

Inverted Emulsion Polymerization Route to Polyaniline-3D Nanofiber Network Using Sulfonated-*p*-Cresol as Novel Dopant

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ABSTRACT: Sulfonated-*p*-cresol (SPC) was used as novel dopant for the first time in the synthesis of polyaniline in 3D nanofiber networks (PANI-3D). Polyaniline in 3D nanofiber network was prepared using organic solvent soluble benzoyl peroxide as oxidizing agent in presence of SPC and sodium lauryl sulfate (SLS) surfactant via inverted emulsion polymerization pathway. The influence of synthesis conditions such as the concentration of the reactants, stirring/static condition, and temperature etc.,

on the properties and formation of polyaniline nanofiber network were investigated. Polyaniline in 3D nanofiber network with 40–160 nm (diameter), high yield (134 wt % with respect to aniline used), and reasonably good conductivity (0.1 S/cm) was obtained in 24 h time. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2421–2427, 2011

Key words: conducting polymers; emulsion polymerization; nanofiber; polyamines; synthesis

INTRODUCTION

Fiber-like structures with nanometer diameter, such as nanotubes, nanofibers, and nanowires, have been the subject of great interest for a number of potential applications.^{1–3} Micro/nanostructured conducting polymers have received great attention because of their unique properties and promising potentiality in nanomaterials and nanodevices.⁴

Conducting polyaniline (PANI), as one of the most important conducting polymers, has been intensively studied in recent years. This is mainly due to its reasonable conductivity, ease of preparation, good environmental stability, and a large variety of applications especially in light-emitting,⁵ electrochromic devices,⁶ sensors,^{7,8} separation membranes,⁹ and antistatic coatings.¹⁰ Synthesis of polyaniline with spherical shapes,¹¹ needle-like particles,¹² hexagonal plates,¹³ oriented

nanowires,^{14–16} dendrites,¹⁷ chiral PANI nanofiber,¹⁸ etc., have attracted much attention because of their technological advances in potentially diverse applications.

PANI nanostructures have been synthesized through polymerization of the aniline by (i) using an external “hard template” such as aluminosilicate MCM-41,¹⁹ the channels of nanoporous membranes,²⁰ and porous alumina.²¹ The main advantage of the hard template synthesis method is that the length and diameter of the products can be controlled by the selected porous membrane. However, the removal of the template is tedious when hard templates are employed, and it is difficult to mass-produce nanostructures by a template synthesis method, (ii) using surfactants as an external “soft template,”^{22–24} (iii) Manohar and coworkers reported a seeding method to synthesize PANI nanostructures that requires very small amounts of seeds of nanofibers, regardless of their chemical nature, which leads to a precipitate with bulk fibrillar morphology,²⁵ (iv) Wan et al. studied on nanostructure of polyaniline through self-assembly method,²⁶ (v) Epstein and coworker prepared polyaniline nanofibers by using dilute solution of aniline,²⁷ (vi) Bertino and coworkers reported radiolytic synthesis of polyaniline nanofibers,²⁸ (vii) interfacial polymerization,^{7,29–31} MacDiarmid and coworkers reported electrospun polyaniline-PEO blend nanofiber from doped polyaniline by using electrospinning technique.^{32,33}

Synthesis of polyaniline nanofiber was reported using acids such as, β -naphthalenesulfonic acid,³⁴

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camphorsulfonic acid,^{17,34} or azobenzenesulfonic acid³⁵ wherein, acid function as dopant as well as soft “internal” template. Zhang et al.³⁶ used Gadolinium chloride (GdCl_3) as dopant to synthesize PANI nanofiber using chemical method. Zhang et al.³⁷ has been prepared highly crystalline PANI nanotubes and nanofibers by a “micelle soft-template” method using dicarboxylic acids as dopants with different number (n) of $-\text{CH}_2-$ groups ($n = 0-4$). Feng et al. reported nanotubes and nanofibers of (PANI)/Au composite through a self-assembly process in the presence of camphorsulfonic acid and hydrochloric acid, as surfactant and dopant, respectively.³⁸ Zhang et al. synthesized nanoscaled PANI fibers by oxidation polymerization using ferric hydrochloride as an oxidant in the presence of *p*-toluenesulfonic acid (*p*-TSA), β -naphthalenesulfonic acid (β -NSA), or camphorsulfonic acid (CSA) as dopant.³⁴ Thus, dopant is playing the main role in controlling the structure and properties of PANI.

The above reasoning lead us to study the use of another novel dopant instead of using the traditionally used dopants to prepare the nanostructured PANI. Herein, we describe the successful synthesis of PANI-3D nanofiber networks by inverted emulsion polymerization pathway using sulfonated-*p*-cresol as novel organic dopant, benzoyl peroxide as oxidant, and sodium dodecyl sulfate as surfactant.

EXPERIMENTAL

Aniline (E. Merck, India) was distilled prior to use. Benzoyl peroxide (BP), sodium lauryl sulfate (SLS), all other reagents (SD fine chemicals, India) and *p*-Cresol (SRL, India) were used as received. All solvents were purified by the reported methods.

Sulfonation of *p*-cresol was carried out by reacting 55 mL *p*-Cresol with 250 mL 98% of concentrated sulfuric acid at 70°C for 30 min. Then the reaction mixture was poured into ice and the reaction mixture was treated with 75 mL *n*-butyl alcohol. The organic layer was separated and washed with cold water in separating funnel. The organic layer was separated and removed the solvent under reduced pressure. A light yellow color powder was obtained.

Sulfonated-*p*-cresol: ¹H-NMR (300 MHz, D₂O): δ 1.95 (3H, s), 6.56–6.59 (1H, d, $J = 8.3$), 6.92–6.95 (1H, dd, $J = 8.3, 7.9$ Hz), 7.18 (1H, d, $J = 1.3$ Hz).

Benzoyl peroxide (0.832 g; 0.12M) was dissolved in 7.5 mL toluene taken in 50-mL round-bottomed flask. 0.216 g (0.03M) sodium lauryl sulfate (SLS) was dissolved in 2.5 mL distilled water and added to the above solution. The reaction mixture was stirred at 40°C. 15 mL aqueous solution containing 1.42 g (0.3M) sulfonated-*p*-cresol and 0.232 g (0.1M) of aniline was added drop wise into the initiator-surfactant mixture for 15 min duration. After the chemical polymerization proceeded for 24 h under

constant stirring at 40°C, the lower solution containing unwanted mixture was discarded and the reaction mixture was poured into acetone for precipitation of polymer. After precipitation, the resultant green precipitate was filtered, washed with water and acetone. The obtained green precipitate was dried in ambient temperature for 24 h.

Polyaniline salt (0.2 g) was stirred in 20 mL of 1N aqueous sodium hydroxide solution for 8 h at ambient temperature. The solution was filtered, washed with 20 mL of 1N sodium hydroxide solution followed by 50 mL water, and finally with 25 mL acetone. The sample was dried at ambient temperature till a constant weight.

Polyaniline base (0.1 g) was stirred with 10 mL of 0.3M sulfonated-*p*-cresol for 4 h at room temperature. The solution was filtered, washed with 25 mL distilled water followed by 25 mL acetone. The sample was dried at ambient temperature till a constant weight.

PANI powders were pressed into disks of 13 mm diameter and about 1.5 mm thickness under a pressure of 400 MPa. Silver paint was applied on both sides of the pellet. The resistance of the pellet was measured by a two probe method using Keithley Digital Multimeter—Model 2010 [Keithley, Cleveland, Ohio]. Conductivity (σ) was calculated by using the formula $\sigma = l/(a \times R)$, where l , a , and R represents the thickness, area, and resistance of the pellet, respectively. A morphological study of PANI was carried out using Hitachi 3000N (Tokyo, Japan) scanning electron microscope instrument operating at 10 kV. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (MODEL 670 Nicolet Nexus, Minnesota). Wide angle X-ray diffraction spectrum of powder sample was obtained using a Bruker/D8-Advance X-ray diffractometer (Karlsruhe, Germany) using Cu K α radiation (wavelength of 1.54 Å) and a continuous scan speed of 0.007°/min. UV-vis spectrum of PANI base in NMP solvent and a green suspension of PANI salt in toluene, which was taken from polymerization vessel were recorded at ambient temperature using LABOMED INC UV-Vis double beam spectrophotometer PC (CA). Elemental analyses of polyaniline samples were determined with an Elementar Vario EL, (Hanau, Germany), elemental analyzer. Elements present on polyaniline sample were also found out by energy dispersive X-ray analysis (EDAX), Link ISIS-300, UK attached to Hitachi S-520-SEM (Tokyo, Japan). Sulfonated-*p*-cresol was analyzed by ¹H-NMR (BRUKER-Avance-300 MHz Spectrometer) using D₂O solvent.

RESULTS AND DISCUSSION

Yield and conductivity

Aniline in presence of acid (aqueous phase) was oxidized by benzoyl peroxide oxidant (organic phase)

TABLE I
The Effect of Acid Strength, Surfactant, Stirring/Static and Temperature on Yield and Conductivity of PANI Salt

Variations	Yield (%)	Conductivity (S/cm)
Aniline: 0.1M; BP: 0.12M; SLS: 0.03M		
[SPC]/[An] ratio		
2.0	126	0.04
2.5	121	0.10
3.0	134	0.10
4.0	137	0.24
5.0	137	0.06
Aniline: 0.1M; BP: 0.12M; SPC: 0.3M		
[SLS]/[SPC] ratio		
0.1	134	0.10
0.2	103	0.07
1.0	78	0.03
Aniline: 0.1M; BP: 0.12M; SLS: 0.03M; SPC: 0.3M		
Stirring		
Stirring (40°C)	134	0.10
Stirring (25°C)	116	0.02
Static (40°C)	98	0.04
Static (25°C)	98	0.04

using sodium lauryl sulfate as surfactant via emulsion polymerization pathway, wherein, sodium lauryl sulfate was converted to dodecylhydrogensulfate (DHS) and incorporated on to polyaniline as

dopant along with acid dopant (SPC). It is difficult to find out the amount of dopants such as SPC and DHS present in the polyaniline chain from the present study.

Polymerization was carried out by varying the effect of acid strength, surfactant strength, reaction condition (stirring/static condition), and temperature of the reaction. The value of yield and conductivity of polyaniline salt with different reaction conditions are reported in Table I. Polyaniline salt was not soluble in most of the common organic solvents and no efforts were made to determine the molecular weight of PANI. Hence, the yield of the polyaniline salt is reported with respect to the amount of aniline used in the reaction.

The value of yield and conductivity of PANI increased with increase of [SPC]/[An] ratio from 2 to 4 (Table I). This is due to increase in the amount of dopants (SPC and DHS) on the polymer backbone. At further increase of [SPC]/[An] ratio from 4 to 5, the amount of dopant was increased and however, the conductivity was decreased from 0.24 to 0.06 S/cm. Reasonably good yield and conductivity (0.1 S/cm) were observed for [SPC]/[An] molar ratio was 3. When we change the molar ratio of [SLS]/[SPC] from 0.1 to 1.0 (by increasing the

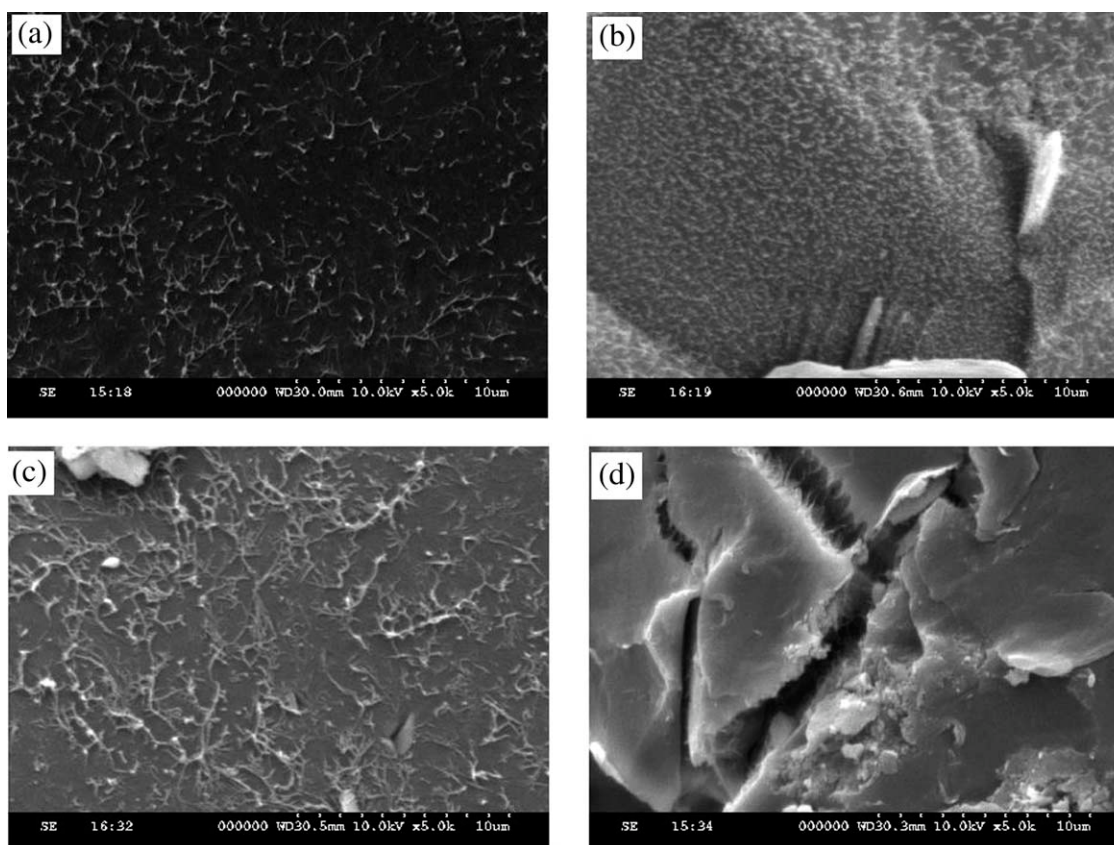


Figure 1 SEM pictures of PANI nanofiber networks synthesized at different [SPC]/[An] ratios such as (a) 2, (b) 2.5, (c) 3, and (d) 4.

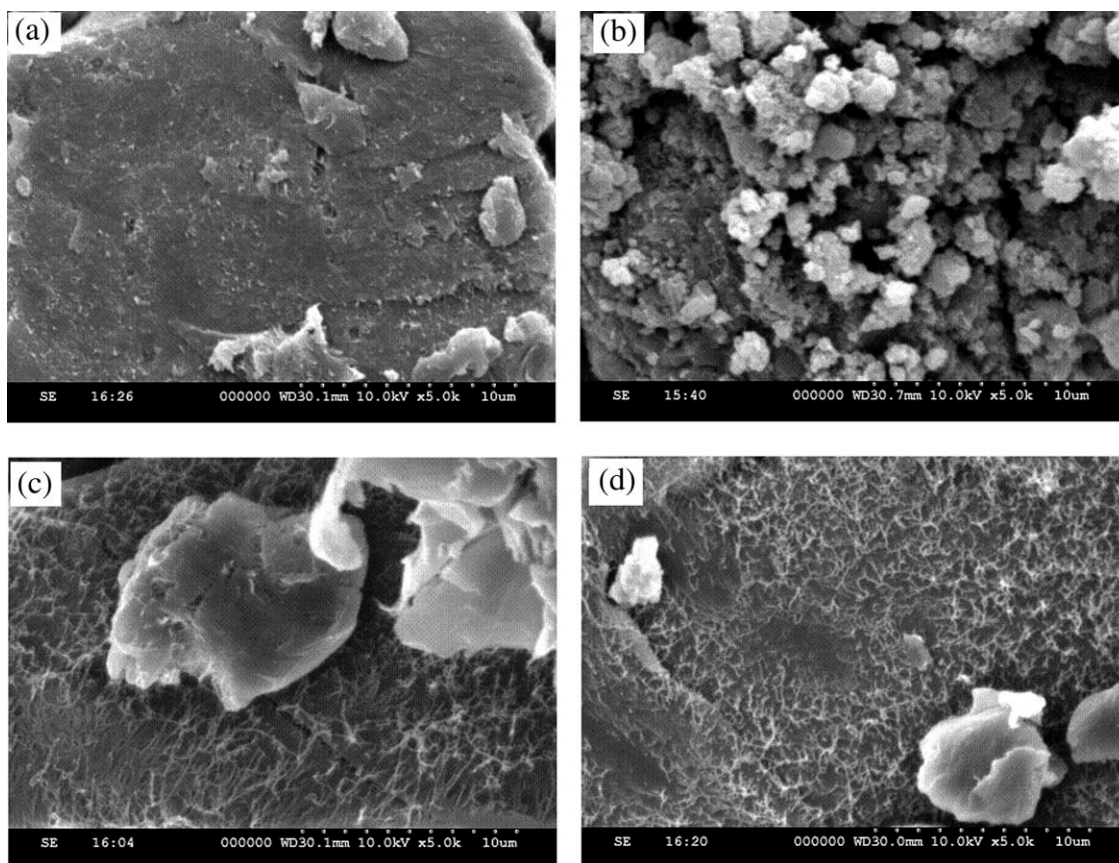


Figure 2 SEM pictures of PANI synthesized with [SPC]/[An] ratio 3 using different [SLS]/[SPC] ratio (a) 0.2 and (b) 1.0; PANI synthesized with [SPC]/[An] ratio 3 and [SLS]/[SPC] ratio 0.1 under (c) stirring condition and (d) static condition at 25°C.

amount of SLS by keeping SPC amount constant), the value of yield and conductivity decreased. This result is due to the excess dopants (SPC and DHS) addition to the PANI, which leads to lower degree of conjugation along the polymer backbone.^{39,40} As a result, [SPC]/[An] molar ratio 3 and [SLS]/[SPC] molar ratio 0.1 were chosen for varying the other reaction condition and temperature of the polymerization reaction. Generally, conductivity of polyaniline salts depends on oxidizing power of oxidant and doping efficiency of protic acid used during the oxidation polymerization of aniline. Higher value of yield and conductivity was obtained at higher temperature (40°C) compared with that of 25°C (Table I). This is because aniline undergoes more oxidation and attracting more dopant at high temperature, wherein, energy of activation is more. However, in the case of static condition, the value of yield and conductivity were found to be temperature independent. This is because the reaction proceeds only at the interface between the aqueous and organic layer in static condition. When the reaction was carried out under static to stirring condition, the value of conductivity drastically increased from 0.04 to 0.1 S/cm and the yield from 98 to 134%. This

result indicates that aniline undergoes more efficiency of oxidation and doping level during stirring condition, wherein, the reaction proceeds homogeneous mixing of whole reaction mixture.

Scanning electron microscopy

Scanning electron microscopic (SEM) images of polyaniline samples are shown in Figures 1–3. Polyaniline nanostructures in 3D-fiber forms having average diameter 40–160 nm, accompanied by decreases in the aspect ratio of the nanostructures were observed as the [SPC]/[An] molar ratio changed from 2, 2.5, to 3 [Fig. 1(a–c)]. However, the PANI nanostructures were affected and became very dense (bulk formation) by increasing the [SPC]/[An] ratio from 3 to 4 [Fig. 1(d)]. This result suggests that [SPC]/[An] molar ratio in the range of about 2–3 is favorable for the formation of PANI nanostructure.

SEM figures of polyaniline salts prepared by keeping constant [SPC]/[An] molar ratio of 3 and varying the molar ratio of [SLS]/[SPC] = 0.2 and 1.0 are shown in Figure 2(a,b), respectively. The excessive usage of DHS makes PANI fibers tend to agglomerate together and became very indistinct

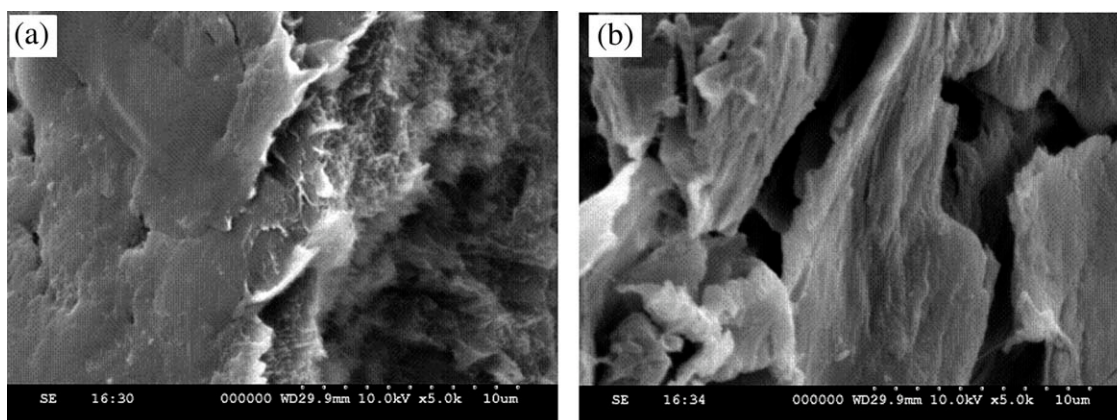


Figure 3 SEM pictures of (a) PANI base and (b) redoped PANI-SPC salt.

[Fig. 2(a,b)]. This result indicates that the molar ratio of $[SPC]/[An] = 3$ and $[SLS]/[SPC] = 0.1$ shows better 3D nanofiber networks. A similar morphology was observed when the reaction was carried out under stirring [Fig. 2(c)] and static conditions [Fig. 2(d)]. The morphology of PANI nanofiber network was partially changed with the treatment of PANI by sodium hydroxide solution to polyaniline base [Fig. 3(a)]. PANI nanofibers are bound together when the dedoped PANI base was redoped with SPC [Fig. 3(b)].

Polyaniline salt in 3D fiber nanostructure with high yield (134%) and reasonable conductivity (0.1 S/cm) was obtained with the use of $[SPC]/[An]$ ratio 3, $[SLS]/[SPC]$ ratio 0.1 and benzoyl peroxide (0.12M) under stirring condition at 40°C. This polyaniline in 3D fiber (PANI-3D) form was characterized by infrared, electronic absorption, X-ray diffraction, and elemental analysis measurements.

Infrared spectra

The FTIR spectrum of PANI-3D salt (Fig. 4) shows the characteristic peaks at 3445 cm^{-1} (N-H str.), 1550 cm^{-1} (C=C ring-stretching vibration of the quinoid form), 1460 cm^{-1} (C=C stretching of the benzenoid ring), 1290 cm^{-1} (C-N stretch), 1230 cm^{-1} (C=N stretch), 1100 cm^{-1} (in-plane bending of C-H) and single band at 785 cm^{-1} (1,4-disubstituted phenyl ring stretch), which are identical to the emeraldine salt form of PANI nanofiber networks.^{38,41}

The presence of bands at 2920 and 2820 cm^{-1} is assigned to asymmetric and symmetric aliphatic C-H stretching vibrations of alkyl substituent, SPC and DHS dopant, respectively. The Peak at 1025 cm^{-1} is attributable to the absorption of $-\text{SO}_3\text{H}$ group³⁸ and band 565 cm^{-1} is due to SO_3- group, which confirms that the PANI is directly doped with SPC.³⁴

The infrared spectrum of redoped PANI salt is similar to that of synthesized PANI salt. The infrared spectrum of polyaniline base is shown in Figure

4. The infrared spectrum of polyaniline base is similar to that of polyaniline salt, but the peaks at 1550 , 1460 , 1290 , and 785 cm^{-1} were shifted to 1580 , 1505 , 1312 , and 825 cm^{-1} respectively.

X-ray diffraction spectra

Figure 5 show XRD pattern of PANI-3D synthesized by inverted emulsion polymerization pathway. Sharp peaks at $2\theta = 15^\circ$, 20° , 25.5° , and 27.3° ($d = 5.9$, 4.4 , 3.5 , and 3.3 \AA , respectively) belong to the crystalline structure of PANI.^{42,43} The characteristic peaks centered at $2\theta = 20^\circ$ and 25.5° are observed in PANI nanostructure, and are attributed, respectively, to the periodicity perpendicular and parallel to the polymer chain.^{37,42} Dufour et al.⁴⁴ suggested that the peak at $2\theta = 25.5^\circ$ ($d = 3.5\text{ \AA}$) is a characteristic of the Vander Waals distances between stacks of phenylene rings (polyaniline ring). Moreover, the sharpness of the PANI peaks indicates that the PANI-3D chains are in a more ordered structure. These results are in good agreement with previous results.^{34,43}

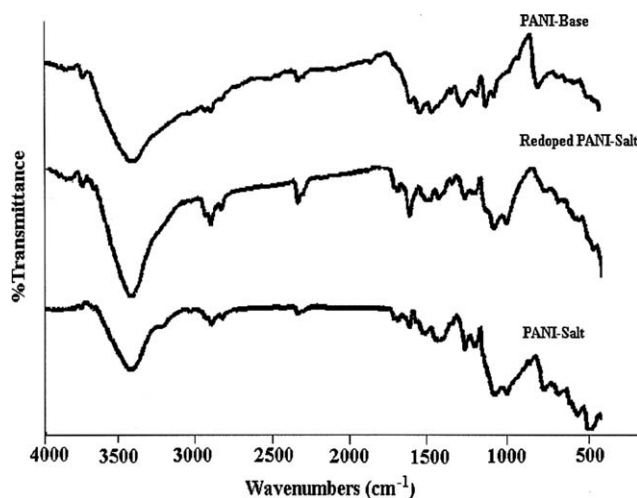


Figure 4 IR spectrum of SPC doped PANI-Salt, Redoped PANI-Salt, and PANI-Base

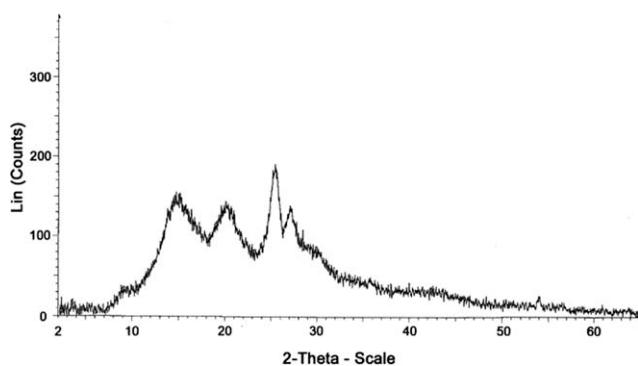


Figure 5 XRD pattern of SPC doped PANI nanofiber network synthesized by inverted emulsion polymerization pathway.

Electronic absorption spectra

The typical UV-vis spectrum of the as-synthesized PANI-3D isolated in toluene during emulsion polymerization is shown in Figure 6 (Spectrum A). It showed three peaks at 340, 415, and 830 nm, which are attributed to $\pi \rightarrow \pi^*$ transition, polaron band $\rightarrow \pi^*$ and $\pi \rightarrow$ localized polaron band of doped PANI in its emeraldine salt form, respectively.^{43,45} Polyaniline base shows peaks at 325 and 635 nm (Fig. 6, Spectrum B), which are related to $\pi \rightarrow \pi^*$ transition of benzenoid and quinonoid rings respectively. This result is similar to that of the dedoped polyaniline in its emeraldine base form.^{27,43,45}

Elemental analysis

The elemental analysis values of the PANI-3D salt, PANI base, and redoped PANI-SPC salt are reported in Table II. The elemental analysis of redoped PANI-SPC salt showed 4.71% of sulfur due to the presence of SPC dopant. Higher amount of sulfur content (6.34%) was observed for PANI-3D when compared with PANI-SPC salt and this result indicates the presence of both SPC and DHS

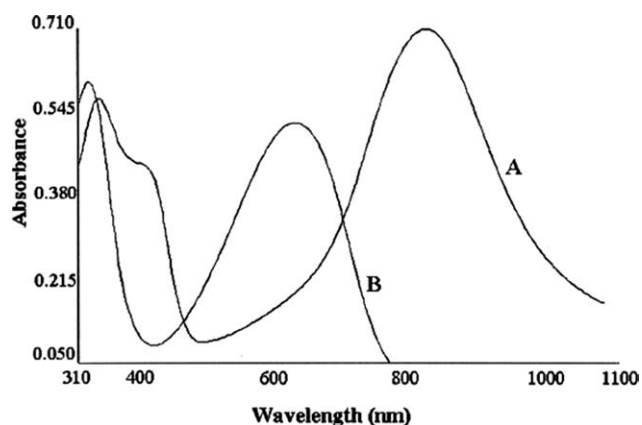


Figure 6 UV-vis spectra of the PANI-3D (A) and its base (B).

TABLE II
Elemental Analysis Values of PANI-3D Salt, PANI-Base and Redoped PANI-SPC Salt

Samples	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)
PANI-3Dsalt	54.35	5.11	6.55	6.34
PANI-base	67.93	5.11	9.47	0.1
Redoped PANI-SPC salt	61.20	4.99	7.02	4.71

dopants on polyaniline salt. Polyaniline base contains negligible amount of sulfur (0.1%) and this result indicates that all the dopants have been removed from the polyaniline salt.

Energy dispersive spectroscopic analysis of PANI-3D showed C (67%), O (19%), and N (13%) and very less amount of S (0.2%) observed for PANI base. Energy dispersive spectroscopy qualitatively indicates the elements present on the surface of the sample. This result also supports that polyaniline base does not contain sulfur.

CONCLUSIONS

Inverted emulsion polymerization process has been successfully used for the synthesis of polyaniline in 3D nanofiber networks with an average diameter \sim 40–160 nm and conductivity of 10^{-1} S/cm. This method provides a wider, simpler, and repeatable route for the preparation of three-dimensional nanofiber networks of polyaniline. Our novel approach will lead to the preparation of nano blends/composites of polyaniline with other insulating polymers because of the solubility of conventional polymers and benzoyl peroxide in most of the organic solvents.

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