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Self-doped Carboxylated Polyaniline: Effect of Hydrogen Bonding on the Doping of Polymers

Seong-Cheol Kim

School of Textiles, Yeungnam University, Gyeongsan, Gyungbuk 712-749, Korea

James Whitten and Jayant Kumar*

The Center for Advanced Materials, Polymer Science Program, Departments of Chemistry and Physics, University of Massachusetts Lowell, MA 01854

Ferdinando F. Bruno and Lynne A. Samuelson*

U. S. Army Natick Soldier Development and Engineering Center, Natick, Massachusetts 01760

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Abstract: This study examined the unique self-doping behavior of carboxylated polyaniline (PCA). The self-doped PCA was synthesized using an environmentally benign enzymatic polymerization method with cationic surfactants. XPS showed that HCl-doped PCA contained approximately 34% of protonated amines but self-doped PCA contained 9.6% of the doped form of nitrogen at pH 4. FTIR and elemental analysis showed that although the PCA was doped with the proton of strong acids at low pH via the protonation of amines, the self-doping mechanism of PCA at pH > 4 was mainly due to hydrogen bonding between the carboxylic acid group and amine group.

Keywords: self-doping, polyaniline, surfactant, H-bonding.

Introduction

In order to improve the stability of doping and the solubility of polymers, researchers have tried to prepare self-doped polymers.¹⁻³ Among conjugated polymers, polyaniline has attracted great attention because of its electronic, electrochemical, and optical properties, and especially because of its good environmental stability.^{4,5} MacDiarmid *et al.* showed that PANI can afford conduction by protonation of the emeraldine base leading to emeraldine salt through acid-base chemistry.⁶ The polyaniline emeraldine base can also

be protonated by the photo-induced formation of triflic acid leading to the formation of emeraldine salt via UV irradiation.⁷ The same doped polymer can be obtained by chemical oxidation of leucoemeraldine base.⁸ The reaction with chlorine solution of carbon tetrachloride proceeds to give emeraldine hydrochloride. In addition, the doping of polyaniline can be induced by applying negative and/or positive potential on the electrochemically polymerized polyaniline.⁹ However, the doping of polyaniline induced by the hydrogen bonding has not been reported to date.

Many possible applications of the carboxylated polyaniline could be as follows: the functionalization of PCA via esterification with other materials, such as bioactive and chemoselective components having hydroxyl or amine groups, the

*Corresponding Authors. E-mails: Jayant_Kumar@uml.edu or Lynne_Samuelson@us.army.mil

layer-by-layer self-assemblies,^{10,11} nanotechnology,¹²⁻¹⁷ and the detection of divalent metal ions.¹⁸ In spite of many potential applications of carboxylated polyaniline (PCA), the chemical synthesis of this polymer has not been successful with chemical oxidative polymerization because of the poor solubility of a monomer in acidic media. Consequently, the carboxylated *oligo*-aniline having poor conductivity was produced by sodium peroxodisulphate.¹⁹

The biocatalytic synthesis of conducting polyaniline has received great attention in recent years since the enzyme-catalyzed process can offer environmentally benign reaction conditions, a higher degree of control over the kinetics of the reaction, and a higher yield of the product.^{20,21} In particular, the recent development of polyanionic template-assisted polymerization of aniline at pH 4.3 has shown that a parallel, linear, and reasonably conducting polyaniline with good solubility in water is generated.²²⁻²⁴

The synthesis of PCA with polycationic templates gave rise to PCA/polycation complexes which is inseparable by physical methods because of the difficulty in breaking all ionic interactions between the polycationic macromolecule and the anionic PCA chain simultaneously.²⁵ This paper discusses the enzymatic synthesis of self-doped PCA in the presence of cationic surfactant micelles which can be easily removed by ion exchange. In addition, the manuscript elucidates the mechanism of self-doping of the PCA at different pH.

Experimental

Materials. 3-Amino-4-methoxybenzoic acid, polyaniline emeraldine base and tetradecyltrimethylammonium bromide were purchased from Aldrich. Horseradish peroxidase (HRP) (EC 1.11.1.7) (200 unit/mg) was purchased from Sigma.

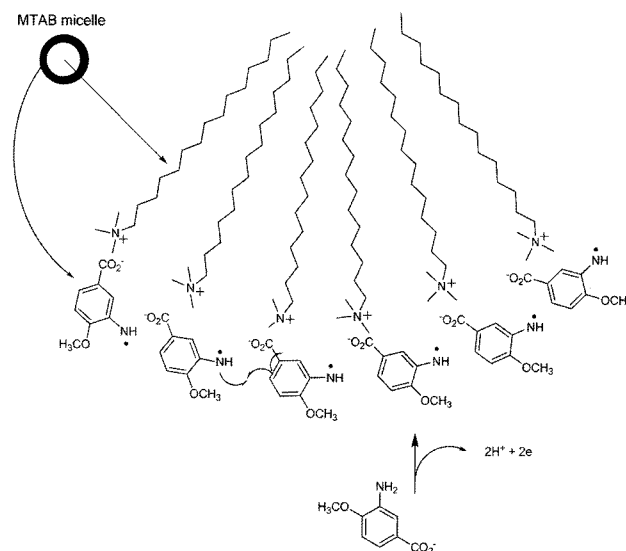
Characterization. The UV-vis-near-IR spectra were recorded on a Perkin-Elmer Lambda-9 UV/vis/near-IR spectrophotometer. FTIR measurements were carried out on a Perkin-Elmer 1760X FTIR spectrometer by using KBr pellets. Cyclic voltammograms were recorded by using a three-electrode cell with a Pt wire as the counter electrode, a saturated calomel electrode as the reference electrode, and platinum foil ($1 \times 1 \text{ cm}^2$) as the working electrode. Cyclic voltammograms were carried out at room temperature in 0.1 M tetrabutylammonium hexafluorophosphate (MTAB) in water with a scan rate of 100 mV/min. The conductivity of the complex was measured using the four-probe method with a Keithley 619 electrometer/multimeter. The X-ray photoelectron spectroscopy studies were performed in a KRATOS AXIS-NOVA photoelectron spectrometer equipped with a concentric hemispherical analyzer, a monochromated aluminum K_{α} ($h\nu = 1486.6 \text{ eV}$) rotating anode X-ray operated at 16 kV and 400 mA. Photoelectrons were detected by a hemispherical analyzer and a two-dimensional position-sensitive detector. The sample solutions containing 20 mg/mL were spin coated at 1,000 rpm for 60 sec on ITO glass before experiment.

The spin coated thin film of the PCA was immersed into an aqueous solution of pH 4 and dried in vacuo for one day at 50 °C. The HCl-doped PCA was fabricated by exposing the pH adjusted PCA thin film to HCl vapor for 1 h and was dried in vacuo for 1 h before XPS experiment.

Polymerization. The polymerization of CA (FW: 167.16) was carried out at room temperature in 100 mL of a 0.05 M sodium dihydrogenphosphate buffer solution at pH 5, which contained a 1:1 molar ratio (2 mM) of the template units to the carboxylated aniline (CA). Template was added first to the buffered solution, followed by addition of CA with constant stirring. To the solution, HRP stock solution containing 10 mg of enzyme was then added. To avoid inhibition of HRP due to excess H_2O_2 , a stoichiometric amount of diluted H_2O_2 (0.3 wt%) was then added dropwise, incrementally, over 2 h to initiate the polymerization. After the addition of H_2O_2 , the reaction mixture was left stirring for at least 1 h and then the final cationic template/PCA complex was first precipitated by the addition of concentrated HCl solution and then washed with acetone/water mixture for several times to remove any unreacted monomer, oligomers, uncomplexed free cationic templates, HRP and phosphate buffer salts. The PCA was then recovered by ion exchange with ammonium nitrate²⁶ and ion exchange resin.²

Results and Discussion

Scheme I represents the complex formation of the PCA in the presence of a surfactant micelle made from tetradecyltrimethylammonium bromide at pH 5. The details of how the electrons are removed in the catalytic oxidation of amine are unclear.^{27,28} The aniline was polymerized via biocatalysis pH below 4.5 to protonate the aniline.²² The polyanionic



Scheme I. Interaction of carboxylated polyaniline and cationic surfactants during the polymerization.

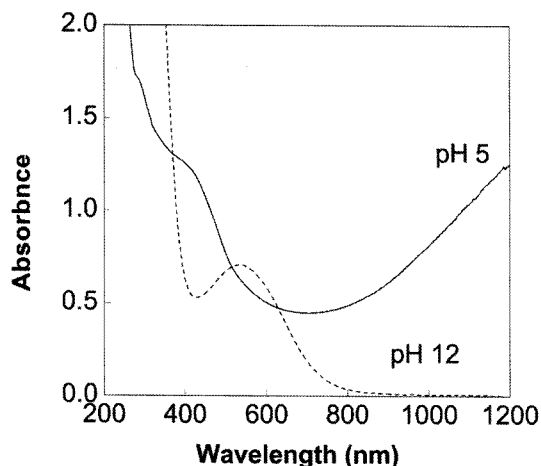
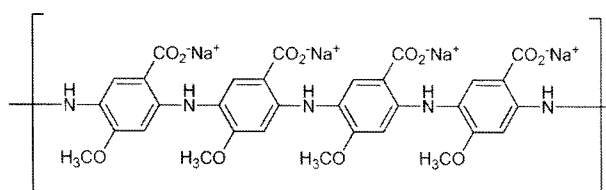


Figure 1. Electronic absorption spectra of PCA/trimethyl(tetradecyl)ammonium bromide [MTAB] at pH 5 and 12.

template was necessary to stabilize and solubilize the *p*-doped polyaniline in water. However, the conditions and mechanisms of polymerization of the monomer, CA, in the presence of a cationic template do not follow that of typical polymerization of aniline. For example, an immediate generation of the polaron transition in the UV-Vis absorption spectra was observed with this system at pH above 4.3. The polyaniline at pH above 4 has emeraldine base form, which does not have the polaron transition due to low concentration of HCl.²⁹⁻³¹ Therefore the UV-vis spectra as shown in Figure 1 demonstrate that the PCA is self-doped at pH 5. The intensity of a polaron transition was highest when the mole ratio between the monomer and MTAB was equal to 1:1. As the mole ratio of MTAB exceeds 1:1, it is expected that the distance between the oxidized monomer/MTAB complexes becomes larger and irregular due to the excess uncomplexed MTAB, which may hinder monomers from polymerization via head-to-tail coupling. A similar phenomenon was observed when the large amount of salt such as NaBr was added into the solution. The abundant bromide ions and the ionized monomers seem to compete to make an ionic bond with the head groups of MTAB, which eventually reduced the rate of a polymerization.

There is an absorption band at 320 nm and two other absorption bands at 425 nm with a strong and broad polaron absorption in the near IR region. The absorption band at 320



Scheme II. Dedoped form of PCA [PCA·Na⁺] with NaOH (aq).

nm is a π - π^* transition^{10,11} and the bands at 430 nm^{29,32} is due to a polaron transition.³³ The blue shift of the π - π^* transition of PCA/MTAB complex compared with the conducting emeraldine hydrochloride is believed to be due to a decreased extent of conjugation caused by increased phenyl ring torsion angle, which may result from the steric repulsion between the carboxyl groups and hydrogens on the adjacent phenyl rings.^{34,35} The conductivities of the self-doped PCA at pH 5 and the unsubstituted emeraldine salt doped with HCl vapor differ by four orders of magnitude. This difference seems to be consistent with the UV-vis results.

However, when the PCA/MTAB complex shown in Scheme I was dedoped with sodium hydroxide as shown in Scheme II, the solution turns purple and an excitonic transition appears at 530 nm.^{32,36-38}

Figure 2 shows the cyclic voltammogram of the PCA at pH 3 buffer solution. Unlike the unsubstituted polyaniline and the self-doped sulfonated polyaniline, it consists of only one quasi-reversible redox peak of which $E_{1/2}$ is 0.48 V vs Ag/AgCl reference electrode.^{9,39-41} During the oxidation process, the color of the PCA film coated on the working electrode changes from pale yellow (reduced state A) to green at

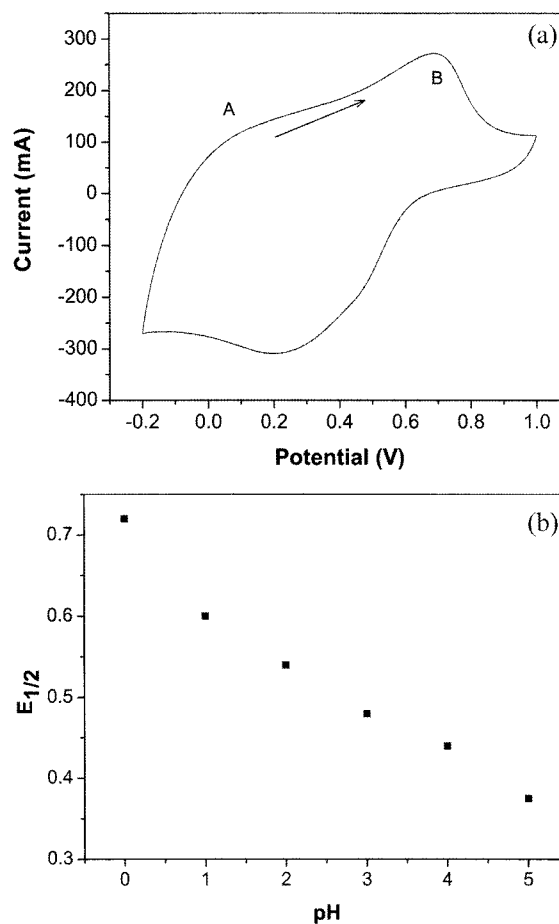


Figure 2. Cyclic voltammogram (50 mV/s) of PCA at pH 3 buffer solution.

0.68 V (emeraldine oxidation state B). The $E_{1/2}$ value shifts to lower potential with increasing pH. The $E_{1/2}$ value above pH 5 could not be obtained due to the dissolution of PCA film on the Pt electrode.

The conductivity of the polyaniline emeraldine base form, the PCA and the PCA complex at different pH was measured by the four point probe method with pellet samples.⁴² The conductivity of reference polyaniline was measured to be 1.3 S/cm when the emeraldine base was converted to the emeraldine salt form by HCl vapor. The measured conductivity of the PCA and the PCA/MTAB complex was in the range of 10^{-4} – 10^{-6} S/cm at pH 5–6. This value is *five to six* orders of magnitude greater than that of the unsubstituted polyaniline in this pH range. In addition, it is quite intriguing to observe the change of conductivity of the PCA/MTAB complex with varying pH as shown in Figure 3. At pH lower than the pKa value of carboxylic acid (pKa ~4.3),⁴³ the conductivity of a PCA/MTAB complex gradually decreases with increasing pH. However, when the pH is greater than the pKa of the carboxylic acid, the conductivity decreased dramatically. The shape of the conductivity trace is quite similar to the curve of weak acid-strong base titration.⁴⁴ This behavior may be explained by the ionization of the carboxyl groups. For unsubstituted polyaniline, the hydrochloric acid is the dominant dopant at low pH. However, at a pH greater than 4, the concentration of HCl is significantly lower and the emeraldine base is essentially undoped, which leads to much lower conductivity.²⁹⁻³¹ The carboxylic acids begin to ionize in a pH range around 5 and seem to function as the dominant dopant due to the proximity and the higher local concentration of carboxylic acids in the vicinity of the nitrogen in the polyaniline backbone. As pH increases from pH 4 to pH 6 in the presence of cationic surfactants, the carboxylic acid seems to lose its proton rapidly and irreversibly due to the strong ionic interaction between the COO⁻ group and the cationic trimethylammonium head group in a surfactant molecule.

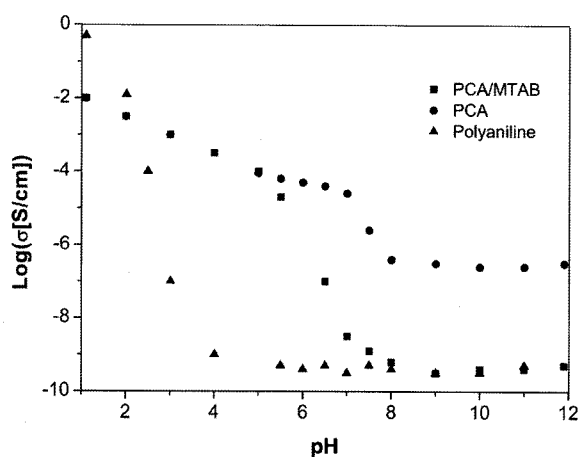


Figure 3. The conductivity of PCA, PCA complex and polyaniline; pH was adjusted with HCl(aq) and NaOH(aq) solution.

The pure PCA (not having the surfactants), however, shows somewhat different behavior from pH 5 to pH 12 and loses its conductivity gradually with increasing pH. The value of conductivity is *three to four* orders of magnitude higher than the unsubstituted polyaniline emeraldine base at the pH range (pH 8–12). This might be related with the lower local pH in the vicinity of the nitrogen of a pure PCA.⁴⁵

X-ray photoelectron spectroscopy (XPS) can give us the information regarding the degree of doping in amines. Figure 4 shows the binding energies of N1s core electron in the self-doped PCA and the HCl-doped PCA. The N1s spectra of the PCA at pH 4 and HCl-doped PCA were fitted smoothly into two component peaks positioned at 399.97 eV and 401.7 eV suggesting the lack of imine and protonated imine.⁴⁶ The large peak is due to the undoped amine. The doping mechanism of the PCA via the protonation of amine is still under investigation. The HCl-doped PCA shows that the area of protonated amines at 401.7 eV consists of 33.9% of total area

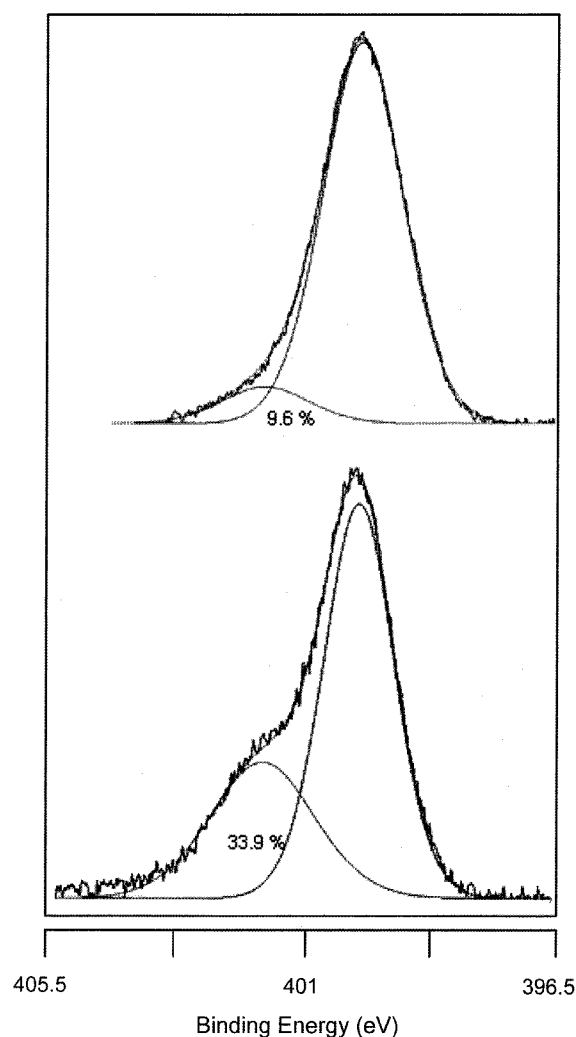


Figure 4. XPS N1s core level spectra of the PCA (above) and HCl-doped PCA.

of amines. In addition, 33.9% of doping of the PCA estimated from N1s XPS spectra explains the reduced conductivity of HCl-doped PCA against the unsubstituted polyaniline emeraldine salt having 50% of a degree of protonation. While, the percentage of the total N1s intensity in the self-doped PCA at pH 4 is 399.97(90.4%) and 401.7 eV (9.6%) respectively. It looks like that the second peak at 401.7 eV is due to the protonated amine in the PCA. However, as the conductivity of self-doped PCA at pH 4 is three orders of magnitude lower than that of the HCl-doped PCA, it is not reasonable to assign the appearance of this peak to the protonated amine.

Figure 5 shows the binding energies of O1s in the pure self-doped PCA at pH 4 and the PCA doped by HCl vapor. The PCA shows three peaks at 532.7, 531.2 and 535.8 eV. The strong O1s peak positioned at 532.7 eV is proposed to correlate with the COOH/COO⁻ groups. The narrow width of the peak at 531.2 eV suggests a uniform chemical environment and seems to be due to the -OCH₃ groups.⁴⁷ The percentage of the total O1s intensity is 532.7 (59.8%), 531.2 (31.2%) and 535.8 eV (9.0%) respectively. As the percent-

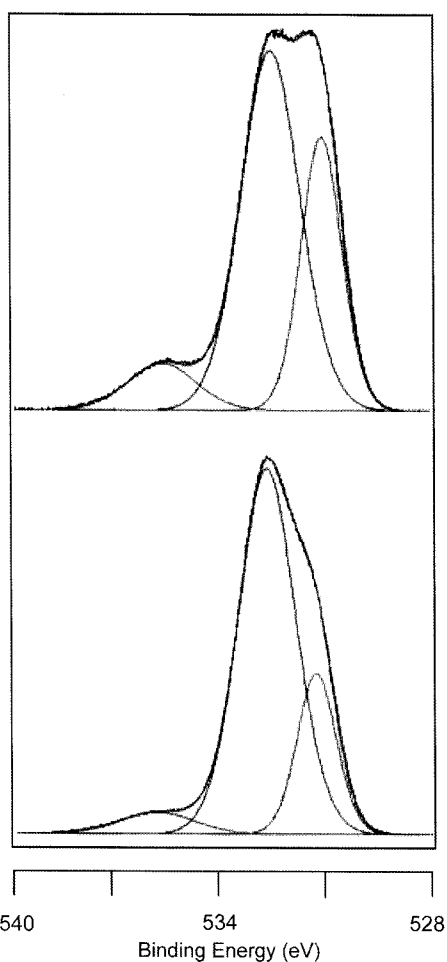
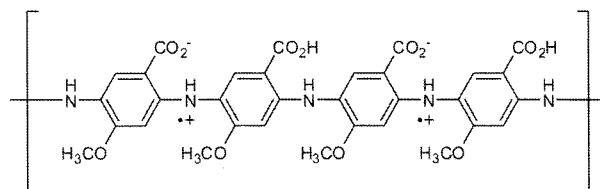


Figure 5. XPS O1s core level spectra of the self-doped PCA (above) and the HCl-doped PCA.

age of the peak at 535.8 eV in O1s is similar to that of the peak at 401.7 eV in the XPS spectra of N1s, the appearance of the peak at 535.8 eV might be related with the doping of amines in N1s. If the carboxyl group protonates the nitrogen of an amine, the peak of COO⁻ groups should appear at the same position with -COOH/COO⁻ groups positioned at 532.7 eV.⁴⁸ Trotter *et al.* and Rodrigues *et al.* showed that the peak at higher binding energy can be generated by the hydrogen bonding.^{49,50} Therefore, it is probable that the peak at 535.8 eV could be generated by the hydrogen bonding between the carboxyl group and the amine group. The area of this peak decreases to 5.7% when the pure PCA is doped with HCl vapor. The decrease of the intensity at 535.8 eV in the HCl-doped PCA might be explained by the decrease in the degree of H-bonding caused by the decrease in electron density of the protonated amine.

Scheme III represents the possible self-doping state of the PCA like the unsubstituted emeraldine salt forms. If the PCA is self-doped by the proton of the COOH as shown in Scheme III, the intensity of the C=O stretch peak in FTIR spectra shown in the Figure 6 should decrease significantly with respect to that of monomer, CA, and should have high conductivity due to a high concentration of the protonated amine in the PCA.

Considering four orders of magnitude lower conductivity of PCA and PCA/MTAB complex than that of the unsubstituted emeraldine salt forms, the concentration of doped



Scheme III. The possible doping structure of the PCA; the source of proton is COOH.

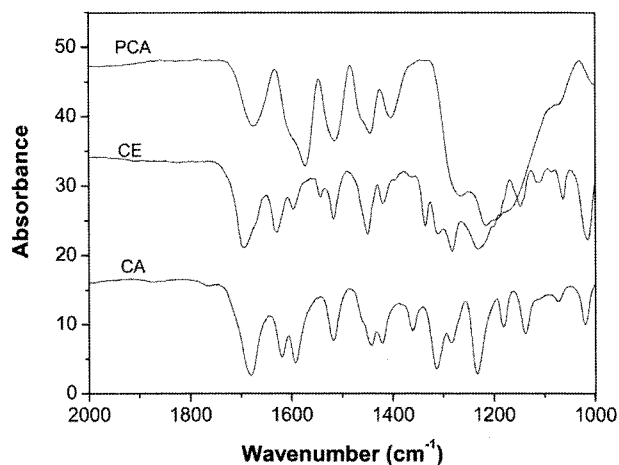
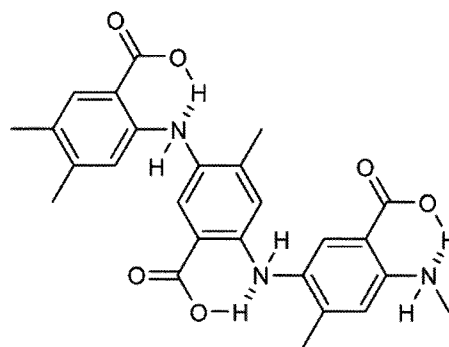


Figure 6. FTIR spectra of CA, CE, PCA and PCA·Na⁺.

form of the nitrogen in the PCA and PCA/MTAB complex should be much lower than that of the emeraldine salt. Therefore, the measured conductivity of the PCA does not correspond with the structure shown in Scheme III. However, it is still possible that only small numbers of the COOH groups protonate the nitrogen of the PCA to generate small numbers of protonated amines. The FTIR spectra show that the C=O stretch of the esterified monomer (CE) with ethanol and sulfuric acid, which does not have an acidic proton, appears at 1690 cm^{-1} due to lack of a hydrogen bonding. The carboxyl groups of the PCA can have the *inter*-molecular hydrogen bonding with adjacent COOH and the *inter*-and/or *intra*-molecular hydrogen bonding with the amine. The dimeric form of COOH group should have an overtone and a combination band at $2700\text{--}2500\text{ cm}^{-1}$ but the PCA does not show a distinct peak at this region.⁵¹ Therefore, it is considered that most of the carboxylic acids in the monomer and the polymer have the monomeric form (*intra*-molecular H-bonding). The C=O stretching peak of the carboxyl group in the PCA red-shifts from 1675 to 1667 cm^{-1} after the polymerization, which suggests that the PCA has an enhanced and systematic hydrogen bonding of COOH groups with amines with respect to CA. The broader band width of C=O stretch in the PCA compared with that of CA also supports the enhanced H-bonding characteristics of the polymer.⁵² The peak at 1356 cm^{-1} in the CA (monomeric COOH) is due to the in-plane OH deformation of COOH, and it disappears when the carboxylic acid is esterified with H_2SO_4 . It is important to notice that the OH deformation peak in the PCA does not appear as well at this region. If small numbers of the carboxylic acids ionize due to the doping process like the fraction of doped amines obtained from XPS data, e.g. 9.6%, most of remnant COOH groups should have an OH deformation peak at this region. Therefore, the FTIR spectra of the PCA clearly demonstrate that almost all carboxyl groups in the PCA are in the same physical environment. Furthermore, unlike any compound with the sulfonic acid group which can dope the polyaniline, the addition of CA and acetic acid to the unsubstituted emeraldine base solution does not generate the polaron peak due to the weak acidity of -COOH groups. These results demonstrate that there is little possibility that the PCA is doped by the proton of the carboxylic acid.

The elemental analysis of PCA shows that the ratio between the hydrogen and the nitrogen is 7.042: 1. Consequently all the carboxyl groups are in the COOH form. While, the HCl-doped form of PCA has the ratio of 7.362:1 (H:N). This result indicates that about a third of amines (~36%) have protonated forms of amines, which is corresponding well with the result obtained from XPS. Therefore it is believed that the self-doped PCA has a *intra*-molecular hydrogen bonding between the amine and the carboxyl group and the probable structure of the self-doped PCA could be as follows:



In this structure the nitrogen loses the electron density because of the hydrogen bonding with the carboxyl group, which makes the nitrogen electron-deficient and eventually may make the PCA self-p-doped at pH greater than 4.

Conclusions

The conductivity results and UV-vis spectra proved that the carboxyl group is the dominant dopant at pH above 4 and the PCA is self-doped at neutral and high pH condition. In the presence of cationic surfactants the polaron intensity of the PCA decreases rapidly with increasing pH, which might be due to the strong ionic interaction between ionized carboxyl groups and tetramethylammonium ion preventing COOH groups from a fast and reversible protonation/deprotonation process in water. The PCA and the PCA complex showed a conductivity of 0.3 S/cm with additional doping with hydrochloric acid vapor. The doping of the PCA at low pH was due to the protonation of amine from HCl. However the doping of the PCA at pH above 4 was caused by the H-bonding between 'COOH' and 'N' of the aniline. Although the conductivity of a self-doped PCA is relatively low, the carboxyl group-functionalized polyaniline offers new opportunities in the area of self-assembly, photovoltaics, and chemical and biological sensors because the carboxyl dopant group is a structural part of the main polymer chain, will not leach away, and can be further functionalized by other guest molecules via esterification, which is not possible for sulfonated polyanilines.

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