

## ARTICLES

## Acid Doping of Polyaniline: Spectroscopic and Electrochemical Studies

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A detailed investigation of the acid doping behavior of polyaniline has led to a robust and reproducible procedure for controlled adjustment of the redox state of dry polyaniline films. The initial step in this procedure is the casting of PANI films from formic acid. The subsequent exchange of the trapped formic acid for other primary dopants obtained from mono- and polyprotic acids (e.g.,  $\text{CH}_3\text{COO}^-$ ,  $\text{BF}_4^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$ ) is demonstrated. The voltammetric and the spectroscopic behavior of the PANI doped with different anions indicate that both the protons and the anions of dopant acids influence the structure and redox properties of the polymer. The redox state of PANI doped with homologous series of chloroacetic and carboxylic acids correlates with the  $\text{p}K_a$  of the dopant acid. These results show that it is possible to prepare the polymer with a desired oxidation state according to the  $\text{p}K_a$  of the dopant acid of a given homologous series. The exchange of the formic acid for both stronger and weaker doping acid can be repeatedly accomplished by electrochemical cycling.

## Introduction

Due to the fact that polyaniline (PANI) is one of the most extensively studied and described conjugated polymers, an extensive review of the polyaniline literature is beyond the scope of this paper. An interested reader is referred to a review of this subject.<sup>1</sup> This work has been motivated by the desire to find a method by which the redox state of dry PANI could be controlled and adjusted. A common way to change the redox state of PANI is by applying a potential to the PANI layer immersed in an acid solution. If this is done by cycling the potential, a characteristic cyclic voltammogram (CV) is obtained in which the anion and proton uptake/expulsion can usually be resolved. The shape of the CV often varies considerably depending on the nature of the electrolyte solution. Therefore a comparison of the voltammetric responses of PANI in solutions containing different ions became the starting point of our study. We have been interested in using these materials as sensing layers for gases (i.e., in dry state).<sup>2</sup> Moreover, it is desirable to prepare dry PANI sensing layers with different stable redox states.

When a PANI film is taken out of the electrolyte solution and rinsed, it always assumes an "open cell" potential corresponding to the amount of the acid remaining in the film after the washing step. Consequently, regardless of the final potential applied to the film the "dry value" is always close to the open cell potential value and is poorly defined. This presents a problem for preparation of PANI and similar polymers for any dry application. To circumvent this problem we describe a systematic study of redox properties of PANI doped with different strong and weak acids.

## Experimental Section

**Chemicals.** Aniline (Aldrich, 99.5+ %, 24,228-4), acetic acid, glacial (Fisher ACS reagent, A38<sup>c</sup>-212), tetrafluoroboric acid (Aldrich, 44% weight percent solution in water, 20,793-4), hydrochloric acid (J. T. Baker, 35.5–38% weight percent solution in water, 9535-01), chloroacetic acid (Aldrich, 99+ %, ACS reagent, 40,292-3), dichloroacetic acid (Aldrich, 98+ %, 11,611-4), trichloroacetic acid (Aldrich, 99+ %, D5-470-2), phosphoric acid (Fisher, ACS reagent, A242–500), sulfuric acid (Fisher, ACS reagent, A300<sup>c</sup>-212), perchloric acid (Fisher, ACS reagent, A229), and ammonium hydroxide (Fisher, ACS reagent, A669-500) were all used as received.

**Preparation of PANI–Formate Solution and Films.** The bulk PANI– $\text{BF}_4$  material was obtained by oxidative electropolymerization of 0.25 M aniline in the presence of 2 M  $\text{HBF}_4$ . It was converted into PANI-base material with ammonium hydroxide.<sup>3</sup> The dry PANI-base material of 250 mg was dissolved in 50 mL of 88% formic acid. The PANI–formic acid solution was then filtered using 0.2  $\mu\text{m}$  pore size syringe tip filters (Gelman Science, Acrodisk). PANI films were cast onto Pt and Au electrodes using glass capillary pipets to minimize material overlap on the insulating body of the microelectrodes. The volumes delivered onto the Pt or Au disk with a surface area of 0.14  $\text{cm}^2$  (Model MF-2014 or MF-2013, Bioanalytical Systems) were typically on the order of 5  $\mu\text{L}$ . The formic acid was then allowed to dry under normal laboratory air for 24 h before further use as working electrodes in electrochemical experiments.

**Electrochemical Experiments.** All electrochemical measurements were performed using CH1660 and CH1680 potentiostat/galvanostats connected in series and controlled by the CH instruments electrochemical software. The experiments were made in a one-compartment cell using a standard three-electrode

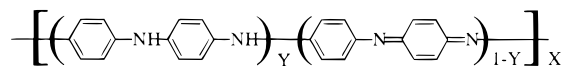
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cell arrangement. The potential of the working electrode was always measured against the saturated calomel electrode (SCE) using a double junction of 2 M acid. The counter electrode was always a platinum sheet. The width of the potential window used for each experiment was selected such that the voltammetric peaks corresponding to the proton and anion doping were fully developed. All cyclic voltammograms were recorded with a scan rate of 50 mV/s.

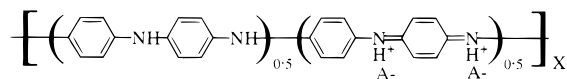
**FT-IR Spectroscopy Apparatus and Conditions.** FT-IR measurements were performed using a BIO-RAD FTS-6000 with a BIO-RAD UMA-500 IR microscope attachment. IR reflectance spectra were obtained using the rapid scan mode at a mirror modulation frequency of 20 kHz, with the aperture open, a filter setting of 5, a resolution setting of 4  $\text{cm}^{-1}$  and a laser wavelength of 15800.8235  $\text{cm}^{-1}$ . An average of 100 scans was used to produce each spectrum. Background spectra were obtained using a mirrored gold surface under the same spectroscopic conditions as the samples. The background was subtracted from the sample spectra using BIO-RAD WIN-IR PRO software. Areas and peak assignments were obtained using the same software.

## Results and Discussion

**Doping Mechanism for the Cast PANI Films.** The structure of PANI is generally represented by the following diagram, where  $Y = 0.5$  for the polyemeraldine salt:<sup>4</sup>

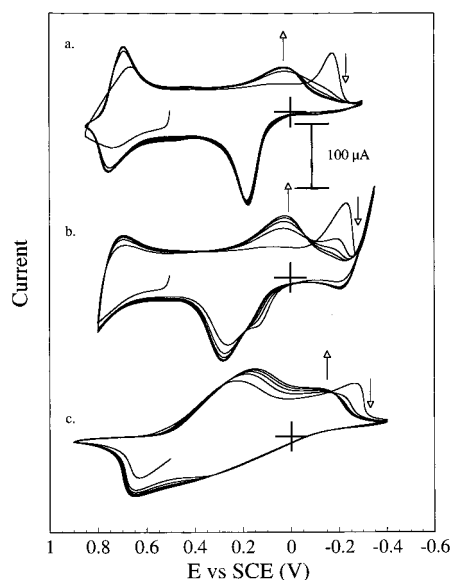


The value of  $Y$  is generally different when the polymer is cast from or cycled in different acids. Both the proton and the anion play important roles in determining the oxidation state of the polymer.<sup>5</sup> Conversely, changes in the oxidation state of the polymer result in the uptake or expulsion of both protons and anions. The doping of the polymer with an acid is governed by the condition of charge neutrality, resulting in the incorporation of positive (proton) and negative (anion) charge as the oxidation state of the polymer is changed. For example, formic acid is incorporated into polymer matrix during the casting procedure. In this case the reflectance IR data indicate that the amounts of benzenoid and quinoid units are equal.<sup>6</sup> Therefore, PANI, cast from formic acid, has the following structure, where  $Y = 0.5$ :



However, doping the polymer with other acids may result in different oxidation state as will be shown later. It has been observed that the conductivity of PANI doped with  $\text{Cl}^-$  from different dilute solutions of HCl increases in conductivity  $\sim 10^{10}$  fold when the pH of the HCl solution is below  $\sim 2.0$ .<sup>7</sup> In this process the degree of proton doping is responsible for the observed increase in conductivity. However, the effect of the anion on the conductivity has not been systematically investigated.

Sariciftci et al. has examined the proton doping of PANI and has shown that deprotonation results in loss of conductivity if the starting material is in the fully reduced state.<sup>5,8</sup> However, the changes in conductivity were also observed for the intercalation of the counterion into the oxidized polymer. The ability of the anion and proton of an acid to interact with the PANI can be related to relative strength of the acid and of the amine and

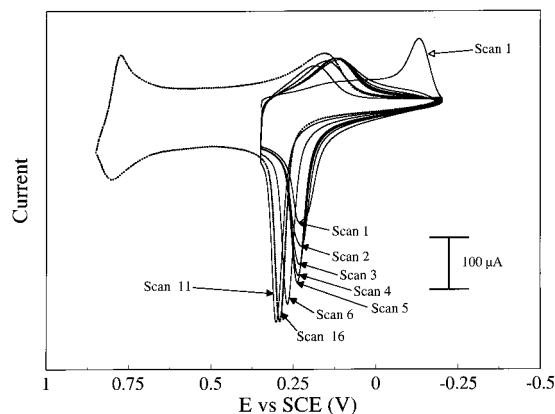


**Figure 1.** Acid doping for PANI films on Pt electrodes in solutions containing 2M (a)  $\text{HBF}_4$ , (b)  $\text{H}_2\text{SO}_4$ , and (c)  $\text{CH}_3\text{COOH}$ .

imine groups within the polymer. The  $\text{p}K_a$  values for the two acidic nitrogen groups within PANI have been determined by titration with NaOH.<sup>9</sup> They are 2.5 and 5.5 for  $(-\text{NH}_2^+)$  and  $(-\text{NH}^+=)$ , respectively. On the basis of these values, we would expect a strong acid ( $\text{p}K_a < 2.5$ ) to protonate both groups. Likewise, a dopant acid with an intermediate  $\text{p}K_a$  value ( $2.5 < \text{p}K_a < 5.5$ ) should result in the protonation of the  $-\text{N}=\text{N}-$  group only. Therefore, the formic acid ( $\text{p}K_a = 3.7$ ) trapped in the cast PANI film acts not only as a solvent but also protonates the film.

To understand how the  $\text{p}K_a$  of the dopant acid influences their properties, the PANI films cast from formic acid were treated in various 2 M acids with different  $\text{p}K_a$  values (Figure 1). The acids used were  $\text{HBF}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{CH}_3\text{COOH}$  for Figure 1a, b, and c, respectively. These acids were selected to include a strong monoprotic acid, a strong diprotic acid and a weak monoprotic acid, respectively. The voltammetric scans for all three acids were started at 0.5 V. The direction of the initial scans was all in the positive direction resulting in the immediate uptake of anions into the polymer films. The subsequent expulsion of the anions was observed upon the potential reversal. The potential scans continued in the negative direction which resulted in the uptake, and after reversal, expulsion of proton from the polymer. A total of five complete cyclic voltammograms at the scan rate of 0.05 V/s were obtained for each acid.

The striking feature of these experiments has been the different shape and evolution of these CVs from the first scan to its steady-state response. The proton uptake at potentials negative of the steady-state response is observed for the first scan for each acid. It is a characteristic feature of the films cast from formic acid. In the case of  $\text{H}_2\text{SO}_4$  and  $\text{CH}_3\text{COOH}$  in the solution a well defined isosbestic points are observed during the cycling. This behavior is attributed to the gradual exchange of the formic acid initially present in the film for the acid in the solution. Because the formate ion trapped in the polymer is a relatively weak Brönsted base, it is protonated on the first scan to form a neutral acid. The internal pH in the polymer is set by the degree of dissociation corresponding to the  $\text{p}K_a$  of the acid and the  $\text{p}K_a$  of the amine groups. Therefore, the relatively basic imine groups are fully protonated when the film is cast. The initial uptake of protons and the expulsion of the formate anions is coupled to a change in the internal pH of the



**Figure 2.** Proton exchange for PANI films cast from formic acid, immersed in solutions containing 2 M HBF<sub>4</sub>. The voltammetric scans are labeled for clarity. The potential limits for voltammetric scans 1–11 were 0.35 to –0.2 V vs SCE. The potential limits were increased to 0.85 to –0.2 for scans 12–16.

PANI film which has a direct effect on the protonation equilibria in the film. With each additional scan the internal pH is influenced by the increasing amount of the new dopant acid taken from the solution, as the original formic acid is being replaced. The voltammetric behavior therefore resembles (i.e., the isosbestic point) the titration of formic acid with the new acid from the doping solution.

Evidence for the displacement of formic acid from the film was obtained from a cyclic voltammetric experiment in which the positive scan was terminated at +0.35 V, well before the uptake of the anion. Therefore, only the proton exchange was directly electrochemically activated. In this experiment the acid in the solution was 2 M HBF<sub>4</sub>. Figure 2 shows that the peak potential of the proton expulsion shifts in the positive direction and becomes progressively narrower. It is necessary to mention here that leaving the film cast from formic acid for 12 h in the solution of HBF<sub>4</sub>, at open circuit potential, *without scanning*, does not result in a change in the CV. This indicates that spontaneous acid exchange does not take place. On the basis of these observation the proton doping of PANI can be examined with respect to three different kinds of labile protons within the polymer: (1) protons that bind to the available (–N=) groups because they are the strongest Brönsted base in this system. The number of these basic sites is determined by the redox state of the polymer (i.e., by the ratio of the amine/imine groups). These protons are exchanged during each scan as the redox state of the polymer changes. (2) protons that exchange between the polymer and the solution phase. Their distribution is given by the equality of the electrochemical potential of protons in the two phases. This leads to the formation of the pH dependent Nernst, phase-boundary potential:

$$E = E' - 0.059 \log \left( \frac{[\text{H}^+]_p}{[\text{H}^+]_s} \right) \quad (\text{at } 25^\circ\text{C}) \quad (1)$$

where the subscripts P and S designate the polymer and solution phases, respectively; (3) the protons in the polymer that are constrained by the weak acid equilibrium. The condition of electroneutrality in the bulk of the polymer requires that

$$[\text{H}^+]_p = [\text{A}^-]_p = (K'_a [\text{HA}]_p)^{1/2} \quad (2)$$

Substitution for  $[\text{H}^+]_p$  to eq 1 yields the dependence of the boundary potential on the concentration of the undissociated acid in the polymer

$$E = \text{constant} - 0.059 \log [\text{HA}]_p^{1/2} \quad (3)$$

The first term on right-hand side of eq 3 contains all the constant parameters, i.e.,  $E'$ ,  $[\text{H}^+]_s$ , and  $K'_a$ . Although the exact values of these parameters are not known, it is safe to assume that they remain constant during the repeated scanning. Thus, eq 3 predicts a positive shift of the peak potential with the decreasing concentration of the formic acid in the polymer. The shift of the proton expulsion peak due to this effect is shown in Figure 2.

If the  $\text{p}K'_a$  of the acid influences the degree of protonation of the PANI and its redox state then it would be expected that the shape and potentials of the voltammetric peaks would be effected. We would further expect that the voltammetric peaks associated with the uptake and expulsion of the different anions would be different. This is clearly observed when the dopant acid is changed in Figure 1. The proton expulsion peaks for the strong acids are sharper than those of the weak acids. The potential for proton expulsion for H<sub>2</sub>SO<sub>4</sub> occurs ~200 mV more positive than that for HBF<sub>4</sub>. This is also due to the fact that H<sub>2</sub>SO<sub>4</sub> is a diprotic acid with two different anions and  $\text{p}K'_a$  values which influence how they interact with the polymer.

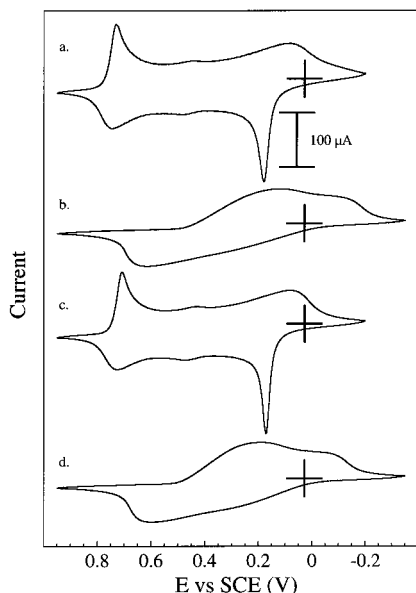
The voltammetric peaks of proton or anion doping for the weak acid (CH<sub>3</sub>COOH) are not well resolved, and significant overlap of the two waves is observed (Figure 1c). Slowing down the scan rate does not fully resolve the waves for the two processes. The lack of resolution is related to the affinity of acetic acid for PANI. This affinity is not surprising considering that acetic acid is also used to dissolve PANI for casting.<sup>10</sup>

The amount of weak acid left in the polymer depends on its  $\text{p}K'_a$  value. The  $\text{p}K'_a$  of acetic acid is 4.7. It is sufficiently strong to protonate the imine groups. However, a significant equivalent amount of undissociated acetic acid must be present within the polymer dictated by its dissociation equilibrium constant. The affinity of the polymer for the acid and the internal equilibrium concentration of acetic acid are both responsible for the lack of voltammetric resolution observed for the doping of PANI with CH<sub>3</sub>COOH. For each acetate anion expelled from the polymer, ~10<sup>4.7</sup> undissociated molecules of acetic acid must leave the polymer.

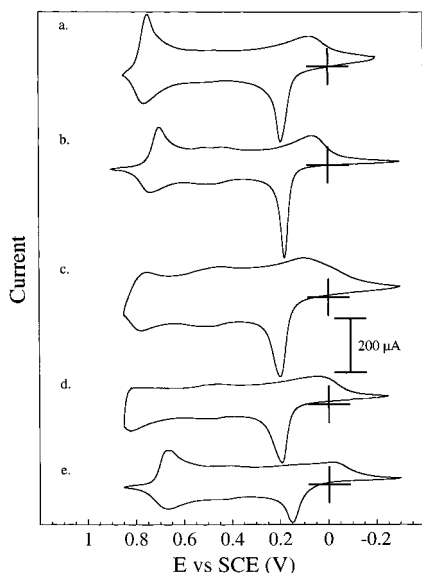
For PANI films to be useful in a dry state, they must be chemically and mechanically stable. The stability of the PANI in the presence of different acid solutions is demonstrated in Figure 3. This figure shows the sequential doping of the same film with weak and strong acid. In this experiment, the PANI film is initially cycled in a solution containing 2 M HBF<sub>4</sub>, until a steady-state voltammetric response is achieved (Figure 3a). The electrode is then removed, rinsed, and placed in a solution containing 2 M CH<sub>3</sub>COOH and the doping process is repeated (Figure 3b). The potential window used to obtain Figure 3b and 3c are identical, while the negative potential limit for CH<sub>3</sub>COOH was extended so the proton wave could be fully displayed. Figure 3a–d shows that repeated exchange of strong acid for weak acid is possible without damaging the PANI film.

**Doping of PANI in Strong Acids.** The differences between the two doping processes for PANI films in 2 M solutions of strong acids are shown in Figure 4. The steady-state voltammetric responses for HBF<sub>4</sub>, HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> are labeled from top to bottom (Figure 4a–e). This series includes acids typically used in the doping and synthesis of PANI.<sup>8,11</sup>

The potential for the doping and expulsion of the proton in strong acids remains fairly constant for the entire series (0.1–0.2V). A slight shift in potential is observed for the proton



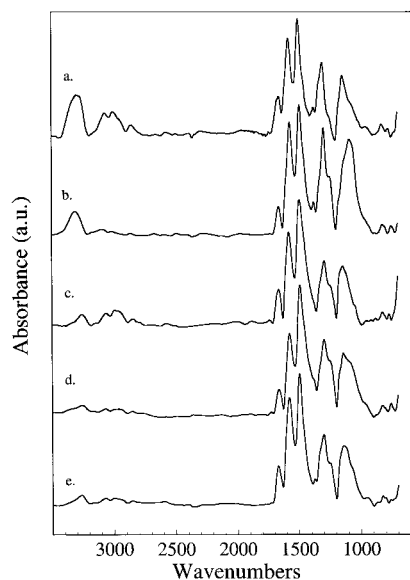
**Figure 3.** Successive acid exchange for a single PANI film cast from formic acid on a Pt disk electrode in solutions containing (a,c) 2 M  $\text{HBF}_4$  and (b, d) 2 M  $\text{CH}_3\text{COOH}$ .



**Figure 4.** Acid doping of PANI films cast from formic acid on Pt electrodes in solutions containing 2 M strong acid: (a)  $\text{HBF}_4$ , (b)  $\text{HClO}_4$ , (c)  $\text{HCl}$ , (d)  $\text{H}_2\text{SO}_4$ , and (e)  $\text{H}_3\text{PO}_4$ .

expulsion with a variance of  $\sim 50$  mV. The potential for proton uptake also remains fairly constant for the series of acids studied as well, with the exception of  $\text{H}_3\text{PO}_4$  (Figure 4e). The proton doping of phosphoric acid occurs at a slightly more negative potential ( $\sim -0.25$  V). This anomaly can be explained by the fact that phosphoric acid is polyprotic and not as strong as the other acids ( $\text{p}K_a = 2.1$ ). The similarity of the proton exchange process is not surprising because  $\text{p}K_a$  for strong acids is less than 1 and the proton behaves independently of the anion.

On the other hand, significant differences for the entire series are observed in the shape and position of the anion doping peaks. Although the amount of incorporated anion is primarily determined by the oxidation state of the polymer, its chemical characteristics also play a significant role in the incorporation interaction. Anions that can hydrogen bond will interact with the amine groups within the polymer more strongly than those that do not. This interaction is reflected in the peak potential corresponding to the anion exchange.



**Figure 5.** FTIR reflectance spectra for PANI after doping with strong acid: (a)  $\text{HBF}_4$ , (b)  $\text{HClO}_4$ , (c)  $\text{HCl}$ , (d)  $\text{H}_2\text{SO}_4$ , and (e)  $\text{H}_3\text{PO}_4$ .

Additional insight into the process of anion doping can be obtained from FTIR spectroscopy. The chemical changes can be observed in the vibrational spectra based on changes in the position and shape of the characteristic IR bands of PANI. For example, the N—H vibrational modes of the IR spectra for PANI can be examined with respect to hydrogen bonding. The reflectance IR spectra for PANI doped with strong acids, are presented in Figure 5a–e. The corresponding spectra are obtained after doping PANI with the same series of acids presented in Figure 4a–e. PANI doped with  $\text{HBF}_4$ ,  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  are labeled from top to bottom (Figure 5a–e).

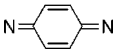
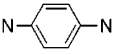
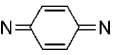
The FTIR reflectance spectra for the acid series show very little change in the fingerprint region. Table 1 gives the band assignments in this region for each acid. An exception is the quinoid band for  $\text{HClO}_4$  at  $1086\text{ cm}^{-1}$  which is  $\sim 50\text{ cm}^{-1}$  lower than the values obtained for the other acids. We stated previously that this band is typically observed at  $1140\text{ cm}^{-1}$ . Our observation suggests there is an increase in the resonance stabilization of the nitrogen groups in the presence of the perchlorate anion.

A better indication of the interaction of the dopant anion in PANI can be obtained by examining the spectroscopic regions which encompass the amine groups and the C—H bands of the benzene rings. These bands should be more sensitive to anion interactions because they are sensitive to hydrogen bonding and electron density changes based on the introduction of electron donating or withdrawing groups within the polymer. Shifts in energy in the region between  $3200$  and  $3350\text{ cm}^{-1}$  are indicative of anion—amine interactions. Shift in the C—H aromatic bands due to electron density changes and resonance changes should be observed between  $2800$  and  $3100\text{ cm}^{-1}$ . The Table 2 gives the band assignments in these two regions for the acid series presented in Figure 5.

A relatively small shift in the wavenumbers is observed in the C—H region for the series of acids. Slight variations are again observed for  $\text{HClO}_4$  which are consistent with the observations made in the fingerprint region of the IR spectra. The three modes for the aromatic C—H are shifted to higher energy for this acid. Shifts to higher wavenumbers are indicative of increasing electron density on the ring. Both spectral regions indicate that the perchlorate anion acts as an electron donor with respect to PANI.<sup>12</sup>



TABLE 1: FTIR Band Assignments in the Fingerprint Region for PANI Doped with Strong Acids

	C-H oop <sup>a</sup>		C-N		
(a) HBF <sub>4</sub>	825 cm <sup>-1</sup>	1142 cm <sup>-1</sup>	1305 cm <sup>-1</sup>	1501 cm <sup>-1</sup>	1579 cm <sup>-1</sup>
(b) HClO <sub>4</sub>	821 cm <sup>-1</sup>	1086 cm <sup>-1</sup>	1295 cm <sup>-1</sup>	1490 cm <sup>-1</sup>	1570 cm <sup>-1</sup>
(c) HCl	822 cm <sup>-1</sup>	1143 cm <sup>-1</sup>	1292 cm <sup>-1</sup>	1493 cm <sup>-1</sup>	1579 cm <sup>-1</sup>
(d) H <sub>2</sub> SO <sub>4</sub>	823 cm <sup>-1</sup>	1140 cm <sup>-1</sup>	1295 cm <sup>-1</sup>	1490 cm <sup>-1</sup>	1575 cm <sup>-1</sup>
(e) H <sub>3</sub> PO <sub>4</sub>	823 cm <sup>-1</sup>	1139 cm <sup>-1</sup>	1299 cm <sup>-1</sup>	1495 cm <sup>-1</sup>	1578 cm <sup>-1</sup>

<sup>a</sup> C-H oop Stands for out-of-plane bending.

TABLE 2: IR Band Assignments for PANI Doped with Strong Acids

	C-H aromatic			N-H
(a) HBF <sub>4</sub>	2854 cm <sup>-1</sup>	3003 cm <sup>-1</sup>	3069 cm <sup>-1</sup>	3297 cm <sup>-1</sup>
(b) HClO <sub>4</sub>	2863 cm <sup>-1</sup>	3012 cm <sup>-1</sup>	3096 cm <sup>-1</sup>	3310 cm <sup>-1</sup>
(c) HCl	2843 cm <sup>-1</sup>	2992 cm <sup>-1</sup>	3060 cm <sup>-1</sup>	3257 cm <sup>-1</sup>
(d) H <sub>2</sub> SO <sub>4</sub>	2851 cm <sup>-1</sup>	2963 cm <sup>-1</sup>	3066 cm <sup>-1</sup>	3255 cm <sup>-1</sup>
(e) H <sub>3</sub> PO <sub>4</sub>	2852 cm <sup>-1</sup>	3000 cm <sup>-1</sup>	3067 cm <sup>-1</sup>	3262 cm <sup>-1</sup>

The N-H region shows a dependence on the doping anion. Hydrogen bonding is observed for two of the five acids studied. The acid doping of PANI with HBF<sub>4</sub> and HClO<sub>4</sub> results in broadening of the N-H stretch which indicates hydrogen bonding. The shift to higher energy is also consistent with an increase in hydrogen bonding with the N-H group. Anions which typically do not hydrogen bond with amine groups such as phosphate, chloride, and sulfate show small variations in the intensity and shape of the N-H band. In contrast, ClO<sub>4</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> show much broader, higher intensity peaks, which shift ~35–55 cm<sup>-1</sup> in comparison to those of the other three acids studied. Thus, the spectral data for both regions discussed indicate that the intercalation of anions within the polymer matrix influences the structure and reactivity through two primary mechanisms. Strong interactions, such as hydrogen or hydrophobic bonding and weaker interactions such as electron withdrawal or donation, both contribute to the structure and chemical reactivity of the polymer.

The ability to examine the structural properties of PANI films after electrochemical doping with reflectance FTIR, allows the redox state of the polymer to be examined. This is based on previous treatments of IR data in which the quinoid and benzenoid units were identified.<sup>13</sup> Therefore, the ratio of the quinoid and benzenoid units (i.e., C=N/C-N) is obtained by taking the ratio of the areas of the IR bands at ~1500 and 1590 cm<sup>-1</sup> (Figure 5). This ratio is then directly related to the oxidation state of the polymer. It follows that the same trend for all strong acids is observed. In each case the ratio of the two bands is less than one indicating that there are more benzene units within the polymer.<sup>3</sup> The ratio *R* is calculated on the basis of the following:

$$\frac{V_{\text{N}=\text{C}}}{V_{\text{N}-\text{C}}} = R = \frac{1 - Y}{Y}$$

The values calculated from the FTIR data are *R* = 0.78, 0.87, 0.53, 0.51, and 0.78 for PANI doped in solutions containing 2M HBF<sub>4</sub>, HClO<sub>4</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub>, respectively. Therefore, the structure of PANI doped with HCl can be represented as

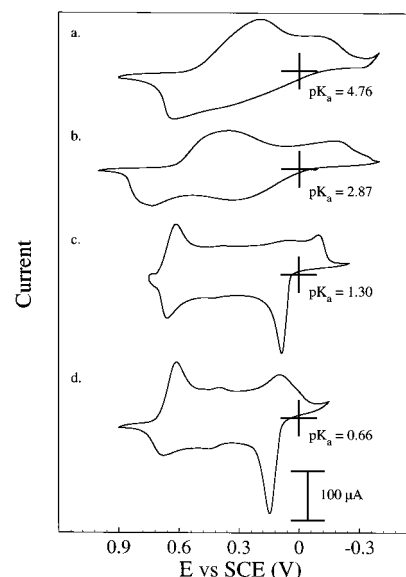
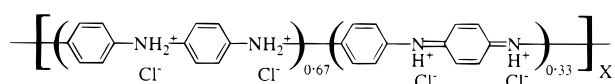






Figure 6. FTIR reflectance spectra for PANI after doping with homologous series of acids: (a) CH<sub>3</sub>COOH, (b) CH<sub>2</sub>ClCOOH, (c) CHCl<sub>2</sub>COOH, (d) CCl<sub>3</sub>COOH.

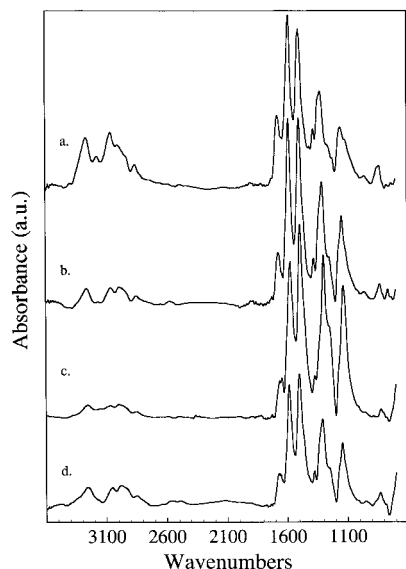
**Doping of PANI with Weak Acids.** The strong acid series provides a valuable insight into the effect of doping on the oxidation state of PANI. However, it is hard to examine the effect of the p*K*<sub>a</sub> value on the properties of PANI with the strong acid series. The primary limitation to this series is the small variation in the p*K*<sub>a</sub> of the dopant acids. On the other hand, weak acids, with higher p*K*<sub>a</sub> values, offer additional information with respect to the doping properties of PANI. This is based on the fact that PANI doped with weak acid results in a material that forms an internal buffer, based on the p*K*<sub>a</sub> of the dopant acid. Therefore, the cyclic voltammetric response of a homologous series of carboxylic acids with different p*K*<sub>a</sub> values (0.66 to 4.7) was obtained (Figure 6).

The acids studied from top to bottom in Figure 6 include (a) acetic, (b) monochloroacetic, (c) dichloroacetic, and (d) trichloroacetic acid. The voltammetric response for the series changes dramatically with the p*K*<sub>a</sub>. As expected the response for dichloroacetic (p*K*<sub>a</sub> = 1.3) and trichloroacetic acid (p*K*<sub>a</sub> = 0.7) is similar to the response observed for other strong acids (Figure 4). In each case, the proton and the anion uptake/expulsion waves are defined and clearly resolved. In contrast, the resolution of the anion and proton doping is poor for the relatively weak monochloroacetic and acetic acid (p*K*<sub>a</sub> = 2.9 and 4.7, respectively). For example, the proton expulsion wave is barely distinguishable from the anion uptake for acetic acid (Figure 6a). The overlap for each process is an indication of the interaction of the anion and proton within the polymer matrix. A significantly higher concentration of undissociated weak acid is needed inside the polymer to satisfy the charge neutrality and the weak acid dissociation equilibrium of the acid, depending on the oxidation state of the polymer.

**TABLE 3: FTIR Band Assignments in the Fingerprint Region for PANI Doped with Acetic Acid Series**

	C-H oop <sup>a</sup>				
HCOOH	824 cm <sup>-1</sup>	1144 cm <sup>-1</sup>	1336 cm <sup>-1</sup>	1505 cm <sup>-1</sup>	1582 cm <sup>-1</sup>
(a) CH <sub>3</sub> COOH	831 cm <sup>-1</sup>	1152 cm <sup>-1</sup>	1319 cm <sup>-1</sup>	1498 cm <sup>-1</sup>	1582 cm <sup>-1</sup>
(b) ClCH <sub>2</sub> COOH	829 cm <sup>-1</sup>	1143 cm <sup>-1</sup>	1305 cm <sup>-1</sup>	1496 cm <sup>-1</sup>	1583 cm <sup>-1</sup>
(c) Cl <sub>2</sub> CHCOOH	825 cm <sup>-1</sup>	1141 cm <sup>-1</sup>	1307 cm <sup>-1</sup>	1499 cm <sup>-1</sup>	1581 cm <sup>-1</sup>
(d) Cl <sub>3</sub> CCOOH	830 cm <sup>-1</sup>	1143 cm <sup>-1</sup>	1306 cm <sup>-1</sup>	1497 cm <sup>-1</sup>	1582 cm <sup>-1</sup>

<sup>a</sup> C-H oop stands for out-of-plane bending.



**Figure 7.** Doping behavior of PANI films cast from formic acid on Pt, for a homologous series of acids. Solutions contain 2 M: (a)  $\text{CH}_3\text{COOH}$ , (b)  $\text{CH}_2\text{ClCOOH}$ , (c)  $\text{CHCl}_2\text{COOH}$ , and (d)  $\text{CCl}_3\text{COOH}$ , respectively.

For comparison, the amount of acetic acid needed would be on the order of  $10^4$  higher than that of a strong acid with a  $\text{pK}_a$  of 1 to dope the polymer equally with the same number of protons. Thus, the difference in  $\text{pK}_a$  is rather significant in terms of the concentration of proton available for doping of the polymer. The position of the peaks for the two processes also provide insight into the effect of  $\text{pK}_a$  on the doping of PANI. Specifically, the potential for proton doping for the carboxylic acid series shifts to more negative potential as the  $\text{pK}_a$  increases. This indicates that the polymer is more reduced when doped with a weak acid.

Anion doping for the acetic acids series can also provide a valuable insight into the effect of the  $pK_a$  of the dopant acid on the polymer. It is not surprising that the potential where anion uptake occurs is similar. That process is primarily determined by the electrostatic interactions of the polymer and the anion. In each case the charge on the anion is one. As the polymer is oxidized, anion uptake occurs in the film so that charge neutrality is maintained. This process is not hindered because there is a large excess of anions available in solution. However, the expulsion of the anion from the polymer is different. The reduction peak shifts to more negative potential as the  $pK_a$  of the acid increases. The difference between the doping and expulsion potential can be attributed to the affinity of the anion for PANI. It is well-known that both acetic and formic acids can be used as solvents for PANI.<sup>10,14</sup> The oxidation state of the polymer and its affinity for the acid determines how much of the anion remains in the polymer. The voltammetric data indicates that the polymer must be reduced to a greater extent for complete anion expulsion to occur in the weak acid.

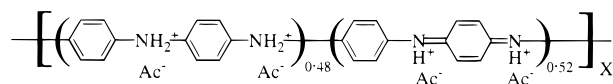
**TABLE 4: FTIR Band Assignments in for PANI Doped with Acetic Acid Series**

	C—H aromati <sup>x</sup>			N—H
HCOOH	2845 cm <sup>-1</sup>	2973 cm <sup>-1</sup>	3059 cm <sup>-1</sup>	3247 cm <sup>-1</sup>
(a) CH <sub>3</sub> COOH	2856 cm <sup>-1</sup>	3002 cm <sup>-1</sup>	3058 cm <sup>-1</sup>	3263 cm <sup>-1</sup>
(b) ClCH <sub>2</sub> COOH	2851 cm <sup>-1</sup>	2988 cm <sup>-1</sup>	3059 cm <sup>-1</sup>	3261 cm <sup>-1</sup>
(c) Cl <sub>2</sub> CHCOOH	2857 cm <sup>-1</sup>	2997 cm <sup>-1</sup>	3065 cm <sup>-1</sup>	3259 cm <sup>-1</sup>
(d) Cl <sub>3</sub> CCOOH	2852 cm <sup>-1</sup>	3000 cm <sup>-1</sup>	3067 cm <sup>-1</sup>	3262 cm <sup>-1</sup>

The cyclic voltammetry data for the weak acids are corroborated by the IR reflectance data (Figure 7). Band assignments for the series are presented for the regions previously discussed for the strong acids and compared to PANI cast from formic acid. The fingerprint region between 800 and 1600  $\text{cm}^{-1}$  shows very little change for the homologous series of acids (Table 3). The band assignments for the benzenoid and quinoid groups are particularly important because they provide information on how the anions for this series of acids interact with the amine groups. The bands in this region show very little change which indicates that the anion of each acid in the series interacts in similar manner with the polymer.

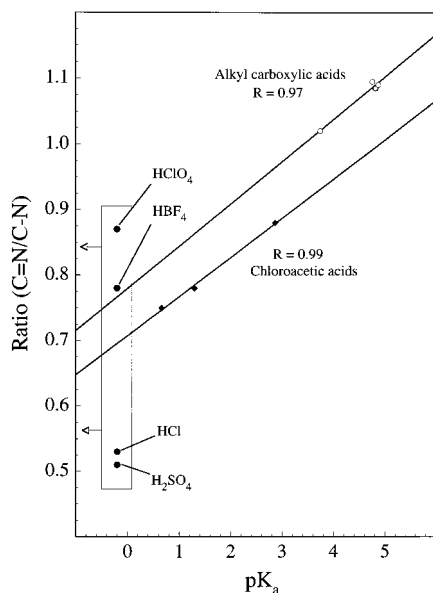
A qualitatively similar result is obtained for the C–H and N–H bands observed at higher wavenumbers. The bands in this region vary slightly which indicates the acid interactions are similar for the entire series (Table 4).

There is no significant hydrogen bonding with the polymer for this series of acids. The most significant change observed in the FTIR data for this series involves the bands for the quinoid and benzenoid units of the polymer. The intensity of these bands change as a function of increasing pH. It has been shown previously that the ratio for the bands is less than one for strong acids and unity for formic acid. In the case of acetic acid (Figure 7a) the ratio of the two bands  $R = 1.1$ , meaning that more quinone units exist in the polymer than the benzenoid units, i.e., that the polymer is more oxidized. The structure of the polymer doped with acetic acid can be represented with the following diagram, where  $\text{Ac}^-$  is the acetate ion.



The difference in the oxidation state for PANI doped with the series of chlorinated carboxylic acids provides the first correlation between the  $pK_a$  of the doping acid and the redox state of the polymer.

Figure 8 shows the values of  $R$  calculated from the FTIR data for two homologous series of acids plotted versus their  $pK_a$  values. A nearly linear trend is clearly observed for the series of aliphatic carboxylic acids (open circles,  $r^2 = 0.97$ ) and chloroacetic acids (filled diamonds,  $r^2 = 0.99$ ). However, their slopes are different. This is a clear indication that the proton interaction is dominating but the nature of the anion also plays an important role in establishing the redox state of the polymer. To our knowledge these plots provide the first direct evidence



**Figure 8.** Correlation between the oxidation state of PANI and the  $pK_a$  of the dopant acid for two homologous series of acids: Aliphatic carboxylic acids (open circles),  $r = 0.97$ , and chloroacetic acids (filled diamonds),  $r = 0.99$ . The ratio of the quinoid and benzenoid structure is obtained from the areas of the bands of aromatic C—C groups at stretching frequencies of 1590 and 1485  $\text{cm}^{-1}$ , respectively.

that the oxidation state of PANI can be predictably adjusted using the  $pK_a$  of the dopant acid.

### Conclusions

This study has shown that there is a fundamental difference between doping of the PANI with a strong and a weak acid. This difference is particularly important for preparation of materials with defined electronic properties for dry applications. The redox state of the polymer, the degree of protonation and the amount of undissociated acid polymer are inter-related parameters. A weak acid forms an internal buffer system which renders the redox state of the polymer stable. Therefore, manipulations such as rinsing the polymer after preparation has little or no effect on its redox state. On the other hand a strong acid is a poorly defined buffer. As its concentration in the polymer changes, e.g., with the rinsing, the redox state of the polymer changes accordingly.

The formic acid solution of PANI is an ideal starting material for any study. The PANI solutions in formic acid can be prepared reproducibly and the exchange for desired doping acid can be readily accomplished by electrochemical cycling *regardless of the relative strength of this acid*. Moreover, the choice of the doping acids within a homologous series allows a rational manipulation of a stable redox state of this material. Despite the nonideal electrochemical appearance of their CVs, PANI materials doped with weak acids are robust and stable.

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