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Communications

Self-Doped Polyaniline/Poly(diallyldimethyl ammonium chloride) Complex: N-Type Doping with High Stability

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The self-doped conducting polymer has received considerable attention recently because of its environmental stability, relatively high conductivity, and potential applications in electronic devices and sensors.^{1,2} Among these polymers, self-doped polyaniline has been studied extensively because of relatively simple synthetic routes and facile control of conductivity.^{3–6} Self-doped polyaniline has relatively good conductivity because of acid moieties in the polymer backbone such as boronic,⁷ sulfonic,^{3–6} and carboxyl acid groups.⁸ However, chemical synthesis of carboxylated poly-

aniline (PCA) was not successful because of poor solubility of the monomer in acidic media.⁸ Yue and Epstein reported that 50% sulfonation of phenyl rings can p-dope polyaniline in acidic and neutral pHs by using X-ray photoelectron spectroscopy.⁶ Krishnamoorthy et al. synthesized fully sulfonated polyaniline using electrochemical methods.⁵ These studies were important in that, although fully sulfonic acid-functionalized polyaniline showed poor conductivity because of the steric effect of sulfonic groups, it demonstrated the possibility of n-doping.

Our group previously synthesized polyaniline with anionic templates such as poly(styrene sulfonate), poly(vinyl phosphate), DNA, and RNA in an environmentally benign method by using the enzyme horseradish peroxidase (HRP).^{9–12}

A PCA using HRP in aqueous media at pH 5 has been synthesized in our group and is the subject of a prior publication.¹³ The cationic template, poly(diallyldimethyl ammonium chloride) (PDAC; MW ~ 20 000) was used as a template to increase the molecular weight of the daughter polymer (PCA) and rate of polymerization and is shown in Scheme 1.¹⁴ This work describes the unusual doping behavior of the PCA/PDAC complex at high pH.

Figure 1 shows the UV–vis–near-infrared (NIR) spectra of the PCA/PDAC complex as a function of pH. The p-doped

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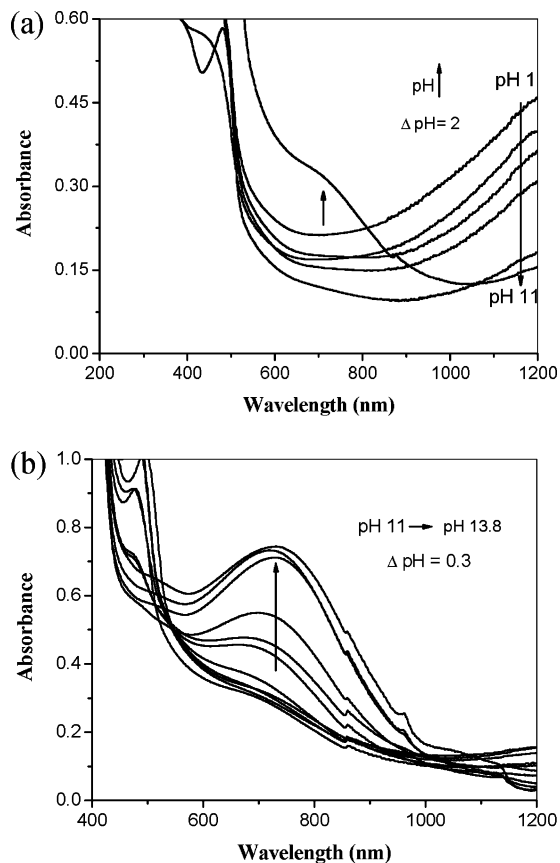
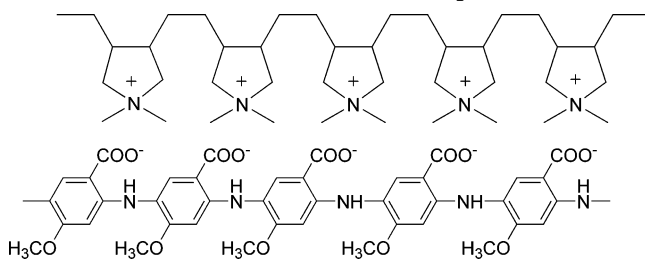


Figure 1. UV-vis-NIR spectra for the PCA/PDAC complex with varying pH. The new peak at 700 nm appears from pH 11, and the color of the solution changes from olive to pale yellow and then finally to green. (a) pH from 1 to 11; (b) pH from 11 to 13.8.

Scheme 1. PCA/PDAC Complex



form of unsubstituted polyaniline shows polaron transitions at 800–1060 nm and 410–420 nm.^{10–12} However, the PCA shows a longer wavelength delocalized polaron transition at low pH.¹⁵ The polaron absorption is observed with the PCA/PDAC complex up to pH 6 and is general to the behavior of a self-doped polyaniline. As pH increases, the polaron transition in the NIR region gradually decreases and a new peak at 700 nm at pH 11 begins to appear. This peak then shifts further to 735 nm with increasing pH. PCA alone shows an exciton transition at 550 nm and a π - π^* transition peak at 325 nm at pH 13, and it shows exactly the same polaron transition at low pH (data is not shown here).

To identify whether the peak at 700 nm originated from an exciton or polaron transition, the conductivity of the PCA/PDAC complex was measured using the four point probe method with pellet samples. Figure 2 shows the conductivity

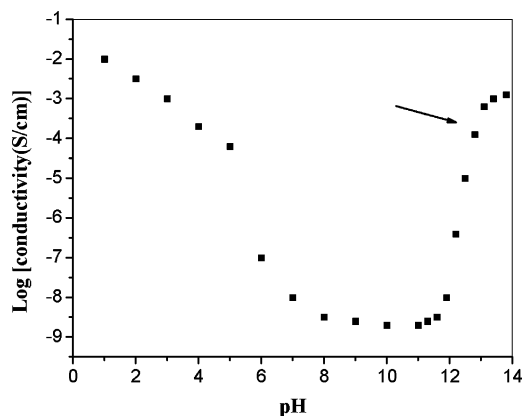


Figure 2. Conductivity of the PCA/PDAC complex as a function of pH.

of this complex. Although the PCA/PDAC complex shows relatively lower conductivity compared to other self-doped polymers, due to the weak doping ability of the carboxylic acid, the conductivity of the PCA/PDAC complex increases up to 0.3 S/cm when it is further doped with hydrochloric acid. As the pH increases, the conductivity of this complex decreases gradually, similar to a curve of acid–base titration. Unsubstituted polyaniline shows a dramatic decrease of conductivity above pH 2.¹⁶ However, the PCA/PDAC complex shows a gradual decrease of conductivity up to pH 5. Because the pK_a value of the carboxyl group in the phenyl ring is approximately 4.3,¹⁷ the dedoping behavior of this complex seems to be related with the ionization of carboxyl groups which lose proton dopants. Even though the complex is dedoped it shows a relatively higher conductivity compared to that of unsubstituted polyaniline which is in the range of 10^{-8} – 10^{-9} S/cm between pH 7 and pH 11. As the pH increases further, another dramatic increase of conductivity appears which corresponds well with the UV-vis spectra. The observed conductivity of this complex is 10^{-3} S/cm, which is *seven orders* of magnitude higher than that observed with PCA and unsubstituted polyaniline dedoped at pH 13.

To study the role of the PDAC template, the mole ratio between PCA and PDAC was varied. As shown in Figure 3, the π - π^* transition peak at 325 nm increases as the mole ratio between PCA and PDAC increases. However, the peak positioned at 700 nm remains constant even though the amount of polymer increases. The peak at 400 nm is only observable at an equimolar ratio, which is considered a localized polaron transition. In addition, the exciton transition at 500 nm, apparent in the spectrum of pure PCA at high pH, is suppressed at a low molar ratio but reappears again at a mole ratio of 3:1 PCA/PDAC. This suggests that PDAC helps to suppress the exciton transition if the mole ratio is close to 1:1. It is also observed that the exciton transition at 550 nm disappears as PDAC is added to pure PCA solution at pH 13, and a new peak at 670 nm appears. Furthermore, the addition of an excess amount of PDAC could increase the intensity of the absorption peak at 700 nm. (Additional data is given in Supporting Information.) In conclusion,

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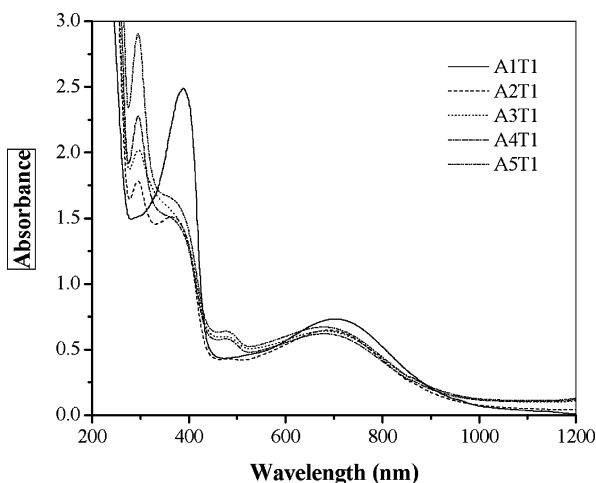
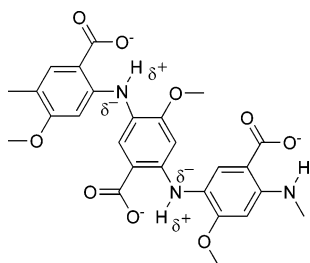


Figure 3. UV-vis-NIR spectra of the PCA/PDAC complex as a function of mole ratio at pH 13. (A and T represent PCA and PDAC, respectively).

Scheme 2. n-Doping of PCA



PDAC is believed to play a vital role in the doping process of PCA at high pH.

As self-doped polyaniline is p-doped at low pH, it is believed that the PCA/PDAC complex might be n-doped at high pH. The ionized carboxyl group and N-H group may generate a six-membered ring at high pH as shown in Scheme 2. The negatively charged oxygen donates an electron pair to the hydrogen, and the hydrogen attached to the nitrogen accordingly weakly bonds with oxygen. Finally the nitrogen in the polyaniline backbone possesses extra negative charge due to the donation of electron density by the oxygen. Although PDAC does not influence the conductivity of the complex at low pH, it seems to stabilize this proposed structure from dedoping at this state. The polaron peak is not observable in pure PCA at high pH, possibly because of fast proton exchange between water and N-H.^{18,19}

To confirm the above structure, Fourier transform infrared (FT-IR) spectroscopy was performed (Figure 4). The IR spectra of PCA homopolymer, PCA/PDAC doped with HCl, and the PCA/PDAC complex are quite similar, which suggests that the PCA is p-doped by carboxyl groups in its backbone. However, PCA/PDAC at pH 13 shows quite different absorption peaks. It was difficult to isolate and observe the band shift of the secondary aromatic amine stretch at 3300 cm^{-1} , which proves the proposed structure clearly, due to the overlapping of the stretching band of hydroxyl groups in NaOH. However, it is observed that the carbonyl stretching peak shifts from 1674 cm^{-1} to 1624 cm^{-1} as

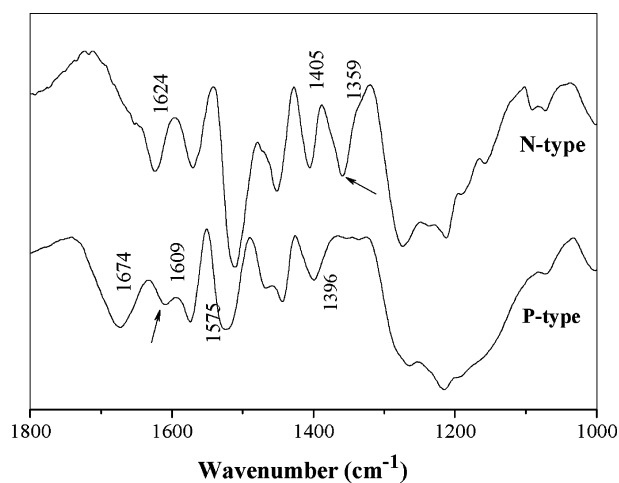


Figure 4. FT-IR transmission spectra of the PCA/PDAC complex. The spectrum of the p-doped state is on the bottom.

a result of the ionization of carboxyl groups as the PCA/PDAC complex transforms from the p-doped state to the possible n-doped state at pH 13. The p-doped PCA shows the C-N-H bending modes at 1609 cm^{-1} and the phenyl ring stretch at 1575 cm^{-1} . However, the base-doped n-type PCA/PDAC complex does not show the C-N-H bending mode at 1609 cm^{-1} , which supports the suggested structure. Two C-N deformation peaks of secondary aromatic amines at 1359 cm^{-1} and 1405 cm^{-1} appear with the PCA/PDAC complex at high pH. However, one of these peaks disappears with the p-doped form during the transformation of secondary amine to the polysemiquinone salt form.¹⁶ This is probably due to the forbidden transition of one of the modes in the p-doped states.

To find additional evidence for n-doping of the PCA/PDAC complex, a secondary amine in PCA was transformed to a tertiary amine by simple alkylation with 2-bromo-2-methylbutane.²⁰ The alkylation of a secondary aromatic amine removes the hydrogen atom, one of the six members to form a ring in PCA at high pH. The alkylated PCA/PDAC complex does not shift the exciton transition at 550 nm to the polaron transition at 700 nm at high pH, which is additional evidence to support the suggested structure.

n-doped polymers are usually generated by reduction of polymer by metal hydride and electrochemical methods.²¹⁻²³ However, the instability of the carbanion in the air, and especially in the water, is an issue that must be solved. The n-doped state of the conducting polymers generated by electrochemical reduction are also unstable, and when the applied potential is removed, the polymer returns to the neutral state.²⁴⁻²⁶ The instability of the n-doped polymer requires an inert condition to measure the optical spectra. The long time stability of the n-doped state with constant conductivity seems to be related to the strong positive/

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negative interaction between the PDAC and PCA. Furthermore, the ratio between the weak acid, COOH, and the conjugate base, COO⁻, in the polymeric chain at certain pH values can be calculated by the Henderson–Hasselbalch equation.²⁷ At pH 11, the [COOH], p-type dopant, might be low enough to generate a stable n-type polaron ($\sim 10^{-6.7}$ times

of [COO⁻]) and may justify the presence of the n-type polaron.

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Supporting Information Available: Synthesis information and additional UV–vis and NMR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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