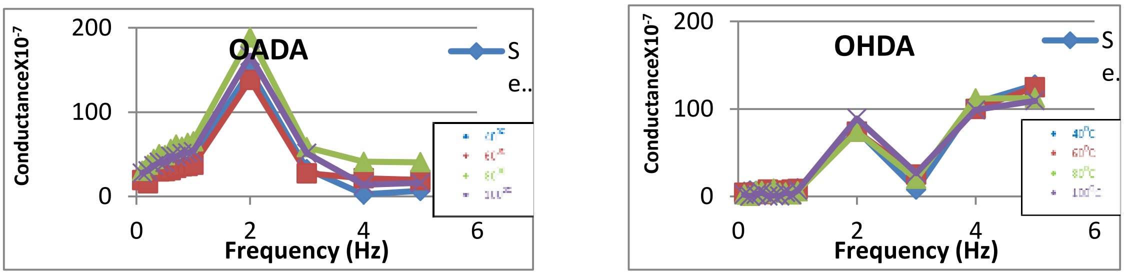


Figure 6 : Variation of conductance with frequency

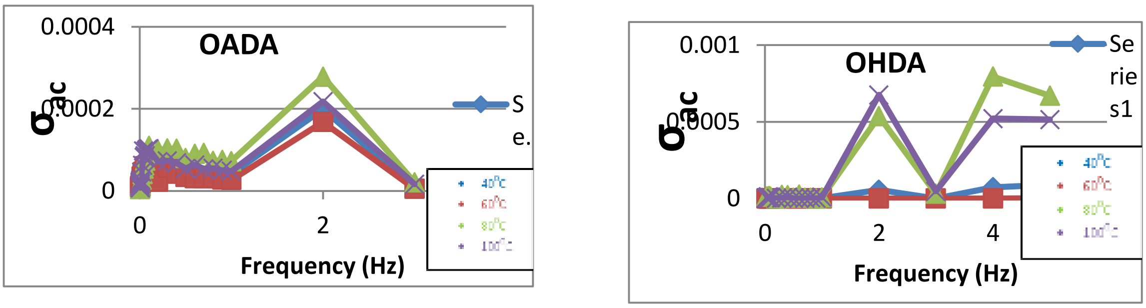


Figure 7: Variation of a.c conductivity with frequency

The polymers are showing increase in conductance with increase in frequency and a maximum conductance of $1.27x10^{-5}$S for OHDA at 40^0C ; $1.52x10^{-5}$S for OADA at 80^0C ; $1.88x10^{-5}$S for OADP at 80^0C; $1.26x10^{-5}$S for OHDM at 40^0C, $1.03x10^{-5}$S for OAHA at100^0C and a.c conductivity of $8x10^{-4}$ Scm^{-1} for OHDA at 80^0 C, $2.8x10^{-4}$ $Scm^{-1}$for OADA at80^0C, $8x10^{-5}Scm^{-1}$ for OADP at 40^0C, $1.4x10^{-4}$ Scm^{-1} for OHDM at 80^0C, $6x10^{-5}Scm^{-1}$ for OAHA at 60^0C were observed. These observations indicate that presence of more aromatic rings and chromophoric groups increase the conductivity due to extended conjugation whereas introduction of aliphatic diol and aliphatic diamine decrease the conductivity due to disruption in conjugation.

4. CONCLUSION

Five new random copolymers OHDA, OADA, OADP, OHDM and OAHA having photocrosslinkability and semi conducting properties were synthesized successfully from 4,4'- oxybibenzoic acid and 2,7-bis[4-hydroxy3-methoxy(benzylidene)cycloheptanone]/ 1,6-hexanediol with two different diols and two different diamines namely 1,8-dihydroxy anthroquinone,4,4'-dihydroxydiphenyl,4,4'-diaminodiphenylmethane and hexamethylenediamine 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 ether linkages has positive effect on solubility of the copolymers. The copolymers 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 reveals semi conducting property of the polymers and this property can be increased by doping techniques. Thus the synthesized polymers having photocrosslinking and semi conducting property could be useful in electrochemical devices and photoactive sensors.

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