Oligomer-Assisted Synthesis of Chiral Polyaniline Nanofibers

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In recent years, there has been increased interest in synthesizing chiral conducting polymers mainly because of their potential applications in chiral separations,[1] surface-modified electrodes,[2] as well as chemical and biological sensors.[3] Chiral polyaniline (PANI) and its derivatives were synthesized usually by either codissolving PANI and a chiral acid in common solvents[4] or by polymerizing aniline in the presence of a chiral acid.[5] Recently, Choli et al. reported a helicity specific synthesis of chiral PANI nanocomposites.[6] However, most of the chiral PANI synthesized from the above methods suffer from low chirality. To achieve highly efficient chemical separations using chiral PANI as the chiral stationary phase, it is essential to have both high chirality and high surface area. PANI nanofibers that provide very high surface areas have been synthesized by using a template-guided synthesis[7] and by employing an electrospinning method.[8] Huang et al. reported a route to synthesize high-quality PANI nanofibers at the organic/inorganic interface. They also demonstrate the use of PANI nanofiber thin films as chemical sensors.[9] Despite all of these synthetic efforts, a need remains for the chemical synthesis of PANI nanofibers with very high chirality.

In this Communication, we report a novel approach to synthesize chiral PANI nanofibers in an aqueous solution. This new approach requires the following conditions: (1) Polymerization was carried out in concentrated camphor sulfonic acid (CSA) solutions. (2) Aniline oligomers[10,11] (Scheme 1) were used to accelerate the polymerization reaction. (3) Ammonium persulfate (oxidant) was added incrementally to the aniline solution.

An optimized procedure for the synthesis of chiral, nanostructured PANI carried out at 25 °C leads to the formation of a dark-green viscous suspension in 2 h after all of the ammonium persulfate was added.[12] (+)-CSA, (−)-CSA, and their racemic mixtures were used to make PANI nanofibers. The as-synthesized nanofibers can be easily separated and purified by centrifuge. After being dispersed in water, these nanofibers form a visually homogeneous dispersion, which is stable for several minutes. Thin films cast from these nanofiber dispersions are highly porous. This porous thin film is similar to that reported by Huang et al.[9] The diameter of individual nanofiber ranges from 20 to 40 nm with lengths up to several micrometers (Figure 1). Most of the nanofibers are twisted and entangled to form a fiber network. The TEM micrograph also shows some helical, single PANI nanofibers embedded in a fiber bundle (Figure 1). The correlation between the direction of the helicity and the handedness of the chirality of nanofibers is not clear. What is more important is that, depending on the experimental parameters, the chiral nanofibers obtained have a molar ellipticity that can vary by 5 orders of magnitude. In addition, the conductivity of the pressed pellets of PANI chiral nanofiber is ~1.0 S cm^{-1}, and the UV−Vis−NIR spectra of these chiral PANI nanofibers are essentially identical to the achiral PANI powder or thin films prepared by using racemic (±)-CSA.

The as-synthesized PANI nanofiber is in its doped form; it can be dedoped by treatment with 0.1 M NH$_4$OH aqueous solution.
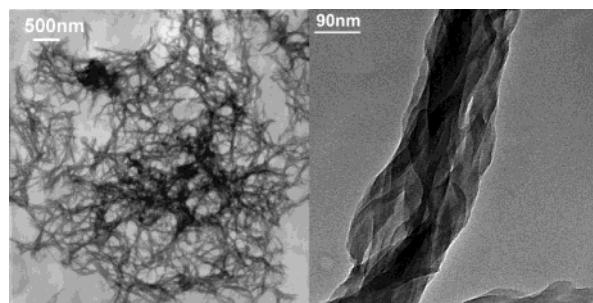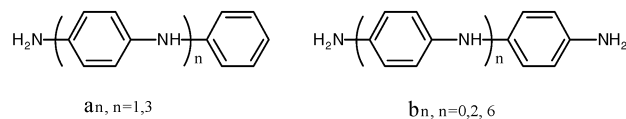

Figure 1. TEM micrograph of the chiral PANI nanofiber network (left) and magnification of a fiber bundle with helical nanofibers embedded (right).

Scheme 1. Molecular Structures of Phenyl−Amine-Capped Oligomers (a_n) and Amine−Amine-Capped Oligomers (b_n)

Because dedoped PANI has no asymmetric carbon, PANI chirality can originate only from the helical conformation of polymer backbones and/or from the helical packing of the polymer chains induced by chiral acids. The formation of chiral PANI results from the polymerization of the aniline/CSA complex (chiral monomers). We observe an increase in the chirality of PANI nanofibers with increasing aniline/CSA concentrations. This increase in fiber chirality is consistent with our previous study, which showed that the enhanced local aniline/CSA concentration near the vicinity of poly(acrylic acid) template results in PANI colloids with a higher chirality.[13,14] The concentrated CSA also prevents aniline from interacting with the achiral sulfate ions, which are generated from the decomposition of the oxidant (ammonium persulfate). However, when the CSA concentration exceeds 2.0 M, the chirality of the PANI starts to drop, presumably due to the increase in the solution viscosity causing a slowing of the polymerization rate. This result suggests that the rate of polymerization can also affect the chirality of the PANI. The newly formed aniline oligomers or PANI are shown to increase the polymerization rate by assisting monomer oxidation (autocatalytic effect).[15,16] Therefore, we designed experiments to carry out the synthesis of the chiral PANI in the presence of aniline oligomers with the incremental addition of oxidant. This approach leads to the formation of nanostructured PANI with a chirality stronger than the PANI synthesized without using oligomers and by adding all of the oxidant at one time by 5 orders of magnitude. We believe that aniline oligomers serve not only to accelerate the polymerization reaction, but also to act as "seeds" for the growth of the chiral PANI. Because oligomers have lower redox potentials as compared to that of aniline monomer,[17] the initiation of chain growth will likely be dominated by these oligomers. In fact, all of the oligomers in Scheme 1 can enhance significantly the chirality of the resulting PANI nanofibers. The trimer (b$_2$) gives the highest anisotropy factor (Figure 2).
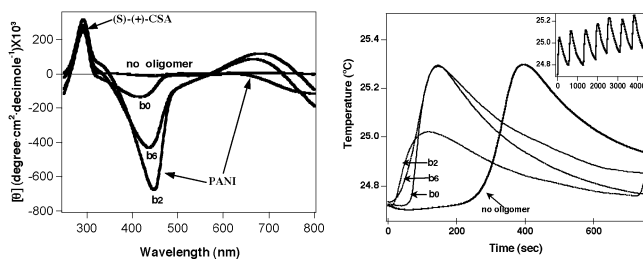
Figure 2. (Left) CD spectra of water-dispersed chiral PANI nanofibers prepared by using (S)-(+)-CSA in the presence of various oligomers. (Right) Monitoring the temperature change during the synthesis of chiral PANI nanofibers in the presence of various oligomers. The inset shows the effect of the incremental addition of ammonium persulfate on the solution temperature.

The early stage of oxidative polymerization, which forms the aniline dimer, trimer, and high molecular weight oligomers, is slow, and the subsequent chain propagation after oligomer formation is much faster. This autocatalytic effect is observed in our synthesis by monitoring the change of the solution temperature. While it takes several minutes for the polymerization to start without the oligomers, it takes only a few seconds for the reaction to start in the presence of b_2 and b_6 (Figure 2). In addition, adding all of the oxidant at once gives rise to PANI nanofibers with very low chirality, presumably due to the overheating in solution and the competing interaction from sulfate with aniline monomers. Adding the oxidant (ammonium persulfate) incrementally can mitigate the above problems, thereby leading to the formation of chiral PANI nanofibers.

After the first portion of oxidant is added, the polymerization starts almost immediately in the presence of b_2 and b_6. When the second portion and the subsequent portions of oxidant are added, the polymerization proceeds very quickly and shows little difference between the systems with and without oligomers. This discrepancy occurs because the polymers and oligomers generated during the addition of the first portion (oxidant) are used to "catalyze" the subsequent polymerization reactions. Although both b_2 and b_6 show similar effects in accelerating the polymerization reaction, the resulting PANI nanofibers synthesized in the presence of b_6 have a lower chirality as compared to the nanofibers synthesized in the presence of b_2. This difference is probably due to the incorporation of b_6 into the initial chain conformation, which limits its ability to develop chiral (helical) conformation. Note that aniline oligomers (a_n) also enhance the chirality of PANI nanofibers and the chirality is comparable to the chiral nanofibers generated by b_n.

Figure 3 shows the UV–Vis and CD spectra of both doped and dedoped chiral PANI nanofibers prepared in the presence of optically active (+)- or (−)-CSA. The as-synthesized chiral PANI nanofibers prepared under the optimized conditions have an anisotropy factor ($g = \Delta\epsilon/\epsilon$) of 2.3×10^{-2}. To the best of our knowledge, this number is by far the highest ever reported for polyaniline. The strong mirror image of CD spectra for the (−)-CSA and the (+)-CSA doped PANI nanofibers suggests that our chemical synthesis of the chiral PANI nanofibers is enantioselective.
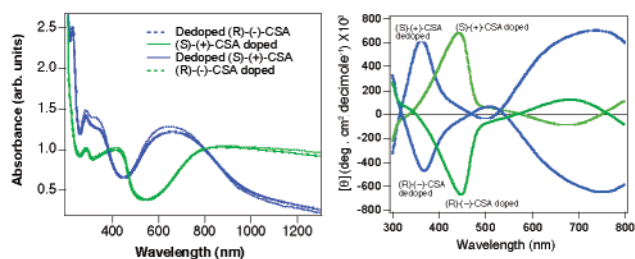

Figure 3. UV–vis (left) and CD (right) spectra of water-dispersed chiral PANI nanofibers prepared from (S)-(+)-CSA (solid line) and (R)-(−)-CSA (dotted line) in both the doped form (green) and the dedoped form (blue).

In summary, using an aniline oligomer to accelerate the polymerization reaction and adding the oxidant to the monomer solution incrementally allowed the synthesis of chiral PANI nanofibers. The chiral PANI nanofibers with extremely high surface areas have great potentials for chiral separations and biological sensors.

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(12) 0.2 g (2.1 mmol) of aniline, 3.5 g of optically active CSA (15 mmol), and 0.063 mmol of oligomer (Scheme 1) were dissolved in 1.5 mL of water, while 0.49 g (2.1 mmol) of ammonium persulfate was dissolved in 1 mL of water. The solution of ammonium persulfate was added incrementally in five separate portions to the solution of aniline and CSA. Each time, 0.2 mL of ammonium persulfate was added. After each addition, the mixed solution was shaken vigorously. The second addition of ammonium persulfate was accomplished after the mixed solution turned from blue to green. The as-synthesized PANI chiral fibers were characterized by using circular dichroism (Jasco 710) and transmission electron microscopy (JEOL JEM 2010). The molar ellipticity [θ] (deg cm² dmol⁻¹) was calculated on the basis of the tetrameric repeat unit of polyaniline.
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