Helical Conformational Specificity of Enzymatically Synthesized Water-Soluble Conducting Polyaniline Nanocomposites

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Polyaniline is one of the most promising electrically conducting polymers because of its chemical stability and relatively high conductivity.[1] In recent years, there has been increased interest in synthesizing chiral conducting polymers because of their potential use in diverse areas such as surface modified electrodes,[2] electrochemical asymmetric synthesis, chiral chromatography, and membrane separation technology.[3] Wallace et al.[4] synthesized chiral polyaniline by electrochemically polymerizing aniline monomer in the presence of a chiral acid dopant. Recently, Wang et al. synthesized water-soluble chiral conducting polymer nanocomposites by a chemical method.[5]

Biocatalytic polymerization using a naturally occurring enzyme is advantageous in that it is a simple, one-step, and environmentally compatible synthesis with the potential for producing industrial polymers in high yield due to the high efficiency of the enzyme catalyst.[6,7] In this paper, we report the template assisted (poly(acrylic acid), PAA) enzymatic synthesis and characterization of chiral-induced conducting polymer nanocomposites,[8] where horseradish peroxidase (HRP) is shown to directly influence the stereospecificity of the polyaniline (PANI) in the nanocomposites PAA/PANI/(+) CSA, PAA/PANI/(−) CSA, and PAA/PANI/(±) CSA (CSA, 10-camphorsulfonic acid).

The UV−vis spectra of the PAA/PANI/(−) CSA nanocomposites are shown in Figure 1. The reversible redox behavior of the polyaniline in the PAA/PANI/(−) CSA nanocomposite was studied by doping and dedoping using 1 M HCl and 1 M NH₄OH aqueous solution, respectively. The PAA/PANI/(−) CSA nanocomposite exists in the self-doped form at pH 4.3 (Figure 1, spectrum a) and has an absorbance peak maximum at 420 nm, which is a signature of the polyaniline. The polaron band in the 750 nm region confirms the presence of PANI in the conducting form. As the pH of the solution is increased from 4.3 to 10, the PANI peak at 420 nm decreases and the polaron band at 750 nm in the near-IR region disappears. A strong absorption peak due to exciton transition of the quinoid ring appears at ca. 550 nm, suggesting that, at pH 10, PANI has been completely dedoped to the base form (Figure 1, spectrum b). These results are comparable to chemically[5] and enzymatically synthesized DNA/polyaniline intertwined complexes.[7d]

The CD spectra of PAA/PANI/(−) CSA and PAA/PANI/(+) CSA nanocomposites are shown in Figure 2 A. The CD spectra of these samples show a positive or negative peak at 310 nm, that is due to (+) or (−) CSA in the nanocomposites, respectively, and the peak at 420 nm is due to the polyaniline. Because the polyaniline does not have an asymmetric carbon atom in the structure, induced optical activity of PANI as observed in the CD spectrum implies the existence of a helical conformation. The induced chiral conformation on the polyaniline may be explained by the influence of either (+) CSA or (−) CSA on the aniline moiety of PANI in
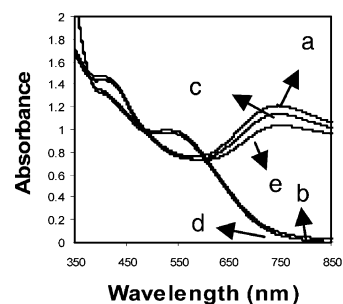

Figure 1. UV−vis spectra of PAA/PANI/(−) CSA nanocomposites. Cycle 1: (a) self-doped at pH 4.3; (b) dedoped with NH₄OH at pH 10; (c) redoped with HCl at pH 4.3. Cycle 2: (d) dedoped at pH 10 and (e) redoped at pH 4.3.
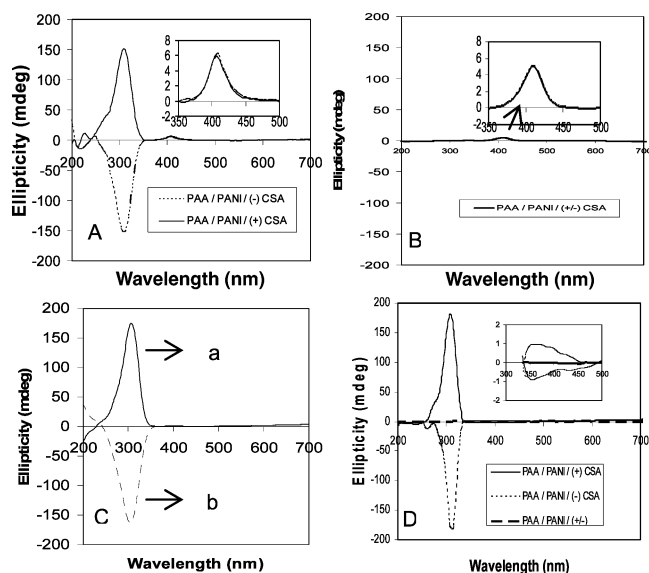

Figure 2. (A) CD spectra of PAA/PANI/(−) CSA and PAA/PANI/(+) CSA nanocomposites formed after enzymatic polymerization; (B) CD spectra of PAA/PANI/(±) CSA nanocomposites; (C) CD spectra of (a) PAA/(+) CSA/H₂O₂/HRP and (b) PAA/AN/(−) CSA/H₂O₂; (D) CD spectra of PAA/PANI/(−) CSA, PAA/PANI/(+) CSA, and PAA/PANI/(±) CSA nanocomposites formed after hematin polymerization.

the nanocomposite. We observe, probably for the first time, however, that only the positive peak is observed in the CD spectrum at 420 nm (Figure 2A), regardless of whether CSA is a (+) or (−) enantiomer in the nanocomposites. This result suggests that, during polymerization, the enzyme plays an important role in preferentially directing polyaniline to a specific helical conformation, thus demonstrating that this biocatalytic polymerization may be enantiospecific.

The CD spectrum of the PAA/PANI/(±) CSA nanocomposite shown in Figure 2 B shows the presence of just the positive peak
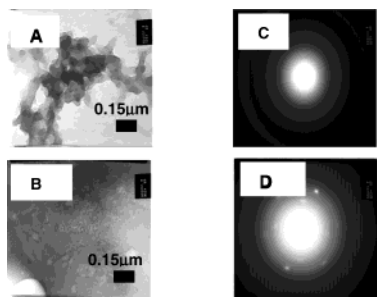
Figure 3. Transmission electron micrograph of chiral PAA/PANI/(−) CSA nanocomposites. (A) PAA:AN (3:1 mmol), (B) PAA:AN (1:1 mmol). The corresponding electron diffraction patterns are shown in (C) and (D), respectively.

at 420 nm for PANI. If the enzyme had no enantiospecificity on the reaction, then it would be expected that there would be no observable peak at 420 nm. Thus, these results further support the stereospecific role of the enzyme on the helical nature of PANI in the nanocomposite. This result is in contrast to that observed for chemically synthesized chiral polyaniline nanocomposites, where a positive CD peak at 420 nm was observed with (−) CSA and a negative peak was observed with (+) CSA[9] for the PANI. To confirm further that the absorption at 420 nm is due to the optical activity of the PANI, we repeated the measurements for samples containing PAA/(+) CSA/HRP/H_2O_2 and PAA/aniline/(−) CSA/H_2O_2 (Figure 2C). The lack of a peak at 420 nm in these CD spectra, as expected, suggests that the peak at 420 nm after polymerization in CD spectra A and B is due to the helical nature of PANI in the nanocomposites.

One final control to show that this stereospecificity is due to the role of the enzyme involved use of the biomimetic catalyst, hematin. The comparative use of hematin to HRP in this study is therefore important to determine that it is the unique enzymatic structure that is influencing the specificity in these reactions. The poly-(ethylene glycol) modified hematin has recently been used for the biomimetic synthesis of a water-soluble conducting polyaniline and lignosulfonate complex.[10] Similar studies were carried out with this PEG-hematin catalyst, and the results in Figure 2D, as expected, show that PANI formed in the presence of (+) and (−) CSA has optical activity similar to that of chemically synthesized Pani,[9] showing no enantiospecificity for Pani. Last, no signature was observed at 420 nm for PANI observed at 420 nm in the presence of a racemic mixture of CSA, suggesting the biomimetic catalyst, hematin, has no capacity to direct enantiospecificity for the PANI chains. These results are strong evidence that the optical activity observed with the HRP is due to its inherent structure and function. Transmission electron micrographs (TEM) and electron diffraction patterns of the polyaniline nanocomposite are shown in Figure 3. For this study, two nanocomposite samples were prepared with different molar ratios of PAA to aniline (i.e., PAA/AN = 1:1 and 1:3). The role of PAA (template) produces linear conducting polyaniline nanocomposites with higher conductivity.[7] The conductivity was measured using a Cascade Microtech four-point probe, which shows conductivity (1.8×10^{-2} S cm^{-1}) for PAA/PANI/

(−) CSA, (2×10^{-3} S cm^{-1}) for PAA/PANI/HCl, and low conductivity ($<10^{-8}$ S cm^{-1}) for PANI doped with HCl.

TEM shows that the nanocomposites are evenly dispersed and have a fairly narrow size dimension of 25−50 nm. The sample with a molar ratio of PAA:AN (3:1) is in the amorphous form (Figure 3A,C), whereas the sample with a molar ratio of PAA:AN (1:1) is in the crystalline phase (Figure 3B,D). Even though the nature of interactions among all of the constituents is not yet clearly understood, it is believed that CSA plays a role in the helical conformation.[9]

In summary, chiral conducting polymer nanocomposites have been synthesized using a biocatalytic route. Our data suggest that these nanocomposites have some interesting optoelectronic properties. Interestingly, it was found that the enzyme HRP plays an important role during the polymerization, which allows polyaniline to prefer a specific helical conformation whether the induced chirality in the monomer-CSA complex is either by (+) CSA or by (−) CSA. Further detailed investigations on optically active conducting polyaniline nanocomposites are now in progress.

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(8) In a typical procedure, 0.093 g (1 mmol) of aniline was added to 10 mL of 0.01 M sodium phosphate buffer. Next, 0.072 g (1 mmol, per monomer unit, MW 250 000) of poly(acrylic acid) was added, and the mixture was stirred for 6 h. To this adduct solution, 0.6 mL of 2 M (−) 10-camphorsulfonic acid was added and adjusted to pH 4.3. A solution of horseradish peroxidase (HRP) (3 mg in 0.5 mL of deionized H_2O) was then added and continuously stirred. The reaction was then initiated with incremental addition of 0.5% H_2O_2 (8 aliquots of 10 μL each). A dark green solution was formed, indicating the formation of doped polyaniline. The molar ratio of 1:1 for PAA:aniline is the optimum condition for the synthesis of chiral polyaniline nanocomposites.
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