Helical Polyaniline Nanofibers Induced by Chiral Dopants by a Polymerization Process**

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Chirality is widely expressed in organic materials, perhaps most notably in biological molecules such as DNA and proteins, owing to the homochirality of their components (d-sugars and l-amino acids). Chiral materials have shown potential applications in materials science, chemical and biological sensors, catalysis, pharmaceutics, and enantioselective separation.[5,6] Chirality can be expressed at different levels, from chiral small molecules to helical conformation of macromolecules, and even to helical nanostructures and supramolecular structures. Weak inter- and intramolecular interactions, including hydrogen bonding, solvophobic interaction, π–π interactions, and chiral templates, play an important role in forming helical architectures.[2]

Conducting polymers are interesting materials because of their multiple applications in electrically and optically active materials and devices. A helical conformation of conducting polymers such as helical polyaniline (PANI) can be obtained by ionic interaction with a chiral dopant, and shows induced circular dichroism (ICD) in circular dichroism (CD) spectra.[3] On the other hand, nanostructured conducting polymers have been produced by template[4] and “template-free” methods.[5,6] In the template-free method, nanotubes or sub-micrometer tubes have been realized by using micelles as a “soft template”.[5] while nanofibers have been obtained as a result of the intrinsic nano fibrillar morphology of PANI by preventing their overgrowth.[6] However, the synthesis of enantioselectively pure helical nanostructures of conducting polymers still remains a scientific challenge.

In this Communication, we report that conducting PANI nanostructures, including sub-micrometer tubes and helical nanofibers, can be produced by means of a polymerization process in the presence of d- or l-camphorsulfonic acid (CSA) as a dopant. CSA has attracted great attention because of the ability to induce the helical conformation of PANI using its enantiomers, which can be realized by either post-processing of PANI or in situ polymerization of aniline in the presence of chiral CSA as a dopant.[7] However, there are only a few reports relating to the synthesis of helical nanostructures of PANI.[8]

In order to controllably synthesize PANI nanostructures, the effect of the molar ratio of d-CSA to aniline (represented by [d-CSA]/[An]) was studied first. When [d-CSA]/[An] is 1/2 or 1 at a fixed aniline concentration of 0.025 M, dendritic PANI tubes with diameters of 120–550 nm were obtained (Fig. 1a and b). When [d-CSA]/[An] was higher than 1, such as 5 or 80, nanofibers with diameters of 30–80 nm were obtained with a large yield (Figs. 1c,d). Sub-micrometer tubes and nanofibers were formed through different mechanisms. At a low ratio of d-CSA to An, aniline monomer is in excess in the system. Since d-CSA has a surfactant-like property, monomer-filled micelles could form in the reaction system. The polymerization on the micelle “soft-template” had a tendency to form one-dimensional (1D) nanostructures due to the rigid polymer chain of PANI. As a result, sub-micrometer hollow tubes were produced.[9] In contrast, at high molar ratio of d-CSA to aniline, the excess d-CSA acted as a protecting agent to prevent the aggregation of the nuclei of PANI in the polymerization process. Therefore, nanofibers were obtained due to the intrinsic nanofibrillar morphology of PANI. Although the formation mechanisms of sub-micrometer tubes and nanofibers are different, the rigid polymer chain of PANI played a key role in forming both kinds of 1D nanostructures. If a soft template existed and the polymerization occurred on their surface, hollow nano- or sub-micrometer tubes were obtained; whereas if there was no soft template, the efficient prevention of the aggregation of PANI nuclei produced nanofibers.[10]

Subsequently, nanostructured PANI was characterized by UV-vis and CD spectrometry. In the UV-vis spectra (Fig. 1e), absorptions at ca. 420 nm and 780 nm were observed due to the π–π* transition of the polarons, indicating that PANI is in the doped state.[11] When the ratio is higher than 1, a free-carrier tail above 800 nm was observed, indicating that the PANI chains are in an extended conformation. Interestingly, negative and positive ICD peaks at 420 nm and 780 nm, respectively, are observed in CD spectra of PANI nanofibers if the ratio of d-CSA to An is higher than 20 (Fig. 1f). Since d-CSA has only a positive peak at 290 nm, the negative peak at 420 nm and the positive peak at 780 nm can be ascribed to the π–π* transition of the polarons in chiral PANI, which is
consistent with its UV-vis spectrum. The peak intensities at 420 nm and 780 nm increased with increasing \([\text{D-CSA}]/[\text{An}]\). The CD spectrum indicates that the PANI chains formed helices of predominantly one type of handedness, obviously assisted by the combination of ionic and hydrogen-bonding interactions with the chiral dopants.[12]

When \([\text{D-CSA}]/[\text{An}]\) was further increased, a maximum intensity at 420 nm was obtained at \([\text{D-CSA}]/[\text{An}] = 80\). At \([\text{D-CSA}]/[\text{An}] = 160\), the ICD intensity at 420 nm decreased again. In principle, a low concentration of PANI means a high \([\text{D-CSA}]/[\text{An}]\) ratio, which should be preferable for a high intensity of ICD. However, too low a concentration of aniline is not beneficial to the polymerization of PANI, in which many defects are formed.[13] Therefore, the maximum of ICD intensity appeared at 0.05 M aniline concentration.

Accordingly, polymerization was carried out at 0 °C with a \(\text{D-CSA}\) concentration of 2.0 M while changing the concentration of aniline monomer from 0.025 to 0.4 M. As shown in Figure 2a, the intensity of ICD at 420 nm increased when aniline concentration increased from 0.025 M to 0.05 M, whereas, when the aniline concentration further increased to 0.4 M, the intensity decreased again. In principle, a low concentration of PANI means a high \([\text{D-CSA}]/[\text{An}]\) ratio, which should be preferable for a high intensity of ICD. However, too low a concentration of aniline is not beneficial to the polymerization of PANI, in which many defects are formed.[13] Therefore, the maximum of ICD intensity appeared at 0.05 M aniline in the
presence of 2.0 M D-CSA at 0 °C. If the polymerization was carried out at 25 °C, the maximum appeared at 0.1 M aniline concentration. Comparing the ICD maxima at 0 °C and 25 °C, we find the latter is higher although the ratio of D-CSA to An is lower. This indicates that higher temperatures are more favorable to induce the chirality of PANI at a high concentration of aniline. In comparison with the chiral PANI obtained in other systems,[8a,14] the optical activity of helical PANI nanofibers is not among the highest. Therefore, we suggest that both the synthetic method and reaction conditions greatly influence the efficiency of the reaction system and polymerization process, and consequently affect the induced optical activity of the PANI.

In order to further prove that helical PANI nanofibers were induced by chiral dopants, PANI was synthesized in the presence of D- and L-enantiomers of CSA separately. As seen in Figures 3a and b, right-handed helical nanofibers were obtained using D-CSA as the dopant, while left-handed helical nanofibers were produced using L-CSA as the dopant. Helical PANI nanofibers further self-assembled into helical bundles. The insets show the helical directions of the helical PANI nanofibers and their bundles. To the best of our knowledge, this is the first time that dopant-induced helical PANI nanofibers have been clearly observed.

The CD spectra of right- and left-handed helical PANI nanofibers are mirror images (Fig. 3c). The positive and negative peaks at 290 nm originate from D-CSA and L-CSA, respectively. The ICD peak from the π→π* transition of the localized polaron in chiral PANI appears at ca. 435 nm, in the opposite direction to the dopant peak at 290 nm. However, its intensity is much weaker than that of the dopant peak even under optimized conditions, and much weaker peaks at wavelengths longer than 800 nm appear due to the delocalized π→π* transition of the polaron in PANI, which indicates the difficulty of twisting the rigid chains of PANI. Two diastereomeric PANIs have exactly the same UV-vis spectra (Fig. 3d), proving they have the same molecular structures.

It has been reported that the optical activity of conjugated polymers and oligomers arises from two different mechanisms. One is that individual conjugated polymer chains preferentially adopt either a left-handed or right-handed screw with chiral induction, due to the electrostatic and hydrogen bonding between the polymer chain and chiral species.[7,15] The other is that chiral species induce either a predominantly left-handed or a predominantly right-handed helical packing of planar molecules into a chiral superstructure.[2,16] Based on our previous discussion, we suggest two mechanisms coexist in the formation of helical PANI nanofibers. The helical conformation of PANI is induced by the chiral D-CSA dopant, and then helical nanofibers are self-assembled due to the π-stacking of the PANI chains. The dark lines in the insets in Figures 3a and b indicate individual PANI chains with helical conformation in the helical nanofibers. In fact, a similar formation mechanism was also observed in mesoporous silica, in which chiral surfactants were used to induce chiral channels, and they further self-assembled into twisted hexagonal nanorods.[17]

As is commonly known, the color as well as the UV-vis spectrum of PANI can be reversibly switched by changing the pH. A similar switching property has been observed in the UV-vis and CD spectra of helical PANI nanofibers. When a helical PANI nanofiber dispersion doped with D-CSA was dedoped with 0.1 M ammonia, its color turned to blue immediately, and the absorptions at ca. 420 nm and 800 nm were blue-shifted to 330 nm and 650 nm, respectively (Fig. 4a). Similarly, the CD absorption at 420 nm was blue-shifted to 350 nm and a new strong absorption at 750 nm appeared (Fig. 4b), which fits well with the absorptions in the UV-vis spectrum. Therefore, we can deduce that the helical conformation was retained in the dedoped state of PANI.

When hydrochloric acid was added to adjust the pH to 2, the color of the solution turned back to green, and the peaks ascribed to the doped state of PANI reappeared in both the
UV-vis and CD spectra, indicating that doped PANI was reobtained.

The molecular structures of the helical PANI nanofibers were measured by Fourier transform infrared (FTIR) spectroscopy. PANI nanofibers showed strong bands at 1576 and 1494 cm\(^{-1}\) (C\(^\equiv\)N stretching of benzenoid and quinoid rings, respectively), and 1300 and 1140 cm\(^{-1}\) (stretching of C–N and C\(^\equiv\)N, respectively), which are identical to the bands found in the emeraldine salt of PANI.\(^{[19]}\) The conductivity of the helical PANI nanofibers were measured with the standard van der Pauwe direct current four-probe method.\(^{[19]}\) The room temperature conductivities of the pressed pellets of helical PANI nanostructures are in the range 0.08–0.6 S cm\(^{-1}\), which is also consistent with conventional PANI.

In summary, two different morphologies of PANI, i.e., submicrometer tubes and helical nanofibers, were obtained by a polymerization process in the presence of chiral d- or l-camphorsulfonic acid as the dopant. Monomer-filled micelles played a “soft-template” role in the formation of sub-micrometer tubes, while nanofibers expressed the intrinsic nanofibrillar property of PANI by the dopant preventing overgrowth of PANI in the polymerization process. Right- and left-handed helical nanofibers were obtained using d-CSA and l-CSA, respectively, as the dopant, and CD spectra exhibited mirror-image induced circular dichroism for the two dopants. We suggest that predominantly one helical conformation of PANI was induced by the chiral dopant, and these further self-assembled into helical nanofibers and nanofibrillar bundles.

**Experimental**

A typical PANI polymerization process was as follows: d- or l-CSA was dissolved in 1.5 mL water, and then aniline was added and the mixture was stirred for 1 h. The amounts of CSA and aniline depended on their concentration and molar ratio. Ammonium persulfate (the same number of moles as the number of moles of aniline) was dissolved in 1 mL water and added in five portions at intervals of 1.5 h. The reaction mixture was stirred for 10 h to finish the polymerization. The as-prepared PANI was divided into two parts: The first portion was washed with water, methanol, and diethyl ether several times, separately, and dried in a dynamic vacuum for 24 h at room temperature. This was used for further characterization by SEM, XRD, FTIR, and conductivity measurements. The second portion was dispersed in water with the same concentration with respect to aniline for CD and UV-vis measurements.

The morphology of the resulting PANI was examined by SEM (Hitachi S-4800). The CD (Jasco J810) and UV-vis (Perkin-Elmer Lambda 950) spectra were recorded for PANI nanofibers dispersed in deionized water. The molecular structures of the PANI were characterized by FTIR spectra (PerkinElmer Spectra One). The conductivity of compressed pellets of PANI at room temperature was measured by a four-probe method with a digital multimeter (Keithley, 196 DMM) and a programmable dc voltage/current generator (Advantest, R6142) as the current source.

Received: April 10, 2007  
Revised: June 8, 2007  
Published online: September 20, 2007

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