

# Toward optimizing synthesis of nanostructured chiral polyaniline

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## Abstract

We report here detailed investigation into optimizing the synthesis of chiral polyaniline nanofibers using an oligomer-assisted route. The effect of temperature, monomer concentration, nature of oligomer, and the rate of oxidant addition on the optical properties of the PANI nanofibers have been carefully determined. Our results indicate that the highest chirality is achieved under conditions that promote interaction of the chiral acid with the growing polymer chain. These chiral polyaniline nanofibers are thermally stable up to 90 °C and are found to be stable against repeated doping–dedoping cycles. The as-synthesized nanofibers are partially crystalline regardless of their chirality. This partial crystallinity may be responsible for their chemical and thermal stability.

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## 1. Introduction

The control of chirality has become a vitally important issue in the pharmaceutical, chemical, and agricultural industries. The differences that make compounds chiral can produce critically different pharmacological effects in biological systems. As a result, demand for stereoselective separation techniques and analytical assays to evaluate the enantiomeric purity of chiral compounds has increased. Amongst many techniques to achieve enantiomerically pure compounds, column chromatography using a chiral stationary phase (CSP) shows promise for large-scale separation (purification) of chiral molecules. Of particular interest is to use chiral polymers as the CSP. The helical structures of chiral polymer result in formation of chiral cavities that are able to discriminate between enantiomers through a recognition mechanism that is not fully understood. This chiral recognition demonstrated by helical polymers may translate into dissimilar retention times in a column-chromatography application. In recent years, there has been increased interest in synthesizing optically active conducting polymers because of their potential application to chiral separations [1], surface-modification of electrodes [2], as well as chemical and biological sensors [3]. Optically active, nanostructured, PANIs are of great interest

because they offer large surface area and shorter penetration distance for analyte molecules, which can influence separation efficiencies. Many groups have attempted to make optically active PANI and its derivatives using chemical and electrochemical routes. Optically active PANI is usually synthesized by either codissolving PANI powder and a chiral acid in common solvents [4] or by polymerizing aniline in the presence of a chiral acid [5]. Recently, Cholli et al. reported a synthesis of chiral PANI nanocomposites that controls the extent of helicity [6]. However, most of the chiral PANI materials synthesized from the above methods suffer from low chirality.

There have been a number of methods reported for the synthesis of PANI nanofibers. For example, Wu and Bein have demonstrated their synthesis by using a template-guided synthesis [7] while Reneker and Chun have employed an electrospinning method [8]. Huang et al. reported a two-phase synthetic route that results in high-quality PANI nanofibers [9]. The latter synthesis is carried out by dispersing aniline monomers and oxidant in organic and aqueous phases, respectively—polymerization occurs at the interface to form PANI nanofibers. Finally, our ‘oligomer-assisted’ synthesis [10] uses aniline oligomers as ‘seeds’ to catalyze the growth of nanofibers possessing a high degree of chirality. A similar approach, reported by Zhang et al., uses ‘nanofiber seeding’ in which polymeric nanostructures formed (or present) during the very early stages of the reaction lead to bulk formation of similar nanostructures [11]. A recent study by Huang et al. shows control over the growth of large quantities of PANI

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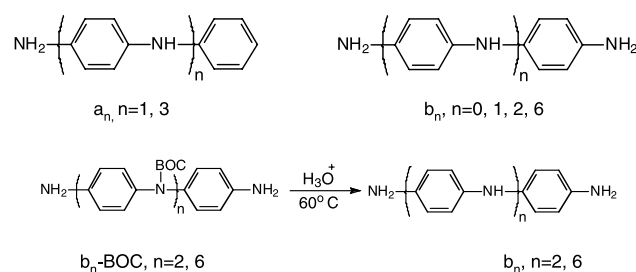
nanofibers by fast mixing to suppress the ‘secondary growth’. This latter work presents a better understanding of the formation mechanism of nanofibers and offers the possibility of preparing other conducting polymer nanostructures using a similar approach [12]. Additionally, Chiou et al. reported a facile synthesis of PANI nanofiber using dilute polymerization with careful control of the nucleation and growth processes [13,14].

Despite all of these synthetic efforts in making high surface area nanofibers, the synthesis of conducting polymer nanofibers with specific chemical or biological function has been realized only recently. Efforts in our labs and elsewhere have focused on making optically active conducting polymers and water-soluble chiral nanocomposites [15,16] with the aim to apply these materials to chiral separations and fabrication of surface modified electrodes. Most of the syntheses, especially the electrochemical ones, result in chiral conducting polymers with low chirality as revealed by the very weak optical activity. To address the above issues, we have developed a new method to synthesize chiral polyaniline nanofibers using the oligomer-assisted route [10]. Using this new process, the preparation of PANI nanofibers with very high optical activity comparable to that of helical peptides or proteins is possible. In this work, we present the systemic study of the effect of experimental parameters, such as concentration, temperature, rate of oxidant addition, and type of oligomer, on the polymerization reactions and on the properties of resulting polyaniline nanofibers. As a result, we have determined the optimal reaction conditions for synthesizing nanofibers with high optical activity. These as-synthesized nanofibers are partially crystalline and show chemical and thermal stability. Ultimately, our study demonstrates that controlled synthesis lays the foundation for preparing nanostructured functional conducting polymers.

## 2. Experimental section

**Materials:** aniline, (1S)-(+)-10-camphor sulfonic acid (CSA), (1R)-(–)-10-camphor sulfonic acid, and ( $\pm$ )-camphor sulfonic acid, 1,4-phenylenediamine ( $b_0$ , Scheme 1), *N*-phenyl-*p*-phenylenediamine ( $a_1$ , Scheme 1), and indium tin oxide (ITO) coated glass were purchased from Aldrich. 4,4'-Diaminodiphenylamine ( $b_1$ , Scheme 1) was also purchased from Aldrich and purified by column chromatography. Synthesis of  $a_3$  was accomplished by oxidative coupling of  $a_1$  by ferric ions in acid solution [17]. The (*N*)-protected species  $b_2$ -BOC and  $b_6$ -BOC were synthesized by Pd-catalyzed coupling reaction [18,19]; the detailed synthesis is published elsewhere [19]. Trimer ( $b_2$ , Scheme 1) and heptamer ( $b_6$ , Scheme 1) were prepared by hydrolysis of their tert-butoxycarbonyl (BOC) groups of the protected precursors ( $b_2$ -BOC and  $b_6$ -BOC) in acid solution (Scheme 1) at 60 °C for 2 h, and then used directly in the synthesis of polyaniline without separation.

**Synthesis of chiral PANI nanofiber:** aniline, CSA, and oligomers (or BOC-protected oligomers) were combined in aqueous solution. For the sake of convenience, concentration of chiral acid (CSA) and aniline is expressed as molality rather



Scheme 1. Oligomers used in the synthesis of chiral polyaniline, and reaction to deprotect  $b_2$ -BOC and  $b_6$ -BOC.

than molarity. The concentration of CSA varies from 0.5 to 10.0 m. In all experiments, the amount of aniline is fixed to 0.20 g (2.1 mmol). Depending on the amount of water, the concentration of aniline is between 0.14 and 0.84 m. The ratio of aniline to oligomer was controlled between 10:1 and 60:1. The solution is sealed in a vial, and heated to 60 °C for 2 h; the solution was then cooled down to 25 °C. To this solution, an aqueous solution of ammonium persulfate is added to achieve a ratio of ammonium persulfate to aniline of 1:1 in most of the experiments. The ammonium persulfate solution can be added as a single aliquot or incrementally.

Incremental addition of ammonium persulfate is achieved by equally dividing ammonium persulfate solution into  $n$  portions; each portion is  $1/n$  of the total oxidant. After addition of each portion, the solution is shaken vigorously, and kept in 20 °C water bath to control the temperature increase. After the addition of ammonium persulfate, the solution usually turned blue followed by return to a dark green color. The next portion of ammonium persulfate was then added. The process is repeated until all ammonium persulfate is added.

The as-synthesized PANI chiral fibers are in an aqueous suspension. The diluted suspension is visually homogenous, and stable up to more than a few hours. The stable suspension allows for characterization using various analytical probes. Optically active polyaniline nanofibers were characterized by using circular dichroism (Jasco 710), UV–vis. spectroscopy (Cary 500 Scan UV–vis-NIR), scanning electron microscopy (JEOL JSM6460), and transmission electron microscopy (JEOL JEM 2010). The molar ellipticity [ $\theta$ ] ( $\text{deg cm}^2 \text{dmol}^{-1}$ ) was calculated on the basis of the tetrameric repeat unit of polyaniline.

## 3. Results and discussion

The optical activity of PANI is induced by the interaction between CSA and aniline or polyaniline. Because there are no asymmetrical centers in PANI chains, optical activity of PANI can only come from helical conformation or helical packing of PANI chains. We have hypothesized that the interaction between optically active CSA and aniline/polyaniline is crucial in forming the helical conformation. Therefore, by maximizing the interaction between CSA and aniline/PANI, the optical activity of PANI should be enhanced. Methods to achieve this increased interaction have been explored in a systematic manner.

### 3.1. Number of persulfate aliquots

The polymerization of aniline is achieved by adding ammonium persulfate to a solution of aniline and CSA. Ammonium persulfate can be added either incrementally or in a single aliquot. The rate of addition has a huge impact on the optical activity of the resulting PANI. As shown in Fig. 1, an incremental addition results in more than 25-fold increase in CD signal intensity. Since, CSA has no CD absorption at wavelengths longer than 300 nm, all CD signals shown in Fig. 1 are due to optically active polyaniline. Incremental addition of oxidant is also used to regulate the polymerization process. After each addition, the solution turns blue suggesting formation of oxidized PANI and aniline oligomers. These PANI and oligomers can further react with aniline monomers to grow longer PANI chains. In the presence of persulfate ions in the solution, PANI and oligomer remain in the oxidized form. Once all persulfate ions are consumed by the oxidative polymerization process, the PANI and oligomers will be reduced from the pernigraniline (oxidized form) to the emeraldine base, which has dark green color in acidic solution. By waiting until the reaction solution changes from blue to green before addition of a further aliquot of ammonium persulfate, we ensure that there is no excess persulfate in the solution, and we have control over the reaction temperature as we limited the extent of reaction by the amount of persulfate added. We can briefly rationalize this result as follows:

- (1) persulfate ions carry two negative charges and they can compete with CSA for positively charged aniline. By adding all of the ammonium persulfate in a single aliquot, an excess of persulfate ions is introduced into the solution. These excess non-chiral anions can displace some interactions with CSA, and consequently lower the optical activity of the resulting PANI;
- (2) single aliquot addition leads to a high polymerization rate, and a sharp increase of the solution temperature. Because of the autocatalytic nature of the polymerization reaction, a high temperature can lead to an excessive rate of

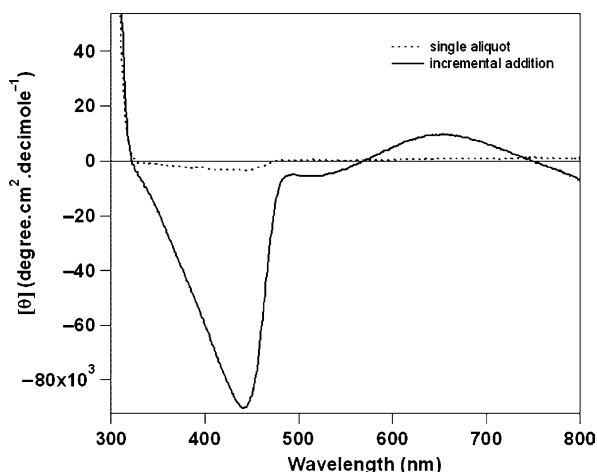


Fig. 1. Effect of method of addition on CD spectra of PANI prepared in 1.5 m CSA. The concentration of aniline is 0.14 m (no oligomer added).

polymerization and results in PANI with random conformations. This result is also consistent with our previous study which showed that high temperature increases the dissociation between CSA and anilinium complex and lowers the optical activity of PANI nanocomposites [15].

### 3.2. Concentration of CSA and aniline

The interaction between CSA and aniline/PANI is mainly electrostatic. In a dilute solution, both anilinium ions and CSA ions are solvated and separated by water molecules. By simply increasing the concentration of CSA, the interaction between CSA and PANI should be enhanced. This prediction is confirmed by our experiments, which shows that optical activity of the resulting PANI is dependent on CSA concentration. Fig. 2 shows that synthesis using a concentrated CSA solution without oligomer can produce PANI with high optical activity. However, when the concentration is too high the optical activity of the resulting PANI drops such that, in this case, 1.5 m CSA is shown to be the optimal concentration for preparing chiral PANI. The reason for the decrease in optical activity at very high [CSA] is unknown. We speculate that it may be due to high viscosity which limits the diffusion of oxidants and causes the polymerization to slow down.

### 3.3. Oligomers

PANI and oligomers have lower redox potentials than aniline monomers. Therefore, in a reaction containing both oligomer and aniline monomer, the oligomer will be oxidized first and initiate the polymerization. By using oligomer  $a_1$  (Scheme 1) as a seed to the polymerization reaction, PANI with very strong CD signals can be synthesized from solutions with very high CSA concentrations. Oligomer  $a_1$  helps to push the optimal CSA concentration for synthesizing chiral PANI

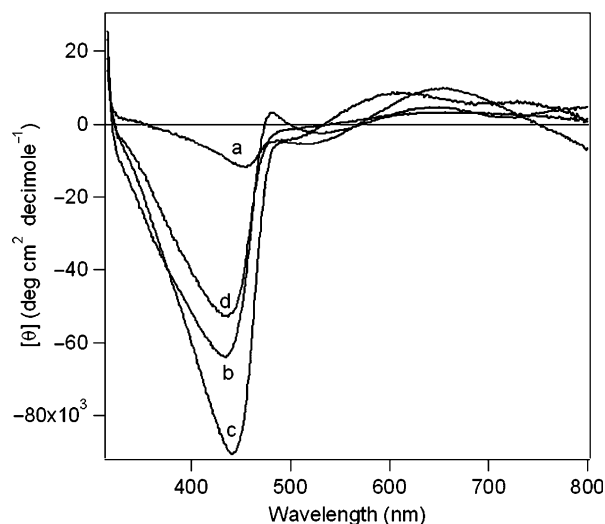


Fig. 2. CD spectra of PANI prepared in different CSA concentration with incremental addition of ammonium persulfate. The concentration of aniline is 0.14 m and no oligomer is used. (a) 0.5 m CSA (b) 1.0 m CSA (c) 1.5 m CSA (d) 2.0 m CSA.

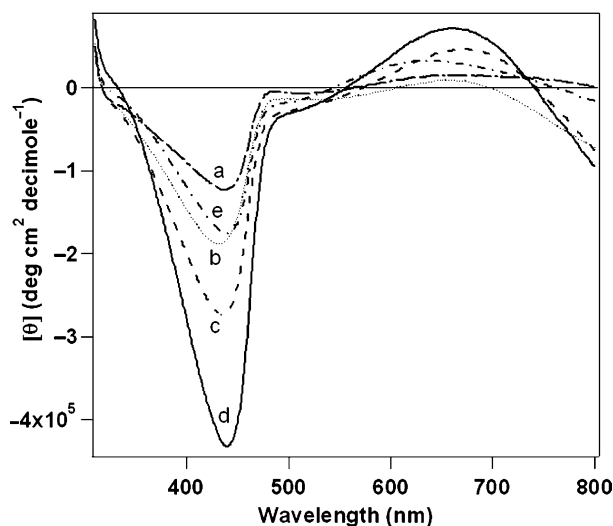


Fig. 3. CD spectra of PANI prepared in the presence of  $a_1$  oligomer. The starting concentration of CSA varies. (a) 0.75 m CSA (b) 2.5 m CSA (c) 5.0 m CSA (d) 10.0 m CSA (e) 15.0 m CSA.

nanofiber from 1.5 to 10.0 m, and enhances the intensity of CD signals by 50-fold.

PANI with the strongest CD signals (Fig. 3, curve d) was prepared from a solution containing 1.5 g water (0.083 mol), 0.20 g anilinium ions (0.0021 mol), 3.5 g CSA (0.015 mol giving 0.015 mol CSA ion and only 0.0129 mol protons as 0.0021 mol are used to form anilinium ions), and 0.02 g  $a_1$  (0.00020 mol). In this solution, there are total of 0.036 mol of ion species that need to be solvated by 0.083 mol of water molecules. On average, one ion gets less than three water molecules, which is not enough to form a hydration sheath of water around these ions. Some anilinium cations and CSA anions probably are exposed without the separation by the hydration layer of water, and have strong interaction between them. Other oligomers were also tested in the same way. The oligomer  $b_2$  was found to be the best in promoting the optical activity of PANI presumably because it has the optimized chain length and redox potentials. Oligomers shorter than  $b_2$  have higher redox potentials, and do not effectively accelerate the polymerization reaction, while oligomers longer than  $b_2$  have poor solubility and may be difficult to rearrange to form structures that lead to a helical conformation. Fig. 4 shows that the optimized molar ratio of aniline to  $b_2$  is 30:1 (0.2 g of aniline: 0.02 g of  $b_2$ ). Oligomer  $b_n$  has a lower redox potential than oligomer  $a_n$ , because  $b_n$  has one more electron donating amino substituent.  $b_n$  cannot form PANI by itself, but it is capable of adding aniline units to both ends. The combination of the lower oxidation potential and polymerization initiated at both ends results in faster polymerization.

### 3.4. Polymerization process

The polymerization of aniline is an exothermic reaction. The temperature of the reaction mixture during the polymerization process is a convenient indicator of polymerization rate upon addition of oxidant to the aniline solution. The solution

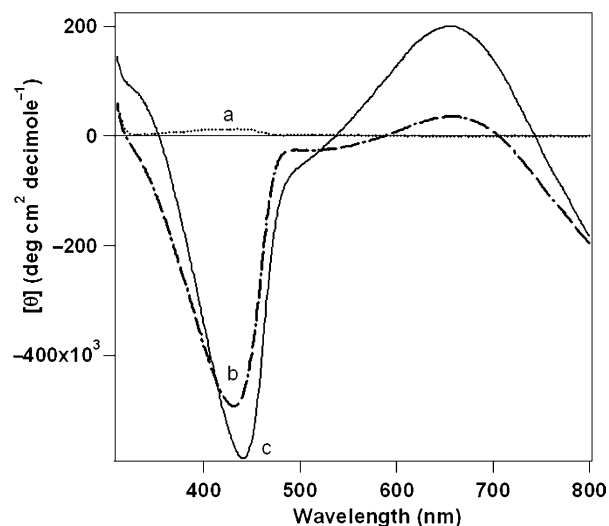


Fig. 4. CD spectra of PANI prepared in the presence of  $b_2$ . The experiments were carried out by adding solution of 0.49 g ammonium persulfate in 1.0 g water into a solution containing 1.5 g water, 0.2 g aniline, 3.5 g CSA and  $b_2$ : (a) 0.01 g (b) 0.02 g (c) 0.04 g.

temperature rises sharply and lasts for a period of  $\sim 100$  s as the oxidant is added. The solution was allowed to cool down before the next addition. In addition to the change in solution color (from blue to green), the change in temperature can also be used as an indicator to track the progress of the reaction.

The effect of the oligomeric seeds is observed by monitoring the temperature of the reaction as a function of time. In the presence of  $b_2$ , polymerization starts within 10 s after the first addition of ammonium persulfate. In contrast, without oligomer, there is an incubation period of more than 7 min after the first addition of ammonium persulfate. The difference between reaction rate with and without oligomers mainly exists in the first addition of oxidants. For subsequent additions of persulfate, the reaction proceeds immediately after addition and little difference can be distinguished between reaction rates for trials with and without oligomers. This result is consistent with the formation of oligomers and polymers after the first addition that can be readily oxidized to form longer PANI chains solutions with subsequent additions.

To better understand the effect of incremental addition of oxidant on the polymerization reaction, both CD and UV-vis (Fig. 5) spectra are taken after each addition of oxidant. Our results show that there is an almost linear increase in the absorbance intensity with increasing amount of oxidant added until it reaches the stoichiometric ratio. The shapes of the CD and UV-vis. spectra are essentially the same for all. This result suggests that the same helical structure is produced each time and adding more oxidant only increases the yield. Since, the polymerization reaction rates with and without oligomers only differ in the first time addition, it is very likely that the reaction initiated by first addition is crucial to the optical activity of the final product.

The fact that nanofibers are obtained after the first incremental addition suggests that the polymerization first starts to form a few oligomers. As these oligomer chains grow

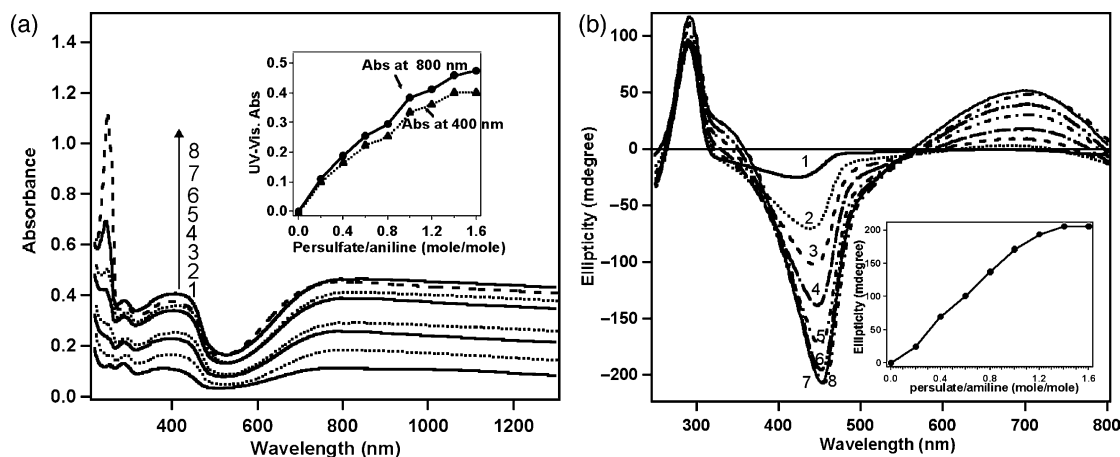


Fig. 5. (a) UV-vis spectra measured after each increment of ammonium persulfate was added. The inset shows UV-vis absorbance at 400 and 800 nm vs. the molar ratio of ammonium persulfate to aniline. (b) CD spectra measured after each addition of ammonium persulfate. Inset shows the absolute intensity of the CD signal at 450 nm vs. molar ratio of ammonium persulfate to aniline.

longer, they are more easily oxidized and hence grow faster, using up the oxidants, and consequently suppress the initiation of new chains. Products after each addition of oxidant were also examined by using SEM. SEM micrographs show that all products are nanofibers and each oxidant addition simply produces more of the same nanofibers. The stoichiometric ratio between aniline to ammonium persulfate is 1:1.5 for producing polyaniline in emeraldine salt form. Excess ammonium persulfate causes degradation or overoxidation of polyaniline. The intensity of CD and UV-vis spectral features drops as a result of the addition of excess (beyond 1.5 equiv total) ammonium persulfate (not shown).

### 3.5. The stability of chiral PANI

The stability of chiral polyaniline, which is critical to its potential applications, can be assessed by thermal treatment and repeated doping and dedoping cycles. Fig. 6 shows the response of the CD spectrum of an aqueous suspension of polyaniline to heating. After treatment at 90 °C for 1 h, the intensity of CD signals drops by only about 10%, i.e.

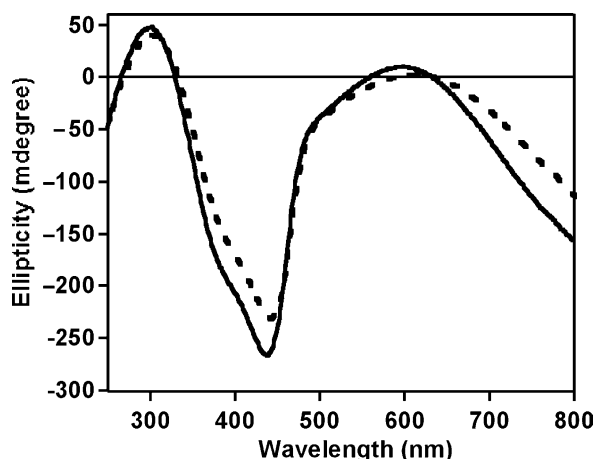


Fig. 6. CD spectra of chiral PANI at different temperatures; solid line: room temperature (25 °C), dashed line: after heating at 90 °C for 1 h.

most chiral PANI chains are able to sustain a helical conformation under these conditions.

Fig. 7 shows the CD spectra of a PANI sample subjected to repeated doping and dedoping cycles. The CD spectra of the doped PANI nanofiber are weakened after each cycle, while the CD spectra from dedoping cycles show a slight increase in intensity at 750 nm. The PANI helical structures are reasonably stable towards repeated doping and dedoping cycles but the spectra do show some minor changes possibly due to relaxation of PANI chains.

### 3.6. Porous films of PANI nanofiber

The morphology of the polyaniline nanofibers obtained is similar for all of our experiments. It is very interesting to note that when CSA is used in the synthesis (either chiral or racemic mixture) the products are always nanofibers. The formation of

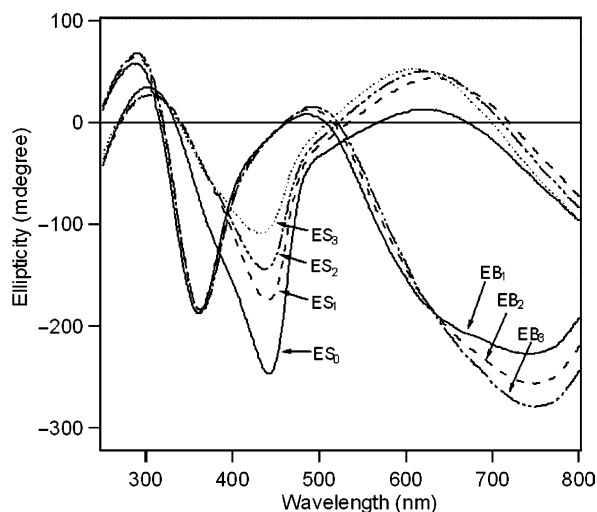


Fig. 7. CD spectra of chiral polyaniline nanofibers dedoped with 0.1 M ammonium hydroxide and then doped with 1.0 M HCl for three repeated cycles. EB1, EB2, and EB3 are dedoped PANI in first, second, and third cycles. ES0 is the original sample. ES1, ES2, and ES3 are doped PANI in first, second, and third cycles.

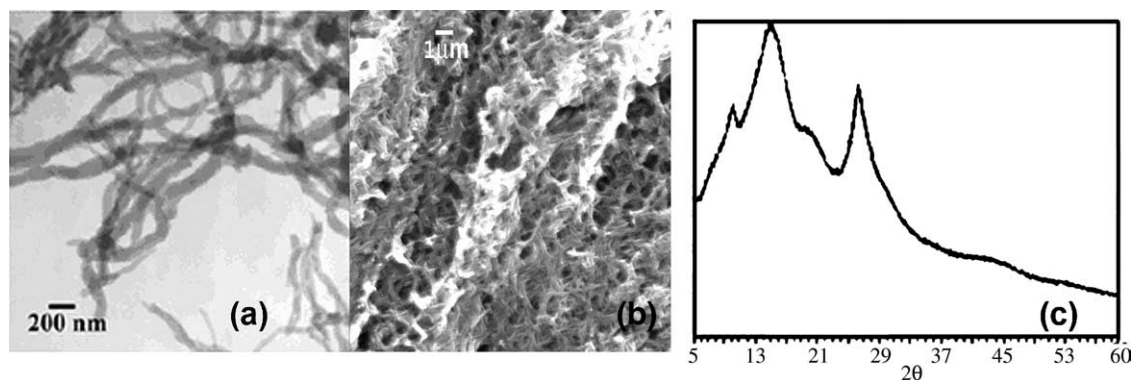


Fig. 8. (a) TEM picture of PANI nanofibers; (b) SEM picture of PANI film cast from nanofiber suspension; (c) X-ray diffraction of PANI nanofiber.

nanofibers must be related to the nature of polymerization of aniline. The nanofibers are twisted and have a diameter between 40 and 100 nm and lengths up to a few micrometers (Fig. 8(a)). Porous films can be cast from the aqueous suspensions of nanofibers (Fig. 8(b)). The fibrous nature visible in the films is due to aggregated PANI nanofibers. The X-ray diffraction profiles obtained from these films (Fig. 8(c)) are consistent with a partially crystalline structure [20]. There is no significant difference in the X-ray diffraction profile obtained from chiral PANI nanofibers prepared from optically active CSA and the achiral PANI nanofibers prepared from CSA racemic mixture. This result suggests that the racemic CSA yields both right-handed and left-handed helices formed in equal amounts (hence the mixture exhibits no CD signal) and the overall packing and resulting crystallinity is similar to that of nanofiber prepared using chiral CSA. It is likely that the partial crystallinity may be responsible for the chemical and thermal stability described previously. It is also interesting to note that the film of PANI nanofibers shows a different CD spectrum than that from the aqueous suspension of PANI nanofibers. Fig. 9 shows the CD spectra of PANI nanofibers in a cast film and an aqueous suspension. The aqueous suspension

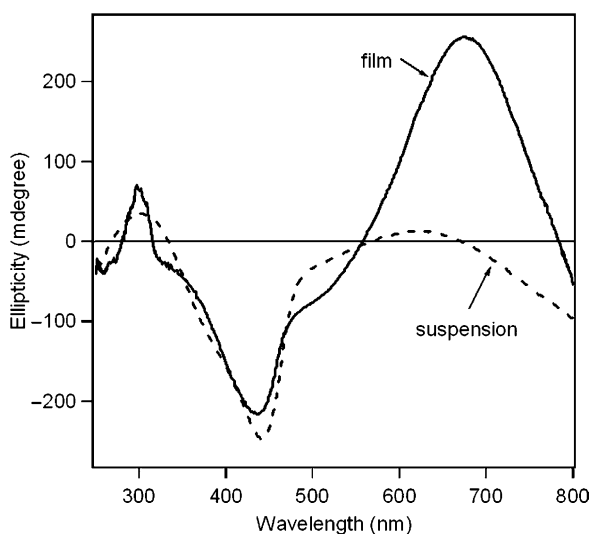


Fig. 9. CD spectra of a PANI film and PANI nanofiber suspension.

of PANI nanofibers has only weak CD signals at wavelengths between 550 and 800 nm, while the CD spectrum of the PANI nanofiber film has a very strong peak at 675 nm. This peak probably arises from the interchain and interfiber interactions. This hypothesis is further validated by the UV–vis–NIR spectra (not shown) from suspension and film which show little difference. The as-cast films do not show a stronger absorption in the NIR. In the aqueous suspension, solvation weakens the inter-chain interactions by enlarging the inter-chain distance. The CD signal of the PANI nanofiber dispersion is mainly contributed by the helical conformation of individual PANI chains.

#### 4. Conclusions

In this paper, we have carefully determined the effects of experimental parameters on the physical and optical properties of optically active PANI nanofibers. Key requirements for production of highly chiral nanofibers are a maximized interaction of CSA with the growing polymer chain and the use of oligomer molecules as ‘seeds’ to catalyze the polymerization. The formation of chiral nanofiber starts with the first aliquot of the oxidant added to the solution and the CD intensity increases with increasing aliquot increments.

The difference in CD spectra in the as-cast thin film and in the aqueous dispersion suggests that interchain and interfiber interactions could generate additional signal intensity at longer wavelength. We also show that these PANI nanofibers are stable against thermal treatment and doping–dedoping cycling. The thermal and chemical stability may be resulting from the fact that these PANI nanofibers are partially crystalline.

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