

Large-Scale Synthesis of Polyaniline Nanofibers Based on Renewable Resource Molecular Template

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Received 27 April 2009; accepted 10 June 2009

DOI 10.1002/app.30962

Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We report reproducible large-scale synthesis of polyaniline (PANI) nanofibers up to 100 g scale via micelle mediated soft template approach. A unique built-in amphiphilic azobenzenesulfonic acid based on renewable resource dopant was synthesized for large-scale production of PANI nanofibers. The amphiphilic surfactant exists as 4.3 nm micelle in water and it self-organized with aniline to form long cylindrical aggregates, which template for PANI nanofibers. The PANI nanofibers were found soluble in water and organic solvents and they were characterized by ¹H-NMR, FT-IR, and viscosity techniques. The mechanism of the PANI nanofiber formation was investigated by dynamic light scattering, scanning electron microscopy, and high resolution transmission

electron microscopy. The width of the nanofibers was precisely controlled from 130–200 nm with length up to ~ 5 μm. The absorption spectroscopic analysis of nanofibers in water revealed that the large-scale samples (10, 50, and 100 g) were found to possess expanded chain conformation compared to that of 1 g scale sample. The wide angle X-ray diffraction patterns showed two new peaks at lower angles at *d* spacing of 25.5 and 13.6 Å corresponding to lamellar ordering of PANI chains followed by interdigitation of the amphiphilic dopant in the nanofibers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3531–3541, 2009

Key words: conducting polymers; WAXS; templates; solid state structure; PANI; morphology

INTRODUCTION

Polyaniline (PANI) nanomaterials have attracted wide interest due to their potential application in electronic devices, chemical, and biosensors.^{1–8} Various polymerization routes such as emulsion,^{9,10} interfacial,¹¹ dispersion,¹² seeding,¹³ dilution,¹⁴ and approach such as soft¹⁵ and hard templates¹⁶ were reported for PANI nanomaterials. It almost appeared that the nanofiber topology is an inherent property of the PANI nanomaterials. Despite, these various routes were documented in the literature, the large-scale synthesis of PANI nanofibers (or any other nanostructures of PANI) has been realized as a challenging task.¹⁷ A detailed literature survey revealed that most of the research works in this area report the synthesis in very small amount, for example, varying from 30 mg to <1 g scale. The important question is why the synthesis of PANI nanomaterials restricted to such low gram scales even though all the starting materials such as monomer (aniline),

oxidizing agent (ammonium persulphate, APS), dopant (like HCl or sulfonic acid), and the solvent (water) are commercially available and not expensive. The nanomaterial synthetic approaches at low quantity scales may not be sufficient enough for practical applications, which required at least few grams of samples (~ 10 g). This issue has been accepted widely as an alarming trend in almost all nanomaterials research and need to be addressed urgently.¹⁸ Recently, efforts have been taken by few researchers to address these issues and they reported that the nanofiber formation was highly sensitive to various experimental parameters such as ultrasonic stirring,¹⁹ magnetic stirring,^{17,19} rate of mixing,²⁰ reaction time and temperature,²¹ reactant compositions and their concentrations,²² etc. It is widely believed that the poor stability of the templates or agglomeration are some main reasons for the non-reproducible nanofiber formation.^{8,17,22} Therefore, new approaches for development of large-scale synthesis of PANI nanofibers are an important issue to be addressed for reproducible and sustainable PANI nanomaterials research. From our research group, we have recently reported a renewable resource strategy for PANI nanomaterials based on a raw material cardanol, which is an industrial waste and pollutant from cashew nut industry.^{23–27} A new amphiphilic molecule,

Additional Supporting Information may be found in the online version of this article

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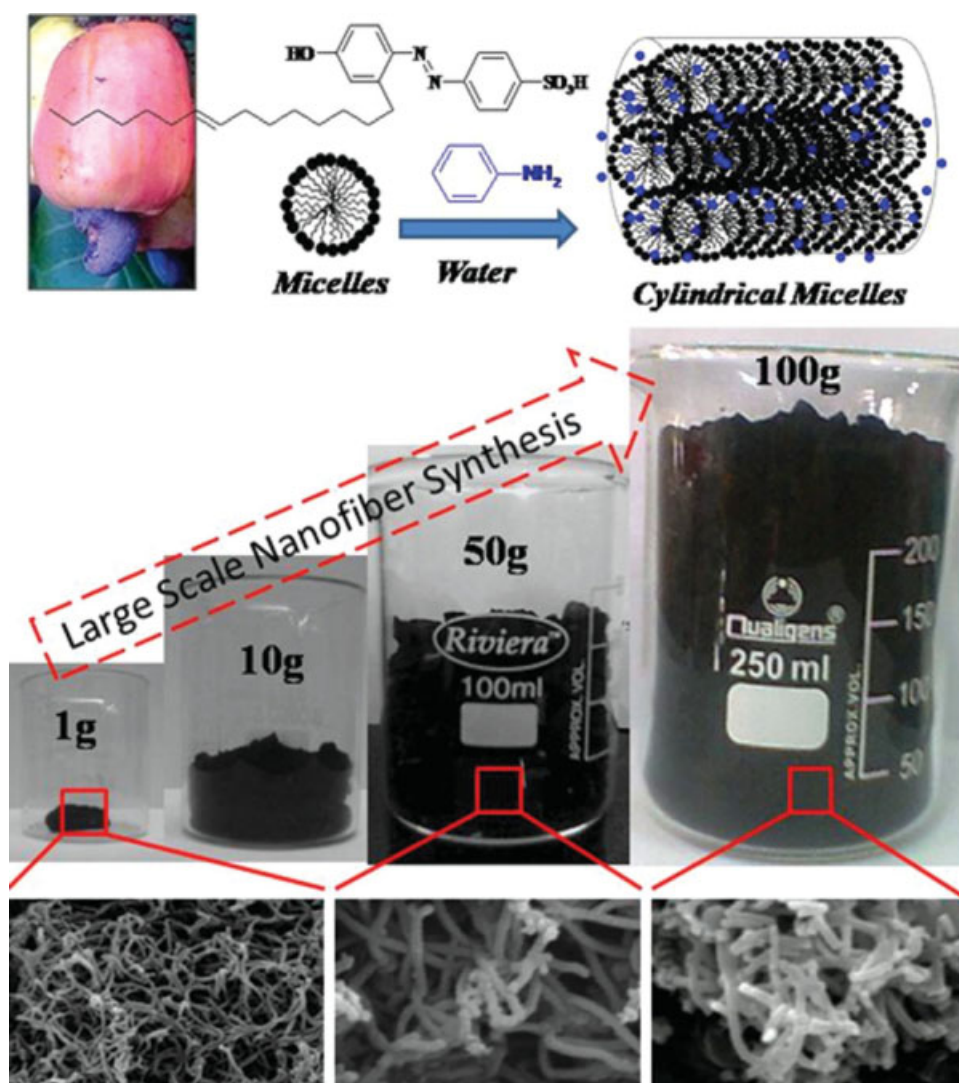


Figure 1 Large-scale synthesis of PANI nanofibers via renewable resource molecular template. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

4-[4-hydroxy-2-((Z)-pentadec-8-enyl) phenylazo]-benzenesulfonic acid, was developed from cardanol and used as a dopant cum structure directing agent to produce PANI nanomaterials. Various PANI nanostructures (fibers, tubes, rods and spheres) were produced by precisely controlling the [aniline]/[dopant] compositions (from 1 to 1500) and concentrations (10^{-3} to $10^{-5}M^{-1}$, 1 g scale) through polymerization routes such as emulsion, interfacial, and dilution routes. However, up to our knowledge, there is no report known for the large-scale synthesis of PANI nanomaterials exclusively nanofibers.

The present investigation is emphasized on the large-scale synthesis of PANI nanofibers using this unique renewable resource surfactant (or dopant) via soft template approach in water. The idea of the current investigation is primarily focused on testing the feasibility of large-scale nanofiber synthesis and investigates new properties associated with these

large-scale produced materials. We have adopted emulsion polymerization route for the large-scale synthesis of the PANI nanofibers using renewable resource dopant and the procedure was established stepwise from 1, 10, and 50 to 100 g scale. The amphiphilic dopant molecules form thermodynamically stable micellar aggregates of inherent nanoscale dimensions in solution (4.3 nm). The complexation of aniline with dopant micelles produce long cylindrical micellar aggregates (refer Fig. 1), which act as template for the overall reproducible nanofiber development. The mechanism of the micelle mediated polymerization process was investigated in detail by dynamic light scattering, SEM, and HR-TEM. The molecular weights of the samples were analyzed by viscosity methods and the structural characterization was done by 1H -NMR, FT-IR, and UV-vis spectrometers. X-ray diffraction studies are also utilized to study the solid state ordering of

polymer chains in nanomaterials and their lamellar chain packing. The results suggests that the renewable resource based approach is very promising for reproducible synthesis of PANI nanofibers up to 100 g scale without altering the morphology, conductivity, solid state ordering, and other electronic properties.

EXPERIMENTAL SECTION

Materials

Aniline, ammonium persulfate (APS), sulfanilic acid, hydrochloric acid, and sodium hydroxide were purchased locally and purified. Cardanol was purified by double vacuum distillation at 3–4 mm of Hg and the fraction distilled at 220–235°C was collected.

General procedures

For SEM measurements, polymer samples were subjected for thin gold coating using JEOL JFC-1200 fine coater. The probing side was inserted into JEOL JSM- 5600 LV scanning electron microscope for taking photographs. Transmission electron microscopic images were recorded using a FEI Tecnai 30G² S Twin HR-TEM instrument at 100 kV. For TEM measurements, the water suspension of nanomaterials were prepared under ultrasonic stirring and deposited on Formvar coated copper grid. Wide angle X-ray diffractions of the finely powdered polymer samples were recorded by Philips Analytical diffractometer using CuK-alpha emission. For dynamic light scattering (DLS) measurements, we used a Nano ZS Malvern instrument employing a 4 mW He-Ne laser ($\lambda = 632.8$ nm) and equipped with a thermo stated sample chamber. For all the DLS measurements, HPLC quality (Merck, India) double distilled water is used. Infrared spectra of the polymers were recorded using a Perkin-Elmer, spectrum one FT-IR spectrophotometer in the range of 4000 to 400 cm^{-1} . For conductivity measurements, the polymer samples were pressed into a 10 mm diameter disk and analyzed using a Keithley four probe conductivity instrument by applying a constant current. The resistivity of the samples was measured at five different positions and at least two pellets were measured for each sample: the average of 10 readings was used for conductivity calculations. UV-Vis spectra of the PANI in water were recorded using Perkin-Elmer Lambda-35 UV-VIS Spectro Photometer. The inherent viscosity values of the nanofibers (PANI-EB form) were measured for 0.5 wt % solutions (0.125 g in 25 mL) in NMP at 30°C. An Ubbelohde viscometer was used for the measurements, and an average of three readings was taken

for the calculation. ¹H-NMR analysis of the polymer samples were carried out in 500-MHz Bruker Avance ii NMR Spectrometer using d₆-DMSO as solvent at 30°C. The cyclic voltametry of the nanofibers was done using a CH Instruments electrochemical analyser with CHI 1121A work station. For electrochemical experiments, the samples in PANI-EB form is well dispersed in 1M HCl solution and were carried out at room temperature. Cyclic voltammograms were recorded using a platinum electrode at a scan rate of 100 mV/s; using Calomel reference electrode and a Pt wire counter electrode.

Preparation of PANI nanofibers (1 g scale)

The dopant (0.053 g, 0.11 mmol) was dissolved in doubly distilled water (20 mL) and stirred under ultrasonic for 1 h at 30°C. Distilled aniline (1 mL, 1.02 g, 11 mmol, [aniline]/[dopant] = 100) was added to the dopant solution and stirred under ultrasonic for additional 1 h at 30°C. To the resultant pale yellow emulsion, ammonium per sulfate (10 mL, 1.1M solution) was added at 30°C and stirred under ultrasonic for 1 h at 5°C. The resultant green color content was allowed to stand at 30°C for 15 h without disturbing. The green solid mass was filtered, washed with distilled water, methanol, and diethyl ether for several times till the filtrate become colorless. The solid product was dried in a vacuum oven at 60°C for 48 h (0.01 m Hg). Yield = 0.80 g (78%). ¹H-NMR (500 MHz, DMSO-d₆): 0.5–3.5 (aliphatic-H, dopant) 6.81(b, Ar-H, dopant), 6.91(Ar-H, dopant), 7.11, 7.18, 7.29 (1/1/1 triplet, -NH+), 7.52(Ar-H), 7.55(Ar-H), 7.81(Ar-H, dopant). FT-IR (KBR, in cm^{-1}): 3010.8, 1579.7, 1500.6, 1305.8, 1224.8, 1159.2, 1031.9, 825, 705.9, and 628.7.

Preparation of PANI nanofibers (10 g scale)

The dopant **1** (0.530 g, 1.1 mmol) was dissolved in doubly distilled water (200 mL) and stirred under ultrasonic for 1 h at 30°C. Distilled aniline (10 mL, 10.2 g, 0.11 mol; [dopant]/[aniline] = 100) was added to the dopant solution and stirred under ultrasonic for additional 1 h at 30°C. To the emulsion, ammonium persulfate (100 mL, 1.1M solution) was added and stirred under ultrasonic for 1 h at 30°C. The rest of the procedures are same as described for 1 g scale. Yield = 6 g (58%). ¹H-NMR (500 MHz, DMSO-d₆): ¹H-NMR (500 MHz): 0.5–3.5 (aliphatic-H, dopant) 6.81(Ar-H, dopant), 6.91(Ar-H, dopant), 7.11, 7.17, 7.28 (1/1/1 triplet, -NH+), 7.51(Ar-H), 7.53(Ar-H), 7.81(Ar-H, dopant). FT-IR (KBr, in cm^{-1}): 3011.8, 1577.7, 1501.6, 1305.8, 1224.8, 1158.2, 1031.9, 827, 705.9, and 626.7.

Preparation of PANI nanofibers-50 g scale

The dopant **1** (2.65 g, 5.5 mmol) was dissolved in doubly distilled water (1 L) and stirred under ultrasonic for 1 h at 30°C. Distilled aniline (50 mL, 51 g, 0.54 mol; dopant/aniline = 1:100) was added to the dopant solution and stirred under ultrasonic for additional 1 h at 30°C. To the resultant emulsion ammonium persulfate (500 mL, 1.1M solution) was added and stirred under ultrasonic for another 1 h at 30°C. The rest of the procedures are same as described for 1 g scale. Yield = 33 g (64%). ¹H-NMR (500 MHz, DMSO-d₆): 0.5–3.5 (aliphatic-H, dopant) 6.81(Ar-H, dopant), 6.91(Ar-H, dopant), 7.11, 7.19, 7.31 (1/1/1 triplet, -NH+), 7.53(Ar-H), 7.56(Ar-H), 7.81(Ar-H, dopant). FT-IR (KBr, in cm⁻¹): 3009.1, 1579.2, 1502.6, 1303.8, 1224.8, 1158.2, 1031.2, 826, 706.1, and 627.2.

Preparation of PANI nanofibers (100 g scale)

The dopant **1** (5.30 g, 11 mmol) was dissolved in doubly distilled water (2 L) and stirred under ultrasonic for 1 h at 30°C. Distilled aniline (100 mL, 102 g, 1.09 mol; dopant/aniline = 1:100) was added to the dopant solution and stirred under ultrasonic for additional 1 h at 30°C. The pale yellow emulsion was oxidized by ammonium persulfate (1 L, 1.1M solution) and further stirred under ultrasonic for 1 h at 30°C. The rest of the procedures are same as described for 1 g scale. Yield = 75 g (74%). ¹H-NMR (500 MHz, DMSO-d₆): 0.5–3.5 (aliphatic-H, dopant) 6.81(Ar-H, dopant), 6.91(Ar-H, dopant), 7.11, 7.21, 7.31 (1/1/1 triplet, -NH+), 7.52(Ar-H), 7.56(Ar-H), 7.81(Ar-H, dopant). FT-IR (KBr, in cm⁻¹): 3011.1, 1577.7, 1502.1, 1306.1, 1225.1, 1158.9, 1032.2, 825, 706, and 627.7

De-doping of PANI nanofibers by aqueous ammonia

Powdered PANI nanofiber (2 g) was taken in a flask containing 25 mL of 10% ammonia solution. The blue suspension was stirred for 4 h at 25°C to ensure the completion of de-doping. The resultant blue emeraldine base was centrifuged, washed with plenty of water until the filtrate become colorless. It was dried in a vacuum oven at 60°C for 12 h (0.1 mm of Hg). Yield = 1.48 g. Insoluble for NMR-characterization. FT-IR (KBr, in cm⁻¹): 3237.1, 3044.3, 1589.7, 1502.1, 1298.1, 1225.1, 1145.9, 825, 693.3, and 627.7.

Re-doping of PANI nanofiber (EB form) with camphor sulfonic acid

PANI nanofiber EB (0.5 g) and of CSA (0.63 g; PANI-EB/CSA = 1:0.5) were taken in a 100 mL flask

with water condenser; 20 mL of ethanol was added and heated to 55–65°C using an oil bath. The whole mixture was stirred for 10 h and then cooled. The resulting mixture was centrifuged and washed with ethanol until the filtrate become colorless. The green colored precipitate was dried in vacuum oven at 60°C (0.1 mm of Hg). The doped polymer weighed 0.72 g (64%). ¹H-NMR (500 MHz, DMSO-d₆): ¹H-NMR (500 MHz): 0.5–3 (aliphatic-H, CSA), 7.11, 7.21, 7.31 (1/1/1 triplet, -NH+), 7.35(Ar-H), 7.51(Ar-H), 7.56(Ar-H). FT-IR (KBr, in cm⁻¹): 3237.1, 2954.3, 1737.2, 1577.7, 1502.1, 1306.1, 1225.1, 1158.9, 1044.2, 825, 706, and 626.9.

RESULTS AND DISCUSSION

The amphiphilic dopant molecule, 4-[4-hydroxy-2-(Z)-pentadec-8-enyl] phenylazo]-benzene sulfonic acid (refer Fig. 1) was synthesized from renewable resource cardanol.^{23,27} The dopant has unique built-in amphiphilic design consisting of hydrophilic sulfonic acid as polar head and long alkyl chain as hydrophobic tail (refer Fig. 1). The amphiphilic azobenzene molecule is freely soluble in water and the addition of aniline produces thick pale yellow emulsion, which was found stable for more than 1 month.²³ Earlier investigation on the effect of aniline/dopant composition and concentration (for 1 g scale) revealed that the fibrous nature was almost unaltered for a wide range of [aniline]/[dopant] = 50 to 900.²⁴ In the present investigation [aniline]/[dopant] ratio was fixed as on 100 (in moles) for the large-scale synthesis of PANI nanofibers based on previous studies. The concentration of the dopant and aniline are fixed as $3.6 \times 10^{-3}M$ and 0.36M, respectively, for all scales of polymerization (starting from 1 to 100 g scale). The total volume of the reaction mixtures for 1, 10, 50, and 100 g scales are 30, 300, 1500, and 3000 mL (refer supporting information for reaction vessels). The polymerization process involved three consecutive steps: (i) dissolving the dopant in water, (ii) addition of aniline and emulsification by stirring in ultrasonic bath, and (iii) polymerization of the resultant emulsion using oxidizing agent (NH₄)₂S₂O₈. The green PANI nanofibers were purified and washed with large amount of water, methanol, and diethyl ether till the filtrate become colorless. The un-reacted aniline, dopant, anilinium salts, APS, oligomers were freely soluble in these solvents, and therefore, they were removed during repetitive washing.²⁵ The green powdered samples were dried in a vacuum oven at 50°C for more than 24 h prior to further analysis. The amounts of dopant, aniline, ammonium persulfate (APS), and water used for the scale of 1, 10, 50, and 100 g was listed in Table I. All the nanomaterials were obtained as dark green solid in good yield

TABLE I
Amount of Reactants Used for Synthesis of PANI Nanofibers

Sample	Amount of dopant (g)	Amount of aniline (g)	Amount of APS (1.1M) in mL	Amount of water (mL)	Yield (%)
E-1g	0.053	1.02	10	30	85
E-10g	0.53	10.2	100	300	60
E-50g	2.65	51	500	1500	60
E-100g	5.3	102	1000	3000	74

from 60–70% (refer Fig. 1 for quantity of the samples). The samples were represented as **E-1g**, **E-10g**, **E-50g**, and **E-100g** in which E-represents emulsion route and the number indicates the scale of reaction.

The polymer samples were characterized by $^1\text{H-NMR}$, FT-IR, and solution viscosity measurements. In general, PANI nanomaterials are not soluble and most of the reports do not report any structural characterization by NMR.²⁸ In the present case, the amphiphilic molecule makes these conducting structures easily dispersible in organic solvents like DMSO for complete structural characterization by NMR. $^1\text{H-NMR}$ spectra of the dopant and PANI nanomaterials were recorded in d_6 -DMSO and the spectra are shown in Figure 2 (the spectra were expanded only for aromatic region for simplicity). The different types of protons in the dopant structure were assigned with alphabets in the structure. It is clearly evident from the spectra of the nanomaterials that the peaks corresponding to the dopant molecule was present in addition to the peaks for the polymer structures. The two broad peaks at 7.65 and 7.52 ppm (peaks g and h) were assigned to the two aromatic peaks in the PANI aromatic ring.^{29,30} Three equally intense peaks (triplet) at 7.1, 7.2, and 7.3 ppm are attributed to the free radical NH proton resonance due to the ^{14}N with unit spin which makes the proton attached to it split into three lines.³⁰ It confirms the strong binding of anionic sulfonic acid dopant to the polymer structure and also the doped stage of the conducting PANI. To check the molecular weights of the synthesized PANI nanofibers, the inherent viscosity (η_{inh}) of the samples (PANI-EB form) were determined in *N*-methylpyrrolidinone (NMP) using an Ubbelohde viscometer. The polymer sample was dissolved in NMP, filtered and 0.5 wt % solutions was subjected to measurements at 30°C. The inherent viscosities of the polymers were obtained in the range of η_{inh} 0.24–0.29 dL/g (refer Table II). The viscosities of the samples indicate the formation of moderate molecular weight samples and the values are in accordance with the earlier reports for PANI materials.^{31–33} FT-IR analysis (refer supporting information) of the PANI nanomaterials showed two peaks at 3200 and 2930 cm^{-1} corresponds to $-\text{NH}$ and $-\text{CH}$ vibrations, respectively.³⁴ It showed peaks at 1583, 1495,

1315, and 830 cm^{-1} corresponding to the quinoid ring $\text{C}=\text{C}$, benzenoid ring $\text{C}=\text{C}$ stretching ring deformations, $\text{C}-\text{N}$ stretching and $\text{C}-\text{H}$ out-of-plane vibrations of 1,4-disubstituted benzene ring, respectively.^{35,36} The appearance of the peaks at 1300, ~ 630 , and 1020 cm^{-1} were attributed to symmetric, un-symmetric stretching vibrations of $\text{O}=\text{S}=\text{O}$ and $\text{S}-\text{O}$ groups and $\text{NH}^+\dots\text{SO}_3^-$ interactions between the polymers chain and the dopant.³⁷ The degree of doping was calculated from the elemental analysis (S/N ratio) as 31.6, 32.2, 36.1, and 41.7% for **E-1g** to **E-100g**, respectively (refer Table II). The degree of doping in the PANI samples matches with the earlier reports for sulfonic acid doped systems.^{26,38} The thermal stability of the samples was analyzed by TGA and all the samples were found thermally stable for more than 300°C (refer supporting information).

The morphologies of the nanomaterials were recorded using scanning electron microscope (SEM) and transmission electron microscope (TEM). The SEM images of the nanomaterials **E-1g** to **E-100G** is given in Figure 3. The average length and diameters of the nanofibers are determined from SEM images and summarized in Table II. The SEM image of **E-1g** clearly indicates the formation of very uniform nanofibers of average diameter 175 nm and a length of 6–8 μm . **E-10g**, **E-50g**, and **E-100g** samples have

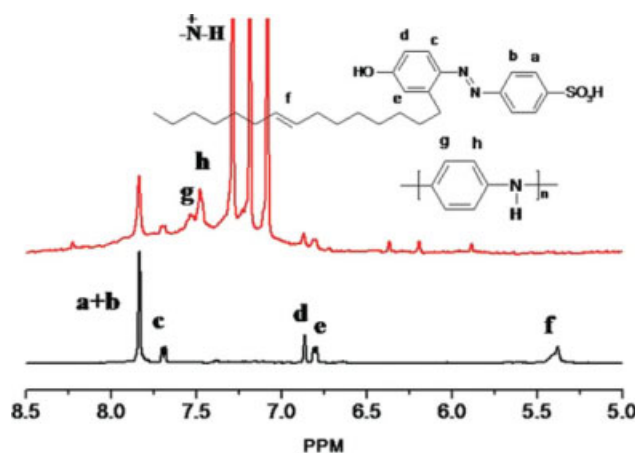


Figure 2 $^1\text{H-NMR}$ spectra of dopant and PANI nanofibers in d_6 -DMSO. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Conductivity, Viscosity, Dimensions, and WXRData of PANI Nanofibers

Sample	S/N ratio ^a	σ (S/cm) ^b	η_{inh} ^c	Fiber diameter (nm) ^d	Peaks in WXRData ^e	
					Peak at (2 θ)	d spacing (Å)
E-1g	31.6	7.5×10^{-3}	0.29	150–220	6.5, 18.5, 25.8	13.6, 4.8, 3.4
E-10g	32.2	1.1×10^{-2}	0.26	145–210	3.4, 19.7, 25.1	25.8, 4.5, 3.5
E-50g	36.1	1.8×10^{-2}	0.29	140–205	3.4, 20.3, 25.4	25.5, 4.3, 3.5
E-100g	41.7	2.2×10^{-2}	0.24	130–200	3.4, 6.4, 17.8, 19.1, 20.4, 23.5, 26.2, 29.2, 30.4	25.5, 13.8, 4.9, 4.6, 4.3, 3.8, 3.4, 3.1, 2.9

^a Determined from elemental analysis.

^b Four probe conductivity at 30°C.

^c Inherent viscosity measured for 0.5 wt % polymer solution in NMP at 30°C.

^d Average fiber size calculated from SEM images.

^e Diffraction peaks at 30°C.

also shown exclusively nanofibers of 160 nm diameters with a straighter rod like nature than E-1g. TEM images (refer Fig. 3) of the nanomaterials have fur-

ther confirmed the fibrous morphology and their diameters were almost same as noticed in the SEM. SEM and TEM images confirmed that in the present

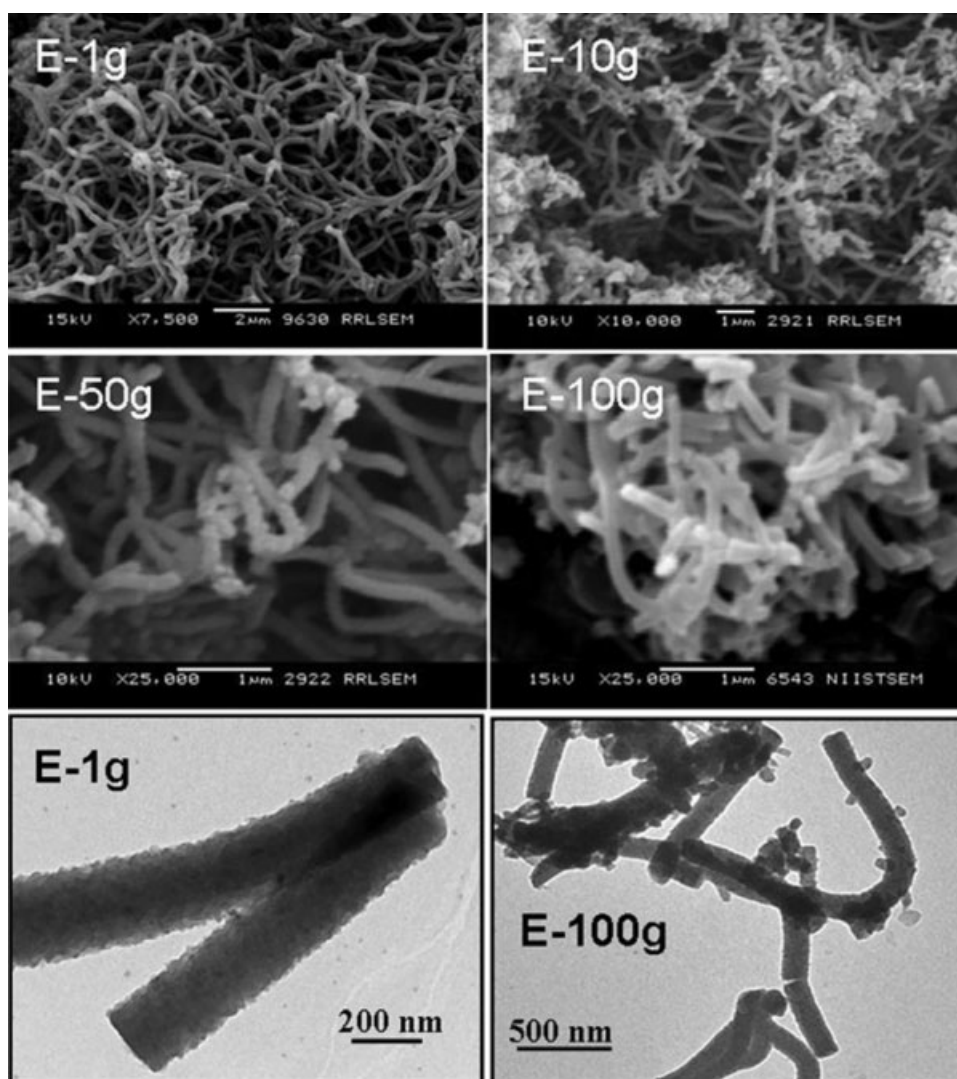


Figure 3 SEM and TEM images of PANI nanofibers.

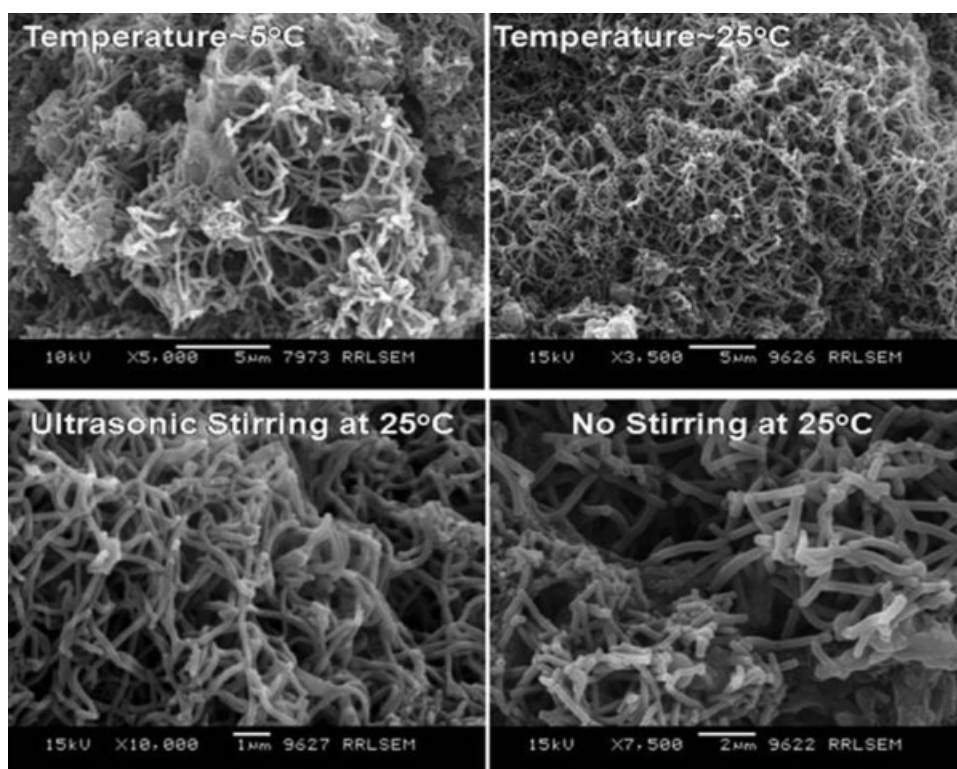


Figure 4 SEM images of nanomaterials synthesized (1 g scale) under various experimental conditions.

investigation, the nanofiber morphology was unaltered from 1 to 100 g scale synthesis. To check the influence of other experimental conditions on the nanomaterial morphology, we have also carried out control experiments (at 1 g scale) by varying temperature (5 and 30°C), under ultrasonic stirring, magnetic stirring, and without any stirring or disturbance. SEM images of the resultant samples under these various conditions (refer Fig. 4) showed only fibrous morphology and confirmed that the present approach is not sensitive to any variation in the experimental conditions such as stirring. Therefore, the present approach is very unique in the sense PANI nanofibers can be prepared in reproducible manner from 1 to 100 g scale with less or no influence of experimental variation.

To understand the mechanism of the amphiphilic dopant mediated synthesis, efforts were taken to utilize dynamic light scattering (DLS) and SEM techniques to characterize the micellar templates.^{39–43} DLS histogram of the amphiphilic dopant (refer Fig. 5, in the supporting information) confirmed the existence of dopant molecule as spherical micelles of 4.3 nm in water. The energy minimized structure of the dopant was calculated using AM1 calculation and based on that the theoretical diameter of the micelle (which is equivalent to the twice the end-to-end distance of the dopant) of was obtained (refer supporting information). The calculated diameters of the micelles (4.8 nm) are matching with that of the DLS

experimental values (4.3 nm). It suggests that the dopant molecule exist in the form of tightly bound micelles in water.⁴⁰ Up on adding aniline in to the dopant micelles in water and stirring under sonication for few minutes, the solution became pale

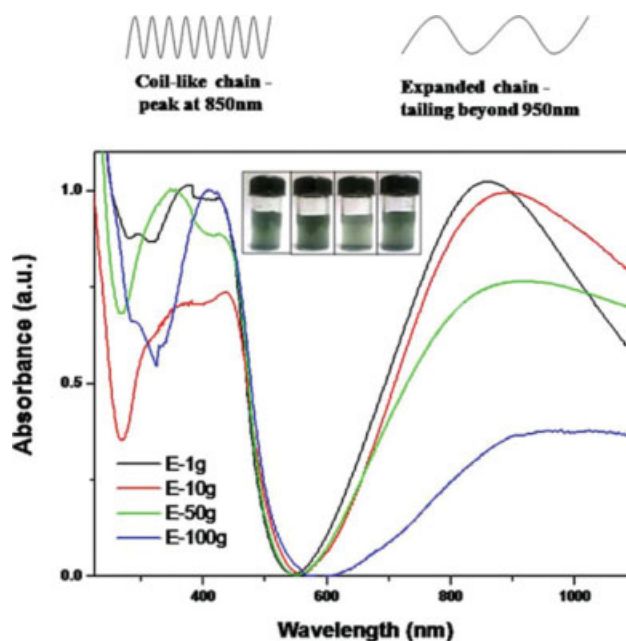


Figure 5 UV-vis absorption of PANI nanofibers in water at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

yellow thick milky emulsion. The emulsion was stable for more than 1 month at ambient conditions without any phase separation. The DLS data of the resultant emulsion showed the existence of aggregates of large size aggregates. DLS experiments clearly evident that amphiphilic molecule has tendency to form stable aggregates with aniline in water under the polymerization conditions.⁴³ The good stability of the template (aniline + dopant) enabled us to characterize the morphology by SEM. For the microscopic analysis, the dopant + aniline emulsion (in water) was drop casted on SEM-stud and the samples was dried under desiccator containing anhydrous calcium chloride for 1 week. SEM image (refer Fig. 5, supporting information) indicates the existence of a net-work morphology of highly entangled cylindrical micelles, which is a typical texture observed for micellar templates.³⁸ The complexation of aniline transform the dopant micelles into long cylindrical aggregates of ~ 180 nm diameter and few micrometer lengths, which template for nanomaterials (refer Fig. 5, supporting information).^{25,26} Further oxidation of these aggregates by APS produces PANI nanofibers. To understand the interactions of aromatic moieties like aniline with anionic surfactant in water, the pH of the polymerization mixtures were also measured. The pH of the dopant (alone) and surfactant + aniline in water were obtained as 2.86 and 7.29, respectively. As expected, the aromatic sulfonic surfactant is highly acidic in nature in water with lower pH of 2.86. Aniline is a strong base and effectively reacted with the surfactant to form the neutral anilinium-salt, which drastically increase the pH of the solution from 2.86 to 7.29 (towards neutral). This results supports that the aniline molecules not only occupy the hydrophobic core of the micelle and it also reacts with the hydrophilic core at the surface of the micelles to bring the micelles together to produce large size aggregates. Since the concentration of aniline and dopant was kept constant for the all the reactions from 1 to 100 g scale, the template assisted mechanism is expected to be same for the entire scale up reactions. Therefore, it can be summarized that the micelle template plays a major role for the reproducible nanofiber synthesis and also for the large-scale production up to 100 g.

The nanofibers were freely suspendable in water and other organic solvents by shaking under ultrasonic at ambient temperature and the resultant solutions were found as green in color (refer vials in Fig. 5). The absorption spectra of PANI nanofibers **E-1g** to **E-100g** are free from quinonid ring (at 650 nm), which confirmed the doped conducting emeraldine salt form. All the nanofibers showed three distinct peaks at 380 nm, 430 nm, and at above 850 nm corresponding to the transitions of π -band to

π^* -band, polaron band to π^* -band and π -band to polaron band as observed in doped conventional PANI samples.^{44,45} Though the features of the absorption spectra were almost identical in all four samples, it is important to note that the near-IR region corresponding to polaron band showed either peak or tail like characteristics. It has been proven earlier by us and other researchers that the conformation of the polymer chain in the PANI highly sensitive to electronic transitions in absorption spectra.^{25,46} Expanded or coil like conformation in PANI chains are expected to show tail or peak like characteristics, respectively, in the near-IR region.^{44,46} It is interesting to note that the spectrum of **E-1g** has a strong polaron peak at 860 nm characteristic with respect to coil like chain conformation in PANI fiber.⁴⁶ On the other hand other three samples **E-10g**, **E-50g**, and **E-100g** showed change from peak to tail like behavior above 890 nm and confirming transformation of conformations from coil to expanded chains at higher gram scale. The four probe bulk conductivity of bulk scale synthesized nanofibers showed a one order increment in conductivity (10^{-2} S/cm) than that of 1 g scale product ($\sim 10^{-3}$ S/cm, refer Table II). It suggests that the more expanded conformation of PANI chains in large-scale products increases the delocalization of charge carriers (evident by UV-Vis spectra, refer Fig. 5) and produced conductivity one order higher than that of 1 g scale products.²⁵ The difference in the conformation of the polymer chains may be associated with the temperature of the polymerization of the 1 to 100 g scale. Oxidation of aniline in to PANI is an exothermic reaction,⁴⁷ and therefore, the temperature of the polymerization medium was monitored at regular interval. Before the addition of APS (before polymerization starts), the temperature of emulsion was noticed as 29°C in all the four cases. After the addition of APS, within 30 min, the temperature of the reaction medium increased to a constant high temperature of 39, 54, 63, and 67°C for the 1, 10, 50, and 100 g scale, respectively. The temperature of the polymerization medium gradually decreased to 29°C after 6 h of reaction. In the 1 g scale reaction, the volume of reaction is relatively small and also the reacting sites are more exposed to atmosphere which will dissipate the heat evolved during polymerization. But in the large-scale synthesis (10 g, 50 g, and 100g), most of the reaction sites are occupied well beneath in the bulk and so the heat generated is trapped inside the reaction medium. This higher temperature favored the effective uncoiling of PANI chains into a more expanded conformation due to the increased thermal motions of PANI chain and subsequent doping by amphiphilic dopant molecules allows crystallization of side chains of dopant to produce highly ordered polymer chains in nanofibers. This thermochromic

effect in absorption spectra due to uncoiling of polymer chains is similar that observed by Nandi and co-workers in the case of poly(*o*-methoxy aniline) and its DNA hybrid.^{48–50} This higher temperature favored the effective penetrating of the dopant molecules into the PANI matrix to produce highly ordered polymer chains.^{48–50} The highly ordered and expanded polymer chain showed one order enhancement in the conductivity. So, we believe that the observed differences in spectral properties and conductivity are due to the conformational variation among polymer chains originated from the difference in the temperature of reaction medium. It is very important to add here that despite the variation in the temperature of the polymerization, the morphology of the nanofiber synthesis is highly reproducible.

The nanofibers were powdered and subjected for Wide angle X-ray diffraction analysis to investigate the solid state ordered properties. The WXR D plots of the PANI nanofibers are shown in Figure 6. The WXR D patterns of the nanofiber **E-1g** showed three distinct peaks at $2\theta = 6.4, 20.1,$ and 25.5° (d spacing = 13.6, 4.4, and 3.5 Å). The two peaks at 20.1 and 25.5° are generally observed in doped PANI and in this case these peaks are more or less super imposed with amorphous scattering.⁵¹ The lower angle peak at $2\theta = 6.4^\circ$ (d spacing = 13.6 Å) is assigned to the ordered (crystalline) domains in the nanofiber followed by the strong penetrating of the dopant molecule into the PANI chains inter-lattices.⁵² A similar peak has been reported by us as well as by other in earlier reported for ordered PANI chains (for 1 g scale reaction).^{22,23,26} Interestingly, the large-scale samples (10, 50, and 100 g) showed a new peak at $2\theta = 3.4^\circ$ (d spacing of 25.5 Å). The presence of this lower angle peak at 3.4° in the WXR D of nanofibers sample is strong indicating for the existence of a lamellar structure.^{53,54} This lamella is formed due to the inter-digitations and crystallization of side chains of the comb-shaped doped PANI. To get more idea regarding d spacing values, the theoretical geometry of the dopant molecule calculated by AM1 calculations (refer supporting information) was correlated to the d spacing of the WXR D patterns. The polar head of the dopant molecules penetrated in to the tunnel between the polymer chains and give d spacing value ($d = 25.5$ Å, refer Fig. 6) equivalent to molecular length (end-to-end distance = 24.4 Å). The WXR D pattern corresponding to the $d = 13.6$ Å is almost equivalent to the second order reflection in the lamellae of the nanofiber.⁵⁴ Among the bulk scale products, **E-100g** is appeared to be more crystalline and showed sharp peaks at even higher angles ($2\theta = 15\text{--}35^\circ$). This may be due to the more expanded nature of the polymer chains (evident from absorption spectra, Fig. 5) in this

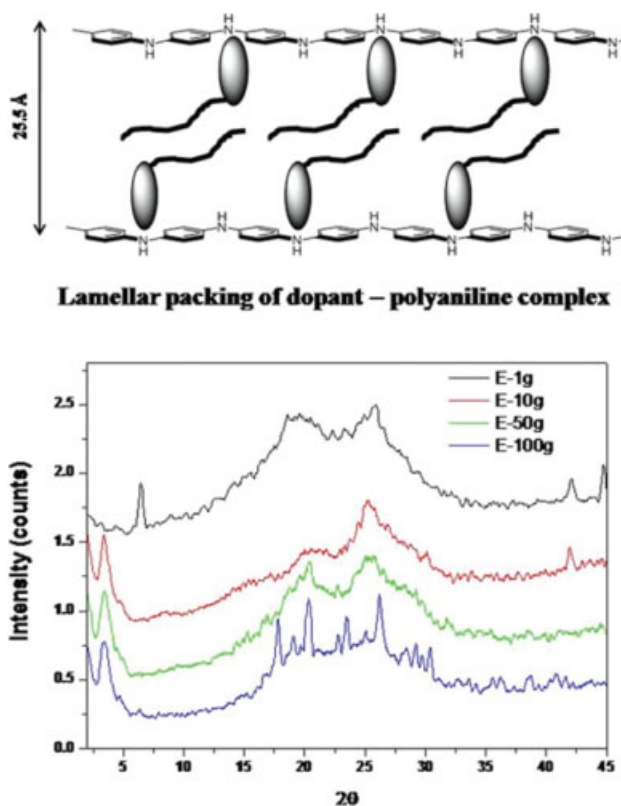


Figure 6 WXR D pattern of PANI nanofibers at 30°C . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sample which can pack in a more ordered fashion to increase the solid state ordering of the nanofibers.^{25,44} We believe that this observed difference in solid state packing is a consequence of heat generated during polymerization. In bulk scale polymerization (**E-10g**, **E-50g**, and **E-100g**), the excess generated heat will improve the diffusion of dopant molecules into the polymer matrix and hence results in peaks with increased d spacing in WXR D. The above data based on the absorption, conductivity, and WXR D indicate that the properties of the samples synthesized from 10 to 100 g scale are almost identical compared to that of 1 g scale. Therefore, the large-scale synthesis of nanomaterials, especially polyaniline nanofibers, and analysis of the bulk samples are important factors which are successfully addressed in the present investigation.

For the facile use of these large-scale synthesized materials, the fiber morphology should be stable and the physical properties such as conductivity, ordering, and absorption characteristics should also be retained in consecutive reversible cycles of doping/de-doping processes. To check the reversibility of the nanofibers, the sample **E-100g** was subjected to doping/de-doping experiments. The sample was de-doped by stirring with 25 mL of 10% solution of aq. NH_3 for 4 h to get PANI-EB form. The sample

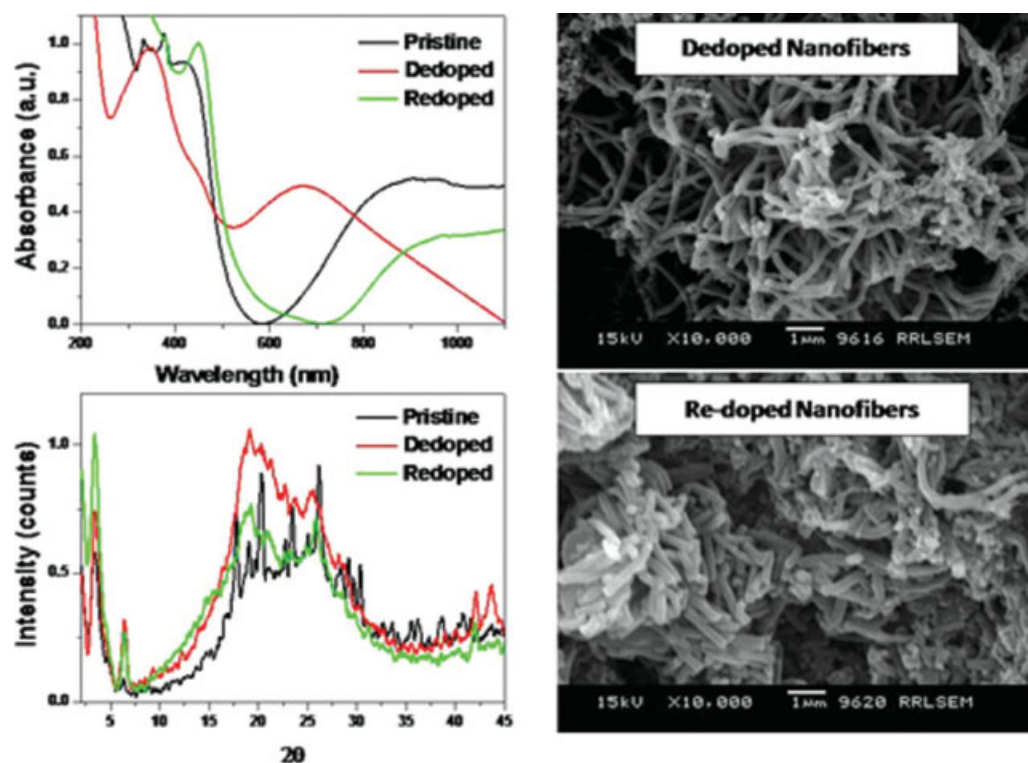


Figure 7 Reversibility studies of PANI nanofibers by acid-base doping/de-doping. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was purified by washing with water till the filtrate become colorless and dried in vacuum oven for 24 h. The morphology and other properties of de-doped sample were given along with the parent sample in Figure 7. Absorption spectra of the de-doped sample showed a peak at 650 nm characteristic of quinoid ring in the emeraldine base, which confirmed the complete de-doped stage. The SEM image of de-doped sample indicated that the fibrous morphology was not altered by the de-doping process. The WAXRD plot of the de-doped sample showed the presence of lower angle peak confirming the retaining of ordered polymer chains even after the removal of the dopant. The conductivity of the de-doped sample was obtained in the range of 10^{-6} to 10^{-7} S/cm, which is 4 order less than that of the original sample (in the range of 10^{-2} S/cm). The de-doped sample was re-doped by treating with camphor sulfonic acid in ethanol (or HCl in water) at 60°C to result green colored emeraldine salt form. The UV-Vis spectrum showed the formation of polaron peak at 850 nm due to the doping and vanishing of peak at 650 nm indicating efficient doping. It is very clear from SEM image that the fiber morphology is still preserved and WAXRD confirmed the complete reversal of solid state properties of PANI. The conductivity values of green colored re-doped pellets showed 10^4 times (in the range of 10^{-2} to 10^{-1} S/cm) increase compared to the de-doped

pellets. The combinations of SEM, WAXRD, UV-Vis, and conductivity measurements reveal that the morphological, solid state, electronic, and optical properties of the PANI nanofibers are reversible and highly intrinsic to the polymer backbone.

CONCLUSIONS

In conclusion, we have successfully utilized the cylindrical micellar template of a renewable resource amphiphilic azobenzenesulfonic acid for the reproducible large-scale synthesis of PANI nanofibers up to 100 g. The importance of the present investigation can be highlighted as follows: (i) for the first time, large-scale synthesis of PANI nanofibers was achieved up to 100 g quantity, (ii) the renewable resource amphiphilic molecule behave as surfactant-cum-dopant and form stable cylindrical micellar aggregates with aniline in water which template for the reproducible synthesis of PANI nanofibers from 1 to 100 g scale, (iii) DLS techniques confirmed the existence of the surfactant micelles in water and its self-organization with aniline, (iv) SEM and TEM analysis confirmed the reproducible formation of nanofibers up to 100 g scale and also provide evidence for the existence of cylindrical aggregates in the polymerization templates, (v) absorption spectra of the nanofibers revealed that the bulk scale nanofibers possesses more expanded confirmation than

small scale products, (vi) wide angle X-ray diffraction indicated that the nanofibers exhibit good solid state ordering and the bulk scale products exhibits more ordering compared with small scale nanofibers, (vii) the expanded and solid state ordered sample was found to show one order higher conductivity, and (viii) the nanofibers showed high reversibility in morphology, optical, and solid state properties in the repetitive doping/de-doping analysis for practical applications. The large quantity of the PANI nanofibers are currently employed as an active layer for chemical and biological sensing applications and the results will be published in future. In a nut shell, for the first time, we have shown that the amphiphilic dopant based emulsion route was very good for reproducible large-scale synthesis of PANI nanofibers and the resultant materials have shown reversibility in their conductivity, morphology, opto-electrical, and solid state properties.

The authors thank Department of Science and Technology, New Delhi, India, under Scheme: NSTI Programe-SR/S5/NM-06/2007 and SR/NM/NS-42/2009 for financial support. The authors thank Mr. M. R. Chandran, Dr. V. S. Prasad, and Mr. P. Gurusamy, NIIST, Trivandrum for SEM, TEM, and WXR analysis. They also thank Mr. Willi Paul, SCTIMST, Trivandrum, for DLS analysis. P. Anilkumar thanks UGC, New Delhi, India, for senior research fellowship.

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