

SYNTHESIS OF CERTAIN RANDOM COPOLYMERS CONTAINING ARYLIDENE DIOL MOIETY AND STUDIES ON THEIR ANTIBACTERIAL ACTIVITY AND PHOTOCROSSLINKING EFFICACY OF BLEND NANOFIBERS

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Abstract- The innovative applications of photocrosslinkable polymers with antibacterial activity, motivated the synthesis of novel random copolyesters/esteramide by the direct polycondensation of 4, 4'-oxybisbenzoic acid and Arylidenediol with 1,8-dihydroxyanthraquinone/4,4'-dihydroxydiphenyl/ 1,4-cyclohexanediol/ hexamethylenediamine in pyridine/LiCl solution using diphenylchlorophosphate as the condensation agent. Their structural features were investigated by viscosity measurements, FTIR, ¹HNMR and ¹³CNMR spectral data and thermal behavior was established by Differential Scanning Calorimetry and Hot stage Optical Polarized Microscopy. 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 before and after UV irradiation were predicted by Scanning Electron Microscopy. Nutrient Agar plates were used to measure the inhibitory activity of the synthesized polyesters/esteramide against pathogenic bacteria. It is anticipated that the synthesized antibacterial and photocrosslinkable polymers might be of promising candidates for biomedical applications and biological water treatment.

Keywords- Antibacterial, Arylidenediol, Electrospinning, Nanofibers, Photocrosslinkable, Polycondensation

I. INTRODUCTION

Polymer chemistry touches many scientific disciplines and is vital in fields that develop products such as plastics and synthetic fibers, agricultural chemicals, paints, adhesives and biomedical applications such as artificial skin, prosthetics and nicotine patch. Recent uptrend in polymer blend research and notably high surface area, small pore size and large pore volume of nanofibers [1] lend many innovative applications such as wound care, filtration, fuel cells and countless others which has attracted considerable attention in the research field because of their interesting mechanical, electrical and optical properties. Presence of photocrosslinkable/ photosensitive moieties like azopolyesters, arylidene esters, arylidene ketones, siloxanes, cinnamate esters and acrylate esters in the polymer backbone [2]-[8] enhance photocrosslinkability of the polymers whereas polymers having photodimerizable groups find applications in immobilization of enzymes[9]-[14]. The residual toxicity associated with biocidal polymers rectify the problems result from the use of conventional antimicrobial agents, which has fascinated the idea of polymeric antimicrobial agents[15]-[17] because of their interesting

advantages of non-volatility, chemical stability, difficulty to permeate through skin of man or animal and minimize environmental problems[18]-[29].

The present investigation is to focus on the synthesis and characterization of novel random photocrosslinkable copolyesters/esteramide with antibacterial efficacy containing arylidene moiety in the main chain and study of their PVC blend nanofibers. The polymers were synthesized by the direct polycondensation of one diacid and two diols/ one diacid, 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°C.

II. MATERIALS AND METHODS

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

A. Synthesis of Monomer- Arylidene diol [30],[31]

Arylidene diol was synthesized by a procedure as reported elsewhere. A mixture of 18.5g (0.15mol) 4-hydroxy 3-methoxy benzaldehyde and 8.4g (0.075mol) 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).

B. Synthesis of Polymers[32]

Polyesters/ polyesteramide were synthesized by the direct polycondensation of two diols/one diol and one diamine with one dicarboxylic acid in the respective mole ratio 1:1:2 using diphenylchlorophosphate in pyridine. 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 m mol) 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, 0.95g (2.5 mmol) of diol ADCH in 5 ml pyridine and 0.6g (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/methanol (1:1, v/v). The product was filtered, washed with hot methanol and dried in vacuum oven at 50 °C.

C. Antimicrobial Studies

The agar diffusion method was followed for antimicrobial susceptibility test. Petri plates were prepared by pouring 10ml of Muller Hinton Agar for bacteria and allowed to solidify. These agar plates were inoculated with 0.1ml of standardized bacterial suspension and uniformly spread. A 6mm well was cut and filled with 10% DMSO of synthetic compounds. A well filled with 10% DMSO served as control. The diameter of the inhibition zone observed around the well was measured for each bacterium. After 48hrs of incubation at 37⁰ C the antimicrobial activities of the polymers were tested against different human pathogens namely Escherichia coli, Staphylococcus aureus, Klebsiella pneumonia, Vibrio cholera and Bacillus cereus.

D. Preparation of Polymer Blend Nanofibers by Electrospinning Process

Blending the synthesized PEs and PEA 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 PEs/ PEA was added and stirring continued for 20 min. The solution was removed and placed in an ultrasonicator. It 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 nonwoven form were collected on an aluminum foil.

E. Characterization of Random Copolymers and Polymer Blend Nanofibers

Infrared spectra were recorded by Perkin Elmer FT-IR 240-c Spectrophotometer using KBr pellet from 450 cm⁻¹ to 4500 cm⁻¹. The solubility of the polymers was determined using 0.005g of the polymer in 1ml of the solvent. The inherent

viscosities (η_{inh}) of the polymers were determined by Ubbelohde viscometer in DMSO solution. 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 ¹H NMR spectra were recorded on a Joel FT-NMR AL 300MHz spectrometer operating at 300 MHz in DMSO-d₆ solvent and with TMS as internal reference. The optical textures were examined on a hot stage optical polarizing microscope. Antimicrobial susceptibility test was done by agar diffusion method. 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 done by recording UV-Visible spectra of the copolyesters/esteramide solution in DMSO solution at regular time intervals.

III. 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 the Higashi method [33]. 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 [34]. The inherent viscosities (η_{inh}) were found to be in the range of 1.005-1.088 dl/g as listed in Table I. The results indicated that the synthesized polymers have high molecular weight. The representative FT-IR spectrum of polyester OADA and polyesteramide OAHA are shown in Fig.1

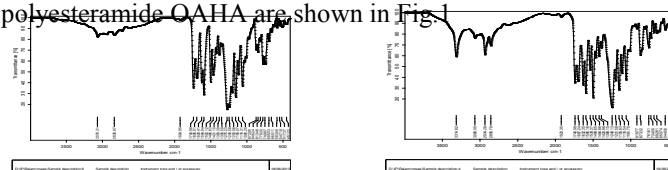


Fig. 1 a. FT-IR spectrum of OADA b. FT-IR spectrum of OAHA

Table II

Polymer code	Monomers	Yield %	η_{inh} dl/g	FTIR Data (cm ⁻¹)			
				CONH	C=O	C=C	C-O-C
OADA	OBBA+AD+DHAQ	75	1.005	-	1741	1595	1275 1156 1060
OADP	OBBA+AD+DHPD	70	1.041	-	1740	1595	1248 1157 1061
OACH	OBBA+AD+CHD	73	1.02	-	1740	1595	1248 1155 1062
OAHA	OBBA+AD+HMDA	69	1.088	2934	1741	1596	1248 1156 1062

Note: OBBA-4,4'-oxybisbenzoic acid, AD-2,7-bis[4-hydroxy-3-methoxy(benzylidene) cycloheptanone], DHAQ-1,8-dihydroxyanthraquinone, DHPD- 4,4'-dihydroxydiphenyl, CHD- 1,4-cyclohexanediol, HMDA-Hexamethylenediamine.

A. Solubility

The polymers reported here are found to be soluble in highly polar solvents, partially soluble in moderately polar solvents and insoluble in non-polar solvents. The results are presented in Table II.

The chemical repeat unit in the synthesized polymers was identified by ¹H and ¹³C NMR spectra. The representative ¹H and ¹³C NMR spectra of OADA and OAHA recorded in DMSO are exposed in Fig 2 and Fig 3. The ¹H NMR spectrum presented in Fig.2 indicate that the signals at 2.5-3.9 ppm show the methylenic protons of cycloheptanone in arylidene keto moiety of OADA and OAHA. The signal for the aromatic protons of dicarboxylic acid lie around 7.3-8.7 ppm and a signal at 2.65 ppm is due to methylenic proton attached to N-atom.



Fig. 2 a. ¹H NMR spectra of OADA b. ¹H NMR spectra of OAHA

The micro structure of repeat units in the polymer chain can be identified satisfactorily using ¹³C NMR spectrum. The signal at 156-164 ppm and 192 ppm indicate the carbonyl carbon of ester and amide groups. The aromatic carbon atoms are indicated by 110-135 ppm. The olefinic protons of arylidene moiety appear at 149 ppm [35].



a. ¹³C NMR spectra of OADA b. ¹³C NMR spectra of OAHA

Fig.3

Solubility of Polymers in common organic solvents
 -- = Insoluble; +- = sparingly soluble; ++ = soluble

Polymer	Hexane	Benzene	CH ₃ OH	CHCl ₃	THF	DM SO	DMF	DM Ac	NMP
OADA	--	--	--	+-	+-	++	++	++	++
OADP	--	--	--	--	+-	++	++	++	++
OACH	--	--	--	--	++	++	++	++	++
OAHA	--	--	--	--	++	++	++	++	++

B. Thermal Properties

The thermal transition temperature of random copolymers was investigated from DSC thermogram and hot stage optical polarized microscopy. The representative DSC thermograms of OADA, OADP, OACH and OAHA are shown in Fig 4 and the data in Table III.

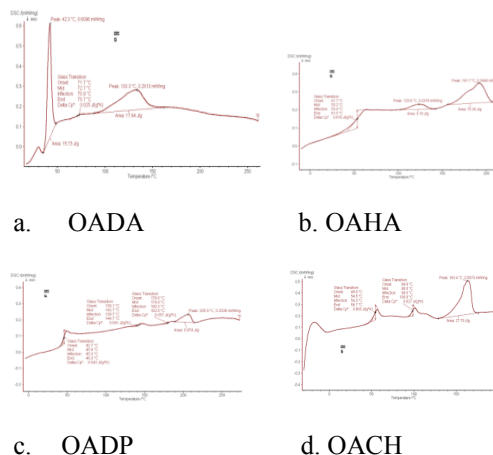


Fig. 4 DSC traces

Table III
 Phase transition temperature of the polymer determined by DSC

Polymer code	T _g	T _m	T _{cl}	T _i
OADA	70.9	-	133.3	-
OADP	45.3	139.7	205.9	180.3

OACH	54.3	98	163.4	-
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 of the synthesized polymers revealed that the polymers become soft and flexible 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 mesophase transition. The OPM pictures are shown in Fig 5.

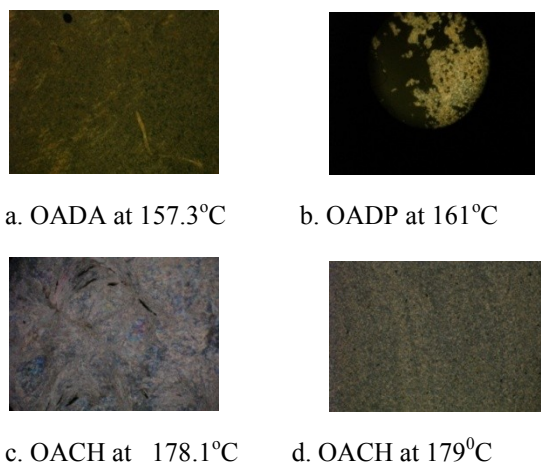


Fig. 5 OPM photographs

C. SEM studies of Nanofibers

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 multifunctionality attracted to choose PVC as a 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.

D. Photocrosslinking Studies

A potential photoactive group such as arylidene keto moiety undergoes photocrosslinking on UV irradiation. The synthesized polymers were tested for their photocrosslinkability by UV irradiation of the polymers in DMSO solution at regular time intervals successfully. The photocrosslinkability of the polymers were accounted to be due to $\pi-\pi^*$ transition of the exocyclic double bond of bis[4-hydroxy(3-methoxy benzylidene)cycloheptanone 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 [36]. The

photocrosslinkability is also attributed to the flexible nature of oxybisbenzoyl unit which enhances the movement of adjacent layers for photocrosslinking. A representative picture of OADA is shown in Fig 6.

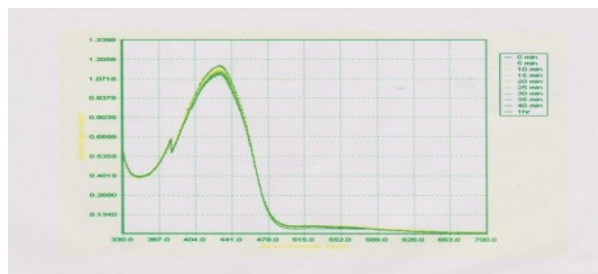


Fig. 6 Photocrosslinking effect of OADA in DMSO on UV irradiation

The photocrosslinkability was also justified by SEM photographs of Polymers/PVC blend nanofibers before and after UV irradiation. The topographical changes observed in the SEM pictures of nanofibers may be attributed to the photocrosslinking of C=C bonds in the arylidene units of adjacent layers. The photo reaction involving $2\pi+2\pi$ addition of the bis[4-hydroxy(3-methoxy benzylidene)cycloheptanone unit in the polymers result in conjoining of the chains [37]. The SEM micrographs obtained from the unirradiated and irradiated electrospun polymers/PVC blend nanofibers are shown in Fig 7

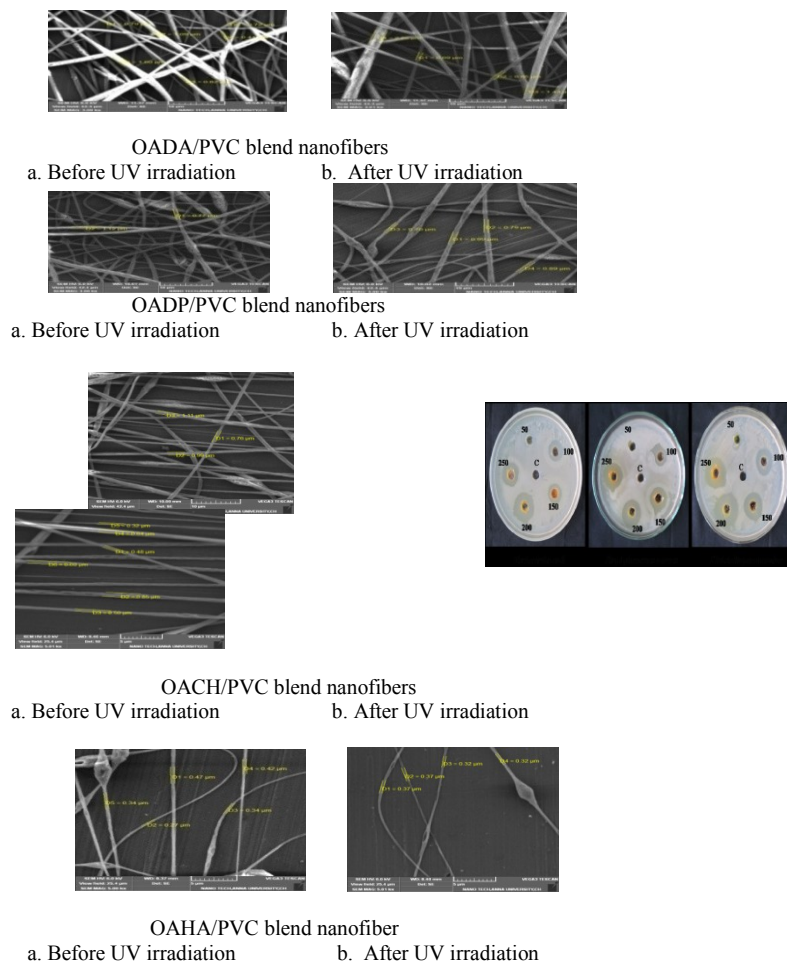


Fig. 7 Scanning Electron Micrographs

E. Antibacterial Assessment

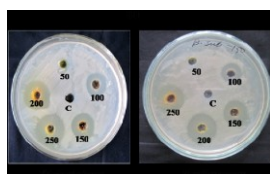
Antibacterial activities of the synthesized polymers were tested against five different human pathogens namely Escherichia coli, Staphylococcus aureus, Klebsiella pneumonia, Vibrio cholera and Bacillus cereus. Nutrient Agar plates in different concentrations were used to measure the inhibitory activity of the polymers by using DMSO as the solvent. The results were summarized in Table 4 and a representative picture of OADA is shown in Fig 8.

Table IV

Inhibition effects of random copolyesters/esteramide on the growth of pathogenic bacteria

P o l y m e r c o d e	E.Coli		S. Aureus		K. Pneumoniae				V. Cholerae			B. Cereus			
	Concentration - mg/ml										Zone of inhibition in diameter(mm)				
	50	100	150	50	100	150	50	100	150	50	100	150	50	100	150
O A D A	9.1	10.5	11.7	11.2	13.5	14.6	10.3	11.5	12.6	9.8	10.6	11.3	9.3	10.5	11.6
O A D P	8.2	9.4	10.7	9.1	10.3	11.6	6.1	7.2	8.5	7.2	8.6	9.8	7.8	8.9	10.1
O A C H	9.6	10.2	11.5	11.1	12.9	13.8	6.3	7.1	8.4	6.9	7.4	8.5	8.1	8.9	9.6
O A H A	2.1	2.7	3.1	1.8	2.1	2.5	2	2.5	3	1.7	2.3	2.7	1.8	2.4	3.1

The antibacterial activity of the synthesized polymers was due to the presence of ether linkage in oxybis(benzoyl) moiety which enhanced the antibacterial activity and also because of methoxy group in vanillin. It is interesting to note that the antibacterial activity of copolyesters was found to be higher than that of copolyesteramide[38],[39], which is justified that the introduction of amide group reduces the antibacterial activity of the polymers.



a,E.coli b.S. aureus c. K. Pneumoniae d. V. Cholerae e. B. Cereus
Fig. 8 Antibacterial activity of random copolyester OADA

IV. CONCLUSION

Four new random copolyesters OADA, OADP, OACH and copolyesteramide OAHA having photocrosslinking and antibacterial activity were synthesized successfully from 4,4'-oxybisbenzoic acid and 2,7-bis[4-hydroxy-3-methoxy-(benzylidene)cycloheptanone] with three different diols and a diamine namely 1,8-dihydroxy anthraquinone, 4,4'-dihydroxy diphenyl, 1,4-cyclohexanediol 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. Presences of arylidene moiety and ether linkages have 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 and the same effect was observed by UV irradiation of the polymers in DMSO solution at regular time intervals. The antibacterial efficacies of the polymers were investigated in different human pathogens using diffusion method. These observations suggest that the synthesized polymers could be useful in optical device technology, biomedical applications and biological water treatment.

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