



## Fabrication and Characterization of Polyvinyl Chloride/Copolyester/Nanoclay Composite Nanofiber

S. JASMINE<sup>1,\*</sup>, D. REUBEN JONATHAN<sup>2</sup>, J. SIDHARTHAN<sup>3</sup> and D. ROOPSINGH<sup>4</sup>

<sup>1</sup>Department of Chemistry, Rajalakshmi Engineering College, Thandalam, Chennai-602105, India

<sup>2</sup>Department of Chemistry, Madras Christian College, Tambaram, Chennai-600059, India

<sup>3</sup>Department of Chemistry, V.O. Chidambaram College, Tuticorin, Chennai-628008, India

<sup>4</sup>Department of Chemistry, Presidency College, Chennai-600005, India

\*Corresponding author: E-mail: jasfranc7@gmail.com

Received: 26 April 2021;

Accepted: 7 June 2021;

Published online: 26 July 2021;

AJC-20440

Four random copolyesters were prepared by the polycondensation reaction of diols namely 1,5-dihydroxyanthraquinone, 4,4'-oxybis(benzoic acid) and variable chalcone diol. Four chalcone diols were produced by acid catalyzed Claisen-Schmidt reaction at room temperature. These random copolyesters were elucidated by solubility tests and viscosity measurements. The FT-IR, <sup>1</sup>H & <sup>13</sup>C NMR techniques were applied to establish the repeating units present in the copolyester backbone. Electrospinning method was employed to derive polyvinyl chloride-copolyester-nanoclay composite nanofiber from tetrahydrofuran medium. Scanning electron microscopy (SEM) was utilized to examine the morphology of the nanofibers. These composite nanofibers are expected to be a potential biomaterial of greater significance.

**Keywords:** Chalcone, Polyvinyl chloride, Copolyesters, Viscosity, Nanofibers.

### INTRODUCTION

Nowadays, the rapid development of nanotechnology created a big forum for the industries in the fabrication of numerous nanostructured materials such as nanofibers, nanowires, nanotubes and nanorods. Among these 1D nanostructured materials, nanofibers are very smart materials [1] because of its uniqueness such as large surface area per unit mass, film thinness, nanofiber diameter of less than 100 nm, small pore size and lighter weight. Shi *et al.* [2] revealed that nanofiber materials synthesized via electrospinning method have number of advantages such as high photoelectric conversion efficiency, the maximum light absorption and hence utilized in the photovoltaic cells, Hydrogen oxygen fuel cells, nano generators, hydrogen generation and lithium ion batteries (LIB) and super capacitors devices. Huang *et al.* [3] has suggested that electrospinning is an efficient method in the production of polymer nanofibers. Caracciolo *et al.* [4] highlighted that polymer based nanofibers fabricated by electrospinning have numerous applications in the drug delivery of therapeutic agents, bioactive materials, tissue engineering scaffolds, sensors and for other biomedical applications because of its porous nature. Sun *et al.* [5] found that composite nanofiber fabrics have shown excellent antimicrobial activity.

Nguyen *et al.* [6] reported that nanofibers scaffolds can be used in tissue/organ failures treatment, in bone, cartilage, skin, heart and blood vessels rejuvenation, in the fabrication of higher sensitivity nanofibers for sensors, photovoltaic cells, lithium ion batteries, respectively. Allen & Cullis [7] reported that polymer-based nanoparticles can enhance the pharmacological and therapeutic properties of drugs that can be administered parentally.

Polymer nanofibers synthesized by electrospinning have been expected for soft tissue prosthetic applications such as blood vessel, vascular, breast, *etc.* [8-11]. Polymer nanofibers also used in the ailment of wounds or burns of human skin and in designing haemostatic devices with some distinctive characters [12-14]. Electrospun polymer nanofibers have been used in skin healing, skin cleansing, possessing therapeutical properties with or without additives [15]. Kenawy *et al.* [16] investigated the fibrous delivery matrices of poly(ethylene-co-vinyl acetate), poly(lactic acid) and their blends. Kim & Lee [17] elucidated the thermal properties of pure polyethyl terephthalate nanofiber and polyethylnaphthalate polymers and PET/PEN blends.

Sathish *et al.* [18] fabricated nanofibers using thermotropic liquid crystalline copolyesters. Waters *et al.* [19] have thrown

reported the progress of a LC device of optical shutter with the help of electrospun nanofibers. Rajam & Roopsingh [20,21] have shown that antimicrobial efficacy of photocrosslinkable copolyesters. Jeong *et al.* [22] synthesized biodegradable electrospun nanofibers composed of photo-crosslinkable alginate, which shows a great impact in wound soothing and tissue rejuvenation. Jeon *et al.* [23] developed the photocrosslinked HP-ALG hydrogel system, for the tissue engineering and regenerative medicine. Jin *et al.* [24] synthesized photo-crosslinked electrospun chitosan based biocompatible nanofibers scaffolds, which can be used as a promising material for the artificial blood vessels. Therefore, in present work, the fabrication and of polyvinyl chloride/copolyester/nanoclay composites nanofibers by electrospinning method is carried out and studied their morphology before and after UV irradiation.

## EXPERIMENTAL

The chemicals *viz.* vanillin and 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, 3-methoxy 4-hydroxyacetophenone, diphenylchlorophosphate (DPCP), 1,5-dihydroxyanthraquinone, 4,4'-oxybis(benzoic acid) (Aldrich), sulphuric acid and lithium chloride (Merck) were procured and used as such. The solvents *e.g.* methanol, ethanol, acetone, chloroform, hexane, dimethyl acetamide (DMAc), tetrahydrofuran (THF) were of AR grade and used as received.

Various solvents were used to determine the solubility of the copolyesters. Ubbelohde viscometer is used to find out the viscosity ( $\eta_{inh}$ ) of the copolyesters using DMAc at 30 °C. The IR spectrum was recorded using Shimadzu Fourier transform infrared instrumentation setup. The BRUKER AV III 500 MHz NMR instrument was involved in recording the  $^1\text{H}$  &  $^{13}\text{C}$  NMR spectrum in DMSO- $d_6$ . Hitachi S-4800 SEM instrument was used to record the SEM micrographs of the copolyester/PVC and copolyester/PVC/nanoclay.

**Synthesis of chalcone diols:** Chalcone diols such as (2E)-1,3-bis-(4-hydroxyphenyl)-prop-2-en-1-one (BHPP), (2E)-1-(4-hydroxyphenyl)-3-(4-hydroxy-3-methoxyphenyl)-prop-2-en-1-one (HMPP), (2E)-1-(4-hydroxy-3-methoxyphenyl)-3-(4-hydroxyphenyl)-prop-2-en-1-one (HMHP) and (2E)-1,3-bis-(4-hydroxy-3-methoxyphenyl)-prop-2-en-1-one (BHMP) were synthesized as reported by Sathya *et al.* [25] and the typical procedure is shown in **Scheme-I**.

**Preparation of BHPP:** In a 250 mL round bottom flask, about 5 g (0.04 mol) of 4-hydroxy benzaldehyde and 5.57 g (0.04 mol) of 4-hydroxy acetophenone were dissolved in 100 mL of absolute ethanol. Dry HCl gas was passed into the reaction mixture with constant stirring for 1 h. Then, the mixture was

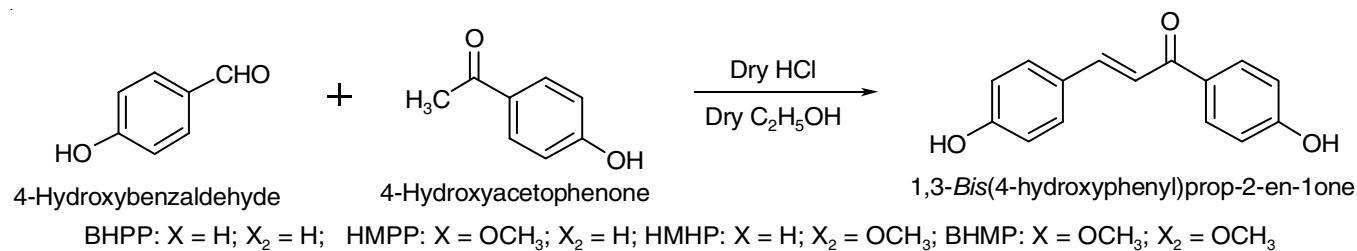
mixed into 200 mL ice cold water, which resulted in the precipitation of yellow coloured crystalline substance of BHPP. It was filtered, purified with distilled water and warm alcohol. Yield: 90%, m.p.: 183.2 °C; IR (KBr,  $\nu_{max}$ ,  $\text{cm}^{-1}$ ): 3301 (b, O-H), 1648 (s, C=O);  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 9.9 ppm (s, 2H, -OH), 7.4-8.4 ppm (m, 8H, aryl ring), 6.7-6.9 ppm (dd, 2H, -CH=CH-); MS (EI)  $m/z$  240  $[\text{M}]^+$ .

**Preparation of copolyesters:** Preparation of copolyester was carried out by polycondensation method with DPCP as a condensing agent [26,27]. Diphenylchlorophosphate (12 mmol) was added to a solution containing LiCl (10 mmol) and 4,4'-oxybis (benzoic acid) (5 mmol) taken in a round bottom flask. At room condition, the mixture was agitated consistently for about 0.5 h. Temperature was increased to 120 °C and stirring was maintained in this elevated temperature for 10 min. After this time frame, the solution containing BHPP (2.5 mmol) and 1,5-dihydroxyanthraquinone (DHQ) (2.5 mmol) was added with steady stirring. The mixture was maintained at the same temperature about 3 h. Then, it was cooled to room conditional temperature and discharged into 200 mL methanol which resulted in the formation of precipitate (**Scheme-II**). The precipitate was filtered, purified with adequate quantity of methyl alcohol and finally dried in air. The details of diols and dicarboxylic acid used in the synthesis of copolyesters PADO, PBDO, PCDO, PDDO are given in Table-1.

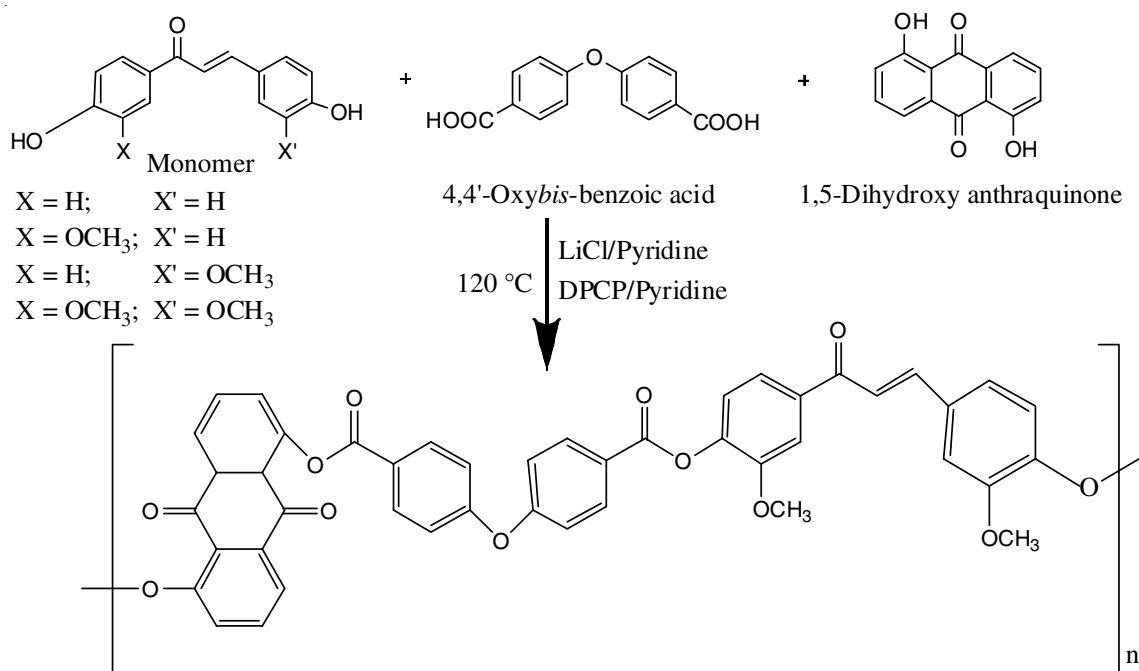
## Synthesis of polymer composite nanofiber

**Preparation of blend solution:** The blend solution was prepared by taking 0.9 g of poly(vinyl chloride), 0.3 g of PDDO and 7 mL of tetrahydrofuran in 10 mL closed flask and agitated for a span of 2 h. Then it can rotate in an ultrasonic bath about 1 h to make sure that the copolyester and the PVC were well spread in THF medium. At last, agitating for a time frame of 24 h was carried out by making use of a magnetic stirrer.

**Preparation of blended nanofibers:** The homogenous blended solution was transferred to a 5 mL syringe and electrical potential was applied to the blended solution through the needle attached with the syringe. When electrical potential of 22 kV was applied, solution jet was obtained due to the electrostatic force. The amount of flow of the solution was adjusted with the help of computer controlled injection system, about 0.4 mL/h. The needle tip and the collector should be at the distance of 10 cm and the drum accumulator rotates at the rate of 1800 rpm. The PDDO/PVC nano fibers obtained in a nonwoven form, allowed to collect on an aluminium foil. The same procedure was employed to produce the copolyester/PVC/nanoclay on an aluminium foil.



**Scheme-I:** Typical procedure adopted for the synthesized chalcone diols



Scheme-II: Typical procedure adopted for the synthesized copolyesters

TABLE-1  
MONOMERS USED, COPOLYESTERS CODE AND STRUCTURE

Copolyester code	Monomers used	Possible copolyester structure
PADO	BHPP, 1,5-dihydroxy anthraquinone, 4,4'-oxybis-benzoic acid	
PBDO	HMPP, 1,5-dihydroxy anthraquinone, 4,4'-oxybis-benzoic acid	
PCDO	HMHP, 1,5-dihydroxy anthraquinone, 4,4'-oxybis-benzoic acid	
PDDO	BHMP, 1,5-dihydroxy anthraquinone, 4,4'-oxybis-benzoic acid	

## RESULTS AND DISCUSSION

**Solubility studies:** Solubility results of the prepared copolyesters in various organic solvents are given in Table-2.

Copolyesters were found to be soluble in aprotic solvents like DMAc, DMF, DMSO, THF, however partially soluble in ODCB,  $\text{CHCl}_3$  and acetone. It was insoluble in solvents like methanol, ethanol, 2-propanol, benzene, toluene, xylene and hexane.

TABLE-2  
SOLUBILITY STUDY OF COPOLYESTERS IN VARIOUS ORGANIC SOLVENTS

Code	Copolyesters											
	CH <sub>3</sub> CN	DMF	DMSO	DMAc	THF	ODCB	EtOAc	CHCl <sub>3</sub>	Acetone	CH <sub>3</sub> OH	C <sub>6</sub> H <sub>6</sub>	Hexane
PADO	++	++	++	++	+-	+-	+-	+-	+-	--	--	--
PBDO	++	++	++	++	++	+-	+-	+-	+-	--	--	--
PCDO	++	++	++	++	++	+-	+-	+-	+-	--	--	--
PDDO	++	++	++	++	++	+-	+-	+-	+-	--	--	--

Furthermore, it was inferred that copolyesters having methoxy groups in the chalcone moiety had greater solubility than those without methoxy group, which might be ascribed to the electron releasing ability of the methoxy group, caused the disruption in the macromolecular chain and thus enhance the easy penetration of solvent molecule into the polymer chain.

**Viscosity measurements:** The inherent viscosity ( $\eta_{inh}$ ) values of the synthesized four copolyesters were determined at 30 °C using Ubbelohde viscometer in DMAc solution. The inherent viscosity values of the copolyesters were about 0.73 dL/g and 1.1 dL/g, respectively (Table-3). These values indicate that these copolyesters are relatively high molecular weight polymers. The copolyesters having one or two methoxy substituent in the aromatic ring exhibit higher viscosity than those of the copolyesters without methoxy substituent. This trend might be ascribed to the interlocking effect exhibited by the methoxy substituents as well as the aromatic rings in the polymer chain [28].

TABLE-3  
SYNTHESIZED COPOLYESTERS INHERENT VISCOSITY

Code	Chalcone diol used	$\eta_{inh}$ (dL/g)
PADO	BHPP	0.73
PBDO	HMPP	0.86
PCDO	HMHP	0.92
PDDO	BHMP	1.10

**Spectral studies:** The FT-IR spectrum of PBDO copolyester is represented in Fig. 1. IR spectra of the four copolyesters

were also obtained. All the copolyesters have shown strong absorption bands due to carbonyl stretching vibration of ester between 1746 and 1730 cm<sup>-1</sup>. The ketonic carbon stretching vibration due to the presence of chalcone and anthraquinone moiety is observed between 1678 and 1675 cm<sup>-1</sup>. The absorption peaks at 1415-1500 cm<sup>-1</sup> are attributed to the C=C stretching vibrations of the ethylene double bonds and aromatic moiety. The absorption peak in the range of 1063-1021 cm<sup>-1</sup> is assigned to -C-O-C- group.

The proton NMR spectrum of PBDO copolyester is shown in Fig. 2. The peaks at  $\delta$  10.1 ppm is attributed to the end phenolic protons. The multiple signals appear between  $\delta$  8.00-8.89 ppm indicates the aromatic protons of chalcone, 4,4'-oxybis-(benzoic acid) and anthraquinone rings. Multiple signals recorded at  $\delta$  6.9 ppm accounts for the deshielded vinylic protons of chalcone moiety. The sharp singlet peak appears in the range of  $\delta$  3.5-3.90 ppm is due to the methoxy protons. The signal peak recorded at  $\delta$  2.5 ppm is due to presence of moisture in the DMSO solvent.

A typical <sup>13</sup>C NMR spectrum of PBDO copolyester is shown in Fig. 3. The  $\alpha,\beta$ -unsaturated ketone carbonyl carbon of chalcone moiety resonance signals appears at 188.6 ppm. The ester carbonyl carbons show signal in the region between  $\delta$  162.7-168.0 ppm. In addition, two resonance signals appear at  $\delta$  155-158.6 and  $\delta$  122-142 ppm are attributed to the aromatic carbons of anthraquinone and chalcone moiety. The olefinic carbons of chalcone moieties resonate in the region of  $\delta$  112.6-152.3 ppm. The chemical shift of methoxy carbon occurs between  $\delta$  56-58 ppm.

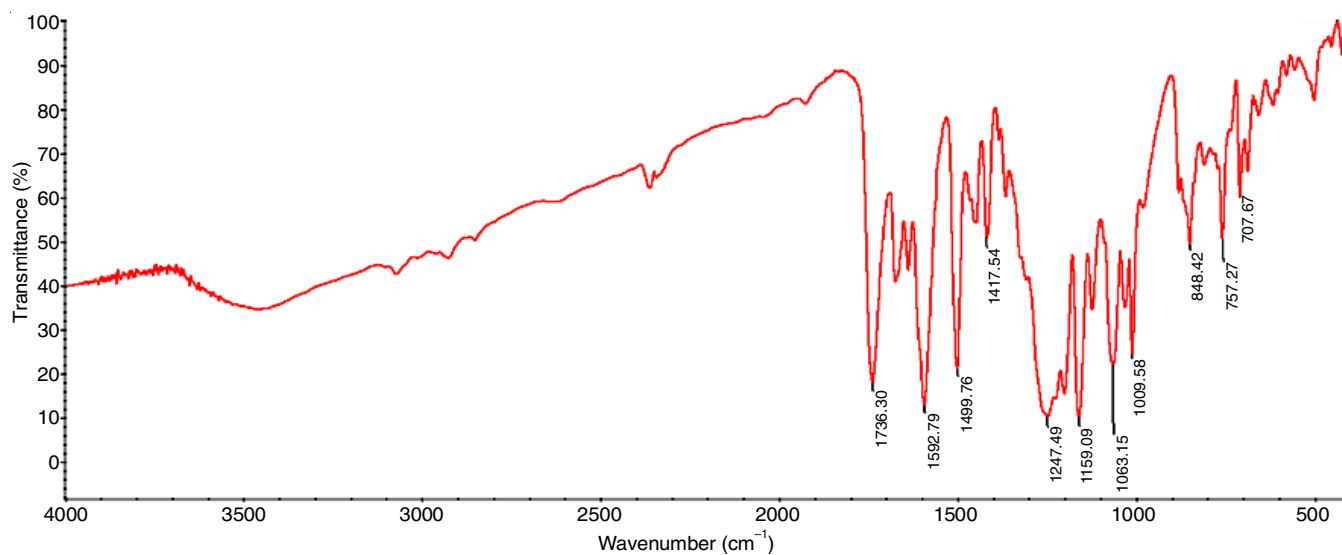


Fig. 1. Fourier transform-IR spectrum of PBDO copolyester

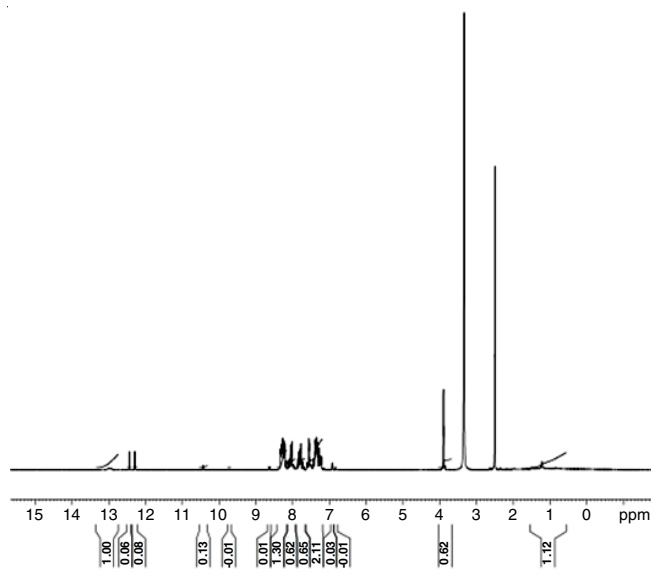


Fig. 2. A typical  $^1\text{H}$  NMR spectrum of PBDO copolyester

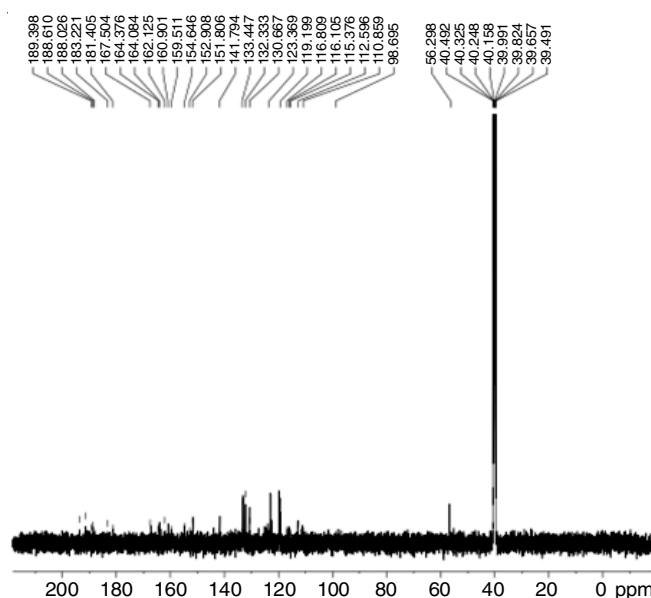


Fig. 3. A typical  $^{13}\text{C}$  NMR spectrum of copolyester PBDO

**Thermal studies:** Heating curves of all the copolyesters were obtained with the help of differential scanning calorimetry. In general, the thermograms give adequate information about thermal transition temperatures such as phase transition temperature ( $T_g$ ), mesophase formation temperature ( $T_m$ ) and isotropic temperature ( $T_{iso}$ ). The phase transition temperature of the copolyester was noted with the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Interestingly, it has been noted that the glass transition tempe-

rate ( $T_g$ ) of the copolyesters is found to be greater than the room temperature. The copolyesters have higher  $T_g$  value ( $> 130\text{ }^\circ\text{C}$ ) due to the aromatic moieties in the polymer backbone (Table-4). The same is observed by Sidharthan *et al.* [29] in thermotropic liquid crystalline copolyesters.

**SEM studies:** The electrospinning technique was utilized successfully to form the blend nanofibers copolyester in a poly(vinyl chloride) matrix. The structure of the photocross-linked polymer blend fibers were studied exactly with the help of scanning electron microscope. The samples were treated with gold particle *via* sputter-coater and scanning done at 5KV electrical potential.

The SEM micrographs (Fig. 4) of the PDDO copolyester in PVC matrix indicate that the copolyester-PVC nanofibers formed by electrospinning technique exhibited sphere shaped fibers in smooth and uniform fashion. The SEM morphology after UV irradiation shows that the nanofibers diameters are well maintained and the nanofibers looked bright and uniform and well dispersed without beads on their surface are shown in Fig. 4. Similar observations were also reported by previous researchers [30-32].

## Conclusion

The outcome of the study reports the efficacious synthesis of four new copolyesters by polycondensation method using diphenylchlorophosphate and lithium chloride in pyridine. The viscosity measurements showed that the copolyesters are relatively high molecular weight polymers. Nanofibers of the copolyester could be efficiently fabricated by electrospinning with PVC matrix polymer solution. DSC thermograms shows excellent thermal stability of copolyesters. The SEM images of copolyester blended nanofibers before and after UV irradiation have shown excellent fibrous structure at the nano level. Therefore, these composite nanofibers are expected to be a potential biomaterial with greater significance.

## ACKNOWLEDGEMENTS

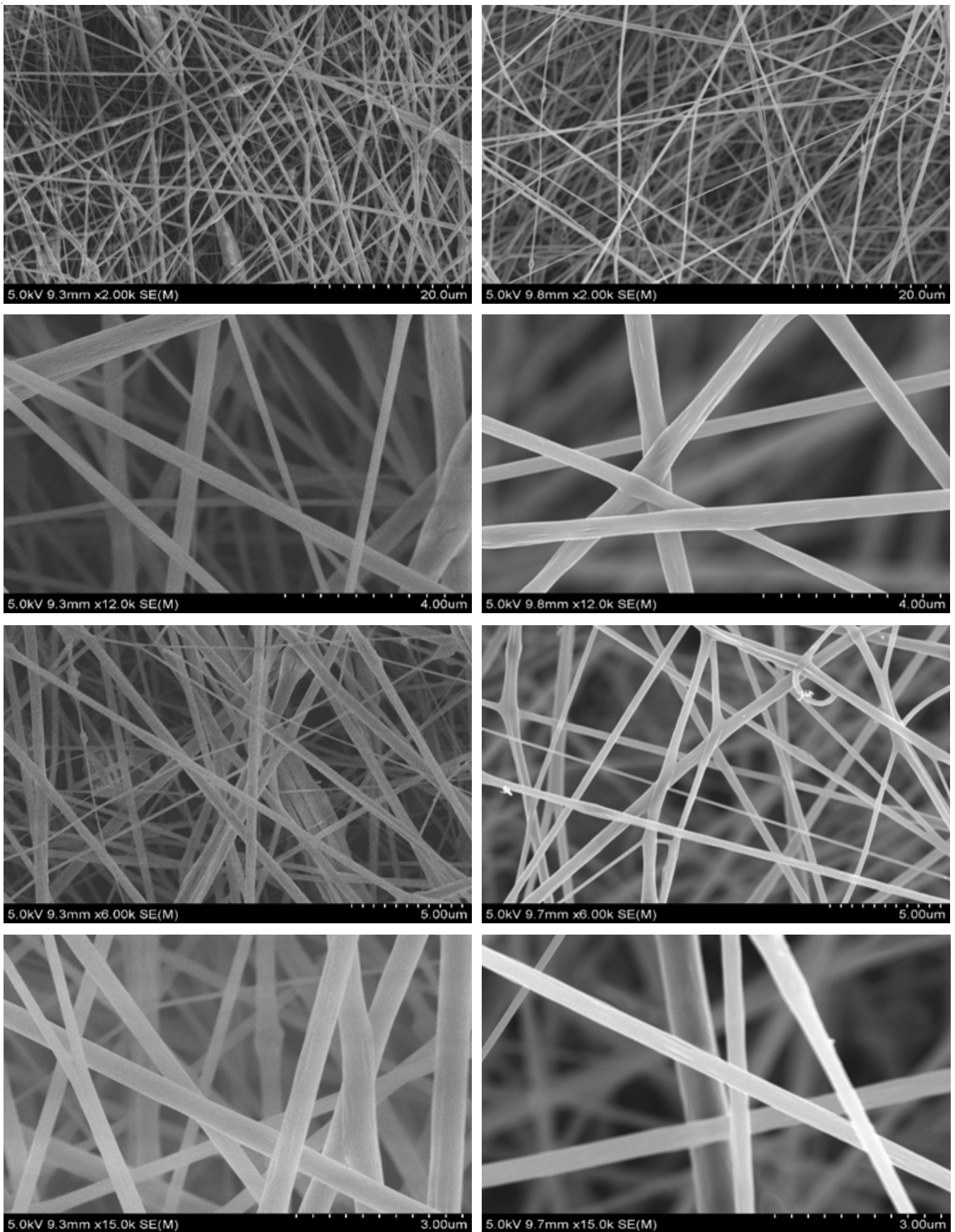
The authors are grateful to SAIF, Indian Institute of Technology, Chennai, India for their great support in spectral analysis and SEM analysis.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-4  
PHASE TRANSITION TEMPERATURE OF COPOLYESTERS

Code	Glass transition temperature ( $T_g$ , $^\circ\text{C}$ )	Mesophase formation temperature ( $T_m$ , $^\circ\text{C}$ )	Isotropic temperature ( $T_{iso}$ , $^\circ\text{C}$ )	Decomposition temperature
PADO	62.5	115.2	152.5	285
PBDO	74.77	123.5	159.8	293
PCDO	90.2	118	165	318
PDDO	85	120	170	350



Before UV irradiation

After UV irradiation

Fig. 4. SEM images of PDDO/PVC/NANOCLAY composites with different magnifications

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