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Synthetic Metals 148 (2005) 237–243

SYNTHETIC METALS

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Controlled interconversion of semiconducting and metallic forms of polyaniline nanofibers

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Received 6 August 2004; received in revised form 26 August 2004; accepted 16 September 2004

Abstract

Self-assembled polyaniline nanofibers doped with 2-acrylamido-2-methyl-1-propanesulfonic acid were prepared by oxidative polymerization of aniline in the presence of a nonionic surfactant. These nanofibers were dedoped to the semiconducting emeraldine base and then redoped to the metallic emeraldine hydrochloride. It was possible to introduce a different dopant anion from that used in the initial synthesis with no significant changes in fiber morphology or diameter, as observed by scanning electron microscopy (SEM). The method of sample preparation for SEM significantly affected the observed morphology. Deposition from aqueous dispersions resulted primarily in nanofibers that ranged in diameter from 28 to 82 nm (average: 56 nm), whereas drying to solid powder resulted in a less fibrous material. UV–vis–NIR absorbance spectroscopy indicated that the electronic structure of the emeraldine base nanofibers was identical to bulk emeraldine base obtained by conventional synthesis. Estimates from X-ray diffraction data suggested that the fractional crystallinity of emeraldine hydrochloride nanofibers did not differ significantly from the bulk powder.

Keywords: Polyaniline; Nanofibers; Doping; Scanning electron microscopy

1. Introduction

Polyaniline is among the most highly studied conducting polymers because of its simple synthesis, easily varied physical, chemical and electronic properties, and good environmental stability [1–11]. It is well known that polyaniline in the emeraldine ("half-oxidized") oxidation state can be reversibly switched between electrically insulating and conducting forms. The insulating (semiconducting) emeraldine base can be converted to the conducting (metallic) emeraldine salt by doping with a wide variety of protonic acids (Fig. 1), with reported increases in conductivity of up to 10 orders of magnitude. The emeraldine salt can be dedoped back to the insulating form via deprotonation with base (e.g., NH_4OH) and the conductivity can be tuned by adjusting the doping level [1–2]. This versatility has made polyaniline attractive for numerous applications, including sensors, battery electrodes, display devices, anticorrosion coatings and field effect transistors [1–11].

Research in the field of nanomaterials (defined as substances or structures which exhibit at least one dimension of less than 100 nm [12]) has lead to the discovery that at this scale, dramatically different properties may be demonstrated with respect to bulk materials [13]. This has inspired recent efforts to synthesize nanostructured polyaniline, especially as fibers and hollow tubes and spheres [8–11]. One-dimensional conducting polymer nanofibers ("nanowires") are of particular interest to the physics and engineering communities for application in electronic devices and molecular sensors due to their extremely high surface area, synthetic versatility and low-cost.

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0379-6779/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.synthmet.2004.09.038

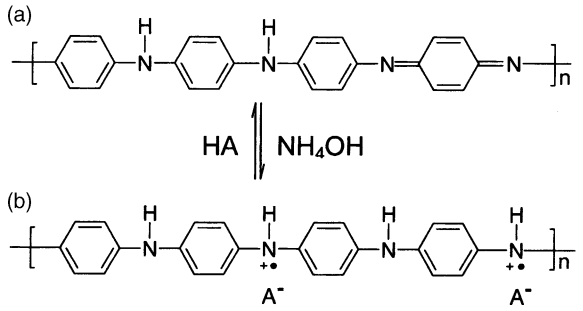

Fig. 1. Reversible doping from (a) semiconducting emeraldine base to (b) metallic emeraldine salt form of polyaniline (HA = HCl, AMPSA, etc.) [1].

Conventional synthesis of polyaniline, based on the oxidative polymerization of aniline in the presence of a strong acid dopant [2], typically results in an irregular granular morphology that is accompanied by a very small percentage of nanoscale fibers [9]. In recent years, however, several approaches have been developed by which nanofibers can be obtained as the dominant nanostructure. For example, the cylindrical pores of nanoporous membranes have been used for the generalized template synthesis of conducting polymers, metals and other materials. Highly monodisperse nanofibers and/or tubules are subsequently obtained by dissolving the membrane template [8]. Electrospinning, a non-mechanical, electrostatic method, has yielded composite polyaniline/polyethylene oxide nanofibers with diameters below 30 nm and lengths of up to hundreds of micrometers [11]. In the absence of an external physical or chemical template, pure polyaniline nanofibers/tubes and spheres can be obtained by making use of large organic acids that serve as both dopants and in situ templates by forming micelles upon which aniline is polymerized [10]. Fiber diameters are observed to be as low as 30–60 nm and are highly influenced by reagent ratios [10]. Uniform nanofibers of pure metallic polyaniline (30–120 nm diameter, depending on the dopant) have also been prepared by polymerization at an aqueous–organic interface. Migration of the product into the aqueous phase is hypothesized to suppress uncontrolled polymer growth by isolating the fibers from excess reagent [9]. It has recently been demonstrated that the addition of certain surfactants to such an interfacial system grants further control over the diameter of the nanofibers [14]. “Seeding” with various nanomaterials has also been used with great effect to initiate polyaniline nanofiber formation in single-phase polymerizations [15]. The template-free interfacial, seeding and micellar methods each employ a different “bottom up” approach to obtain pure polyaniline nanofibers. The combination of self-assembly with minimal post-synthesis processing warrants further study and application of these nanofibers, especially in the field of electronic nanomaterials.

We have prepared self-assembled polyaniline nanofibers doped with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) by polymerization of aniline in the presence of the nonionic surfactant Triton X-100. The present study was carried out in order to ascertain (1) whether these nanofibers could be interconverted between the semiconducting and metallic forms with retention of morphology; (2) if nanofibers of the metallic form of polyaniline could be obtained by doping the emeraldine base form with an acid different from that used in the initial synthesis; (3) whether the method of sample preparation for SEM studies (as distinct from the method of synthesis) had an effect on the observed morphology. In addition to characterization by SEM, the electronic and molecular structure of the polyaniline nanofibers has been probed by UV–vis–NIR absorbance spectroscopy and X-ray diffraction. All results have been compared to data previously obtained from conventionally prepared polyaniline.

2. Experimental

2.1. Synthesis of polyaniline emeraldine base nanofibers

All materials were used as received. Aniline (Aldrich) was stored in a sealed container in a refrigerator. The dopant 2-acrylamido-2-methyl-l-propanesulfonic acid (AMPSA; Aldrich; 4.15 g, 0.0200 mol) was weighed into a 150 mL beaker and dissolved in 20 mL of deionized water at room temperature by magnetic stirring for ∼5 min. Approximately 5 mL of the surfactant Triton X-100 (polyoxyethylene(10) isooctylphenyl ether; Acros) was dissolved in the 1 M AMPSA solution by sonication for 1 h, during which time the solution became warm. The clear, colorless and slightly viscous solution was allowed to return to room temperature. Approximately 1 mL of aniline was added to the solution, which was then magnetically stirred for 20 min. Solid ammonium peroxydisulfate (APS; Fisher; 0.58 g, 2.5 mmol) was added to the solution, which was then magnetically stirred for ∼5 min. The APS was not fully soluble and the system became cloudy. Stirring was stopped, the stir bar removed and the beaker covered to prevent contamination by dust, etc. After ∼3 min, small blue–green particles could be observed suspended in the slightly turbid, colorless solution. Within ∼5 min, the color deepened and the blue–green mixture became opaque. Within ∼10 min, it had become deep green in color, typical of metallic polyaniline [2], in this case doped with AMPSA.

After 2.5 h at room temperature, the reaction was stopped by pouring the thick, opaque green precipitate mixture into ∼1 L of 0.1 M ammonium hydroxide, which deprotonated the doped polymer. The mixture immediately became blue–purple in color (pH ∼9.5, pH paper) and it was added, in portions, to a Buchner funnel (Whatman 41 filter paper, 9 cm). The volume of liquid in the funnel was very slowly decreased and ∼4 L of 0.1 M NH_4OH was added to continuously wash the precipitate, which was not allowed to dry. The product was washed with the aqueous base until the filtrate became colorless and was free of foam, indicating that excess surfactant had been removed. When ∼20 mL of solution remained in the funnel, the upper portion only of the precipitate/NH_4OH mixture was decanted to a glass vial to prevent contamination by filter paper fibers. The product was characterized by UV–vis–NIR spectroscopy, confirming that it was the emeraldine base form of polyaniline. Portions were set aside for study by SEM and X-ray diffraction (see below).

2.2. Interconversion of emeraldine base nanofibers to emeraldine hydrochloride

Approximately 10 mL of the above dispersion of emeraldine base was added to ∼250 mL 1 M HC1 and magnetically stirred overnight. The resulting green suspension was slowly filtered in a Buchner funnel as described above and was continuously washed with ∼2.5 L hydrochloric acid until the filtrate was colorless. When the volume had been reduced to ∼20 mL, the upper portion only of the green dispersion (pH ∼0) in the funnel was decanted to a glass vial to prevent contamination by filter paper fibers. Conversion to emeraldine hydrochloride was confirmed by UV–vis–NIR spectroscopy and portions of the product were set aside for SEM and X-ray diffraction studies (see below). Nanofibers of the emeraldine hydrochloride could be readily dedoped to the emeraldine base in an identical manner to the deprotonation of AMPSA-doped polyaniline, as described above.

2.3. Sample preparation

The morphology of the nanofibers was significantly affected by the method of sample preparation. As will be described below, nanofibers of the emeraldine base and hydrochloride could be destroyed by filtration, drying and mechanical handling (e.g., scraping). It was found that the polyaniline nanofibers remained intact if they were prevented from drying. Therefore, characterization by absorbance spectroscopy, scanning electron microscopy and X-ray diffraction was performed using only samples prepared directly from the aqueous dispersions obtained as described above.

2.4. UV–vis–NIR absorbance spectroscopy

Absorbance spectra from 1300 to 200 nm were obtained on a Perkin-EImer Lambda 9 spectrometer using quartz cuvettes (1 cm path length). A few drops of the dispersion of emeraldine base nanofibers prepared above were dissolved in *N*-methyl-2-pyrrolidone (NMP) to obtain a light blue solution. NMP was used as a reference solvent. Similarly, a few drops of the dispersion of HCl-doped nanofibers were added to 1 M HCl to produce a pale green dispersion. The spectrum of the dispersion was obtained using 1 M HCl as a reference solvent.

2.5. Scanning electron microscopy

One to three drops of the dispersion of emeraldine base in ammonium hydroxide were diluted by addition to 3 mL of 0.1 M NH_4OH and then briefly shaken to produce a transparent, pale blue dispersion. Similarly, one to three drops of the dispersion of redoped nanofibers in hydrochloric acid were added to 3 mL of 1 M HCl and then shaken to produce a transparent, pale green dispersion. The nanofiber dispersions could also be diluted by addition to 3 mL of ethanol instead of NH_4OH or HCl. The dispersions were deposited drop-wise on small segments of microscope slide glass that had been rinsed with methanol and air-dried. The solvent evaporated in air and small particles became visible on the glass surface. After vacuum-drying in a desiccator for 1.5 h, the samples were then attached to aluminum sample stubs using double-sided carbon tape. Electrical contact was maintained between the sample surface and the aluminum stub with a short strip of copper tape. All samples were sputter coated with a gold–palladium alloy prior to imaging on a JEOL 6300 FV field emission scanning electron microscope, operating at an accelerating voltage of 5 kV. Average nanofiber diameters were measured on at least 25 randomly chosen fibers at several regions on each sample. All measurements were made on images obtained at 30,000× magnification (using standard imaging software, 1 pixel = 3.9 nm).

2.6. X-ray diffraction of polyaniline nanofibers

Glass microscope slides were cut into segments of approximately 2 cm × 1.6 cm, rinsed with methanol and then dried in air. Enough of the opaque, deep blue–purple dispersion of polyaniline emeraldine base in 0.1 M NH_4OH was deposited on the substrate to cover the entire surface. The sample dried in air at room temperature, coating the substrate with a layer of dark blue powder. This process was repeated several times as needed to increase the thickness of the sample. The same steps were taken to prepare samples from the emeraldine hydrochloride dispersed in 1 M HCl. Samples were then mounted in a stainless steel sample holder and inserted into the sample compartment of a Rikagu Geigerflex X-ray diffractometer using Cu Kα radiation (λ = 1.54 Å) and a graphite monochromater.

3. Results and discussion

3.1. Oxidation and protonation states of polyaniline nanofibers

The initially prepared AMPSA-doped polyaniline was green in color and became blue–purple upon washing with copious amounts of 0.1 M NH_4OH. This color change qualitatively indicated that the doped emeraldine salt had been deprotonated to the emeraldine base. A few drops of this aqueous dispersion formed a clear blue solution in NMP that yielded UV–vis–NIR absorbance spectra with maxima at 634 and 328 nm (Fig. 2). The peak positions and relative peak heights were in excellent agreement with literature results for conventionally prepared semiconducting emeraldine base in

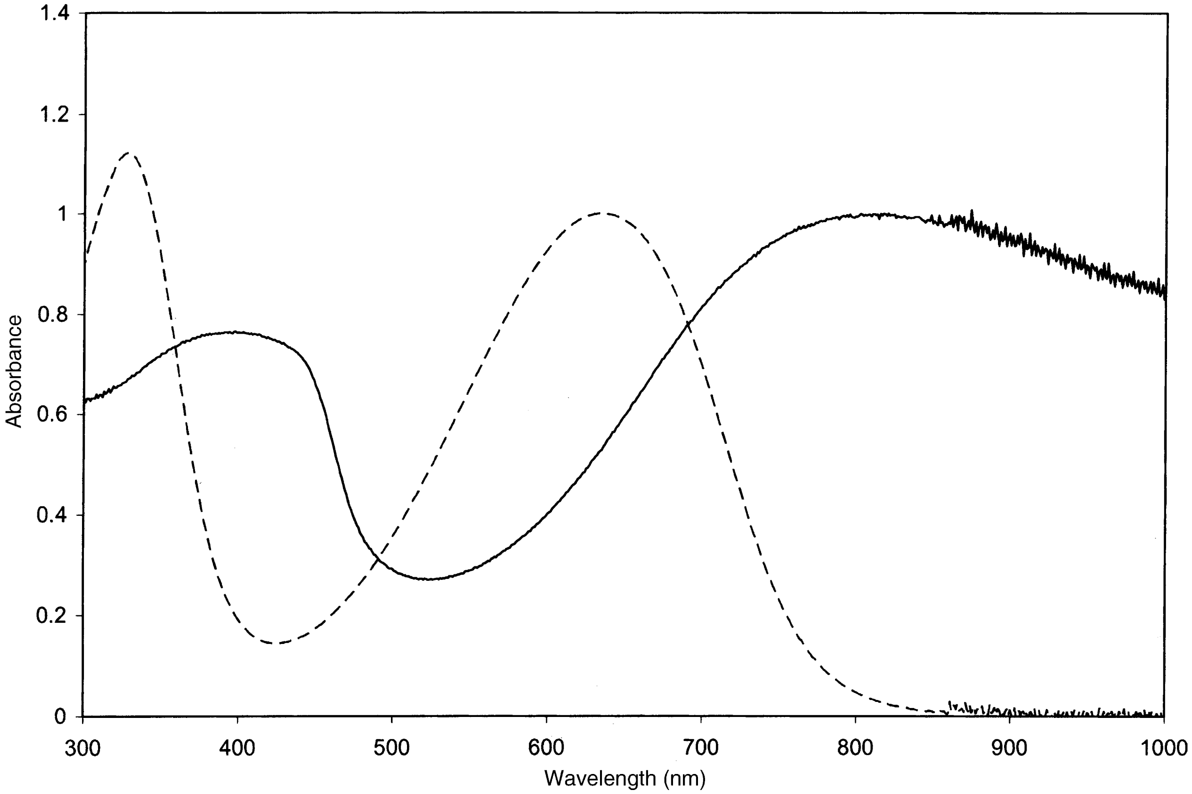

Fig. 2. UV–vis–NIR absorbance spectra of dedoped emeraldine base dissolved in NMP (dotted line) and redoped emeraldine hydrochloride dispersed in 1 M HCl (solid line). Noise observed at wavelengths >860 nm is attributed to an instrumental artifact.

NMP solution [16,17]. Washing with 1 M HCl resulted in a return to the characteristic green color of metallic emeraldine hydrochloride. UV–vis–NIR spectra of the redoped aqueous dispersion diluted with 1 M HCl showed absorbance maxima at 820 and 398 nm (Fig. 2), in close agreement with previously reported emeraldine hydrochloride thin films deposited in situ on glass slides [5,18], as well as nanofibers dispersed in water [9]. From the above spectra, it was concluded that polyaniline in these aqueous dispersions could be completely and controllably interconverted between the semiconducting and metallic regimes, in a manner similar to the conventionally prepared material [2].

3.2. Morphology and structure of polyaniline nanofibers

After confirming doping and redoping by UV–vis–NIR, it was determined by scanning electron microscopy (SEM) that polyaniline prepared by oxidative polymerization in the presence of Triton X-100 results primarily in nanofibers (Fig. 3). However, it was found that when both the metallic and semiconducting forms were completely dried, irregular nanostructures became far more prevalent than nanofibers, typically appearing fused, flattened and/or broken, as shown in Fig. 4. In order to preserve the nanofibrous morphology, the aqueous dispersions of polyaniline were prevented from drying to solid powders, as described in Section 2. This measure significantly increased the content of nanofibers, relative to all other morphologies, as shown by comparison of Figs. 3 and 4.

Representative images of dedoped emeraldine base and subsequently redoped emeraldine hydrochloride are shown in Fig. 3. Examination of several regions on every sample revealed mats of interwoven and twisted nanofibers. Though fibers were the dominant morphology, they were typically accompanied by some small, non-fibrous particles. We have hypothesized that dust and/or other particulate contaminants in the polymerizing solution, including insoluble ammonium peroxydisulfate (see Section 2), might have served as nucleation sites for the observed irregular material [15]. Current studies are directed towards understanding the polymerization process at its earliest stages in an effort to improve nanofiber monodispersity. It could not be determined by these SEM studies if the nanofibers were hollow tubes or solid fibers. Though preliminary transmission electron microscopy experiments have suggested that AMPSA-doped polyaniline consists partially of hollow tubes, this technique has not yet been used to investigate the effects of dedoping and redoping [19].

Fiber dimensions were measured in regions where they were less densely packed, usually near the edges of the mats. The average diameter of emeraldine base nanofibers deposited from dispersions in 0.1 M NH_4OH was 53 nm, ranging from 37 to 71 nm. When deposited from ethanol, diameters ranged from 32 to 75 nm, with an average of 59 nm.

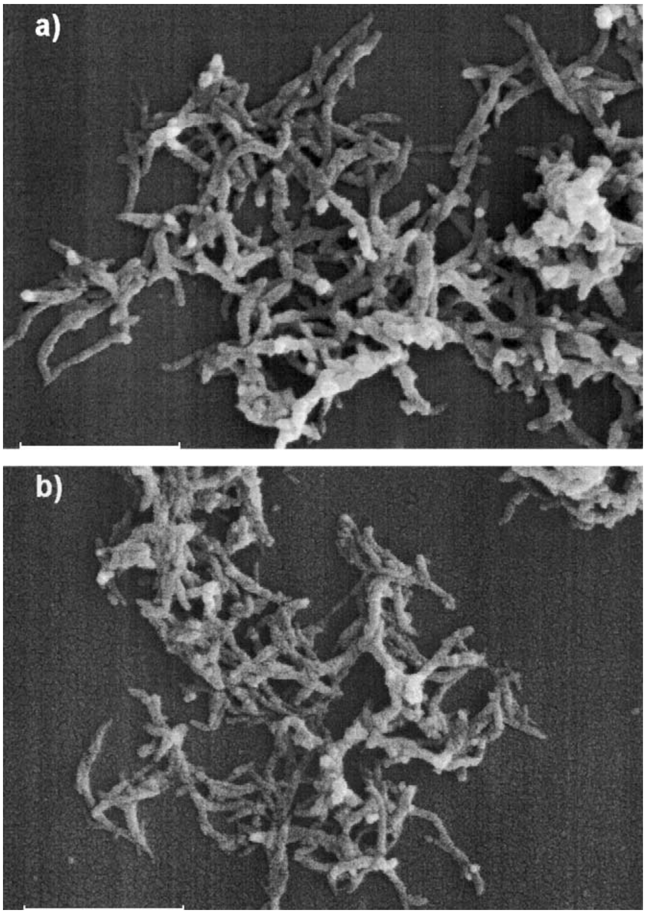

Fig. 3. SEM images of (a) emeraldine base and (b) emeraldine hydrochloride nanofibers both deposited from aqueous dispersions diluted in ethanol. Magnification is 30,000× and scale bar is 1 μm.

Emeraldine hydrochloride nanofibers deposited from dispersions in 1 M HCl ranged in diameter from 28 to 82 nm, with an average of 58 nm. When deposited from ethanol, the average diameter was 54 nm, ranging from 28 to 70 nm. Differences in these averages measured by counting pixels in the SEM images (∼4 nm/pixel) were within experimental error. Estimates of fiber length ranged from ∼400 nm to 2 μm. It was concluded that the interconversion between metallic and semiconducting states by dedoping and redoping did not cause any obvious change to the morphology or dimensions of the nanofibers, nor were there any discernable effects based on the solvent in which they were suspended. However, repetitive dedoping and redoping of the nanofibers appeared to result in changes in morphology, such as more densely packed fiber mats, and fused, and/or broken fibers.

From the absorbance data and SEM images described above, it is most important to note that the polyaniline nanofibers could be redoped with a different acid (i.e., HCl) from that used in their initial synthesis (i.e., AMPSA). This implies that although a certain dopant may he required to obtain a certain type of nanofiher, this dopant can then be removed and replaced with a different dopant for modification of selected properties with retention of morphology.

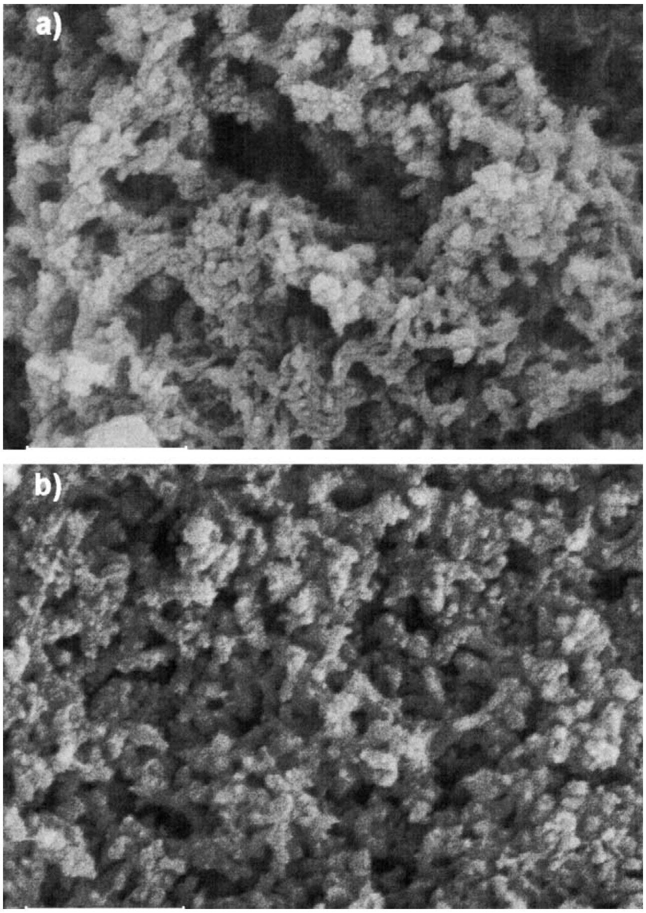

Fig. 4. SEM images of nanofibers of (a) emeraldine base and (b) emeraldine hydrochloride both dried to solid powders. Magnification is 30,000× and scale bar is 1 μm.

X-ray diffraction was used to further probe the structure of the polyaniline nanofibers. The emeraldine base presented a broad signal centered at $2\theta \sim 22^\circ$ with a shoulder at $2\theta \sim 15^\circ$ (Fig. 5a). This broad X-ray structure suggested an amorphous polymer, similar to bulk emeraldine base prepared by standard methods [20]. Subsequent doping to emeraldine hydrochloride resulted in a more sharply defined diffraction pattern with an intense peak at $2\theta = 22.5^\circ$ and two weaker peaks at $2\theta = 16.2^\circ$ and 14.5° (Fig. 5b). As expected from previous results from the bulk material [20], the apparent crystallinity of the metallic form of the polymer was greater than that of the semiconducting form from which it was prepared. The metallic nanofibers were compared with commercially available polyaniline (Aldrich; emeraldine base, mol. wt. ∼100,000) that had been doped to the emeraldine hydrochloride form. It was found that only the lowest angle diffraction from the nanofibers agreed well with the diffraction pattern of the doped bulk polymer. It is unknown what differences in molecular structure this result may imply. However, there was no obvious, pronounced difference in the estimated fractional crystallinity of emeraldine hydrochloride when prepared as either nanofibers or as bulk material.

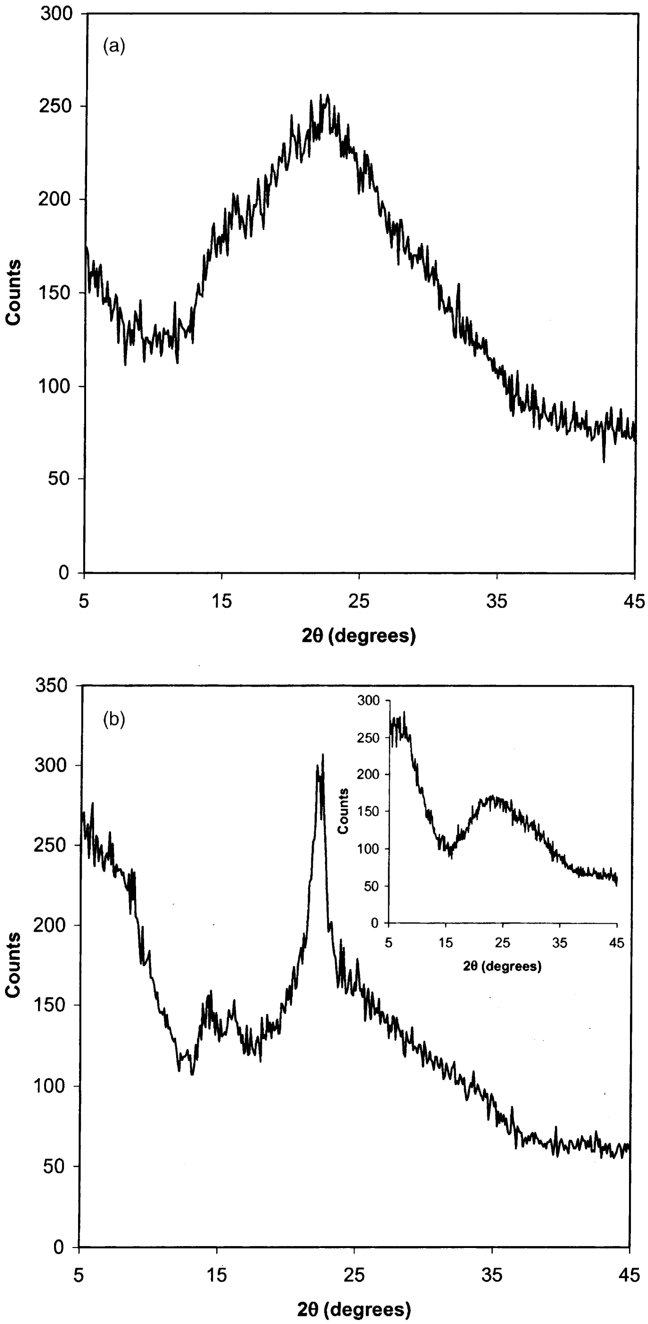

Fig. 5. X-ray diffraction patterns from nanofibers of (a) emeraldine base and (b) emeraldine hydrochloride on glass slides. Diffraction from the glass substrate (see inset, b) may obscure signals below $2\theta \sim 12^\circ$ and above $\sim 25^\circ$.

4. Summary

Nanofibers of semiconducting and metallic polyaniline with diameters of 28–82 nm (56 nm average diameter) have been prepared by oxidative polymerization of aniline in 2-acrylamido-2-methyl-l-propanesulfonic acid (AMPSA) solution in the presence of high concentrations of the nonionic surfactant Triton X-100. As with other similar systems that employ surfactants [10], it is hypothesized that fiber formation probably occurs on a micellar template, though the exact shape and composition of this template is not currently understood. AMPSA-doped polyaniline can be deprotonated to the semiconducting emeraldine base with ammonium hydroxide. Redoping to the metallic emeraldine hydrochloride form is readily achieved by protonation with hydrochloric acid. These nanofibers are electronically identical to the emeraldine base or hydrochloride forms, respectively, of conventionally prepared polyaniline. X-ray diffraction from emeraldine hydrochloride nanofibers indicates approximately the same fractional crystallinity as the analogous bulk material.

SEM images reveal that the nanofiber morphology is unchanged by interconversion between the semiconducting and metallic forms. Furthermore, emeraldine base nanofibers can be redoped with an acid different from that used in their initial preparation. Therefore, regardless of the conditions necessary to obtain a particular type of nanofiber, selected chemical, physical and electronic properties may be subsequently modified. Notably, the observation of nanofibers is greatly favored for samples that are prepared as aqueous dispersions and prevented from drying to solid powders. Extensive filtration and drying damages the nanofibers and significantly increases the content of non-fibrous material. The above studies show that electronic nanofibers of organic polymers represent a potentially very important class of new material in the area of nanoscience/technology.

Acknowledgements

The authors gratefully acknowledge the Office of Naval Research (Contract no. N00014-01-1-0933) and The University of Texas at Dallas for their support of this work. They also acknowledge the Laboratory for Research on the Structure of Matter at the University of Pennsylvania for the use of SEM facilities (MRSEC NSF Award no. DMR00-79909).

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