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Electroactivity of Electrochemically Synthesized Poly(Aniline Boronic Acid) as a Function of pH: Role of Self-Doping

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The influence of pH on the electrochemical behavior of electropolymerized, self-doped poly(aniline boronic acid) thin films in the presence of D-fructose has been investigated with voltammetry and potentiometry in phosphate-buffered saline solution. It was found that the complexation of boronic acid with D-fructose and subsequent formation of self-doped polymer extends the electroactivity of poly(aniline boronic acid) to neutral and alkaline media in a manner similar to that of other self-doped polyanilines. However, the electroactivity exhibits more complex pH-dependent behavior, suggesting a transition between species involved in the self-doping process. Results obtained with in situ UV−vis spectroscopy and ex situ FTIR spectroscopy in conjunction with ^{11}B and ^{19}F NMR studies of monomeric species indicate that the self-doped structure of poly(aniline boronic acid) is pH sensitive and that the anionic boronic acid complex involves either fluoride or hydroxide depending on pH.

Introduction

Conducting polymers have been extensively investigated in recent years because of their potential use in applications such as rechargeable batteries, electronic shielding, sensors, and electrochromic display devices. Polyaniline (PANI) is unique among conducting polymers in that it possesses well-behaved electrochemistry, good environmental stability, and electrochroism, in addition to its low cost and ease of preparation.[1] Despite these attractive features, PANI has not been widely used because of its poor solubility in various solvents and its loss of electroactivity in neutral and alkaline solutions. It is generally accepted that PANI has three oxidation states: the fully reduced leucoemeraldine, half-oxidized emeraldine, and fully oxidized pernigraniline form.[2−5] The only electrically conducting form is the emeraldine salt, which is the protonated form of emeraldine base. The emeraldine base form of PANI can be protonated with sufficiently strong acids to emeraldine salt due to the presence of basic sites (amine and imine groups) in the polymer backbone. This is the source of the pH sensitivity of PANI.

Self-doped PANI derivatives present an important class of conducting polymers which exhibit redox activity over a much wider pH range than PANI.[6−11] The source of this behavior is the presence of acidic functional groups along the backbone of the polymer which replace anions typically present in PANI to balance the positive charge associated with the emeraldine salt form of the polymer. Self-doping occurs when the conjugated backbone is sufficiently basic and the acid functionality is sufficiently strong that protonation of the polymer backbone occurs. This intramolecular doping determines many distinctive properties of self-doped PANI that are inherently different from those of the parent PANI. For example, the redox activity of PANI is lost at pH values greater than 3 or 4, but self-doped derivatives are active up to pH 14 in some cases. This behavior extends the usefulness of PANI to a wide range of fields including electrocatalytic conversion of solution species,[12] sensors, and biosensors. In addition to redox activity, self-doped PANI possesses water solubility. In general, PANI is insoluble in aqueous solvents and most common organic solvents; however, solubility is essential to facilitate processing. The presence of functional groups such as sulfonates along the backbone of self-doped PANI greatly improves the solubility.[13] For example, self-doped PANI dissolves in basic aqueous solutions, in contrast to PANI, which exists in an insoluble insulating form when treated with basic aqueous solutions.

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Recently, it has been demonstrated that boronic acid-substituted PANI can be electrochemically polymerized in the presence of fluoride.[14] This breakthrough has opened up the possibility of developing new sensing strategies for fluoride,[14] saccharides[15] and new methods for producing chemically modified PANI[16] using poly(aniline boronic acid) (PABA) as a precursor. In their original work, Fabre et al. suggested that in the presence of fluoride, PABA should be a self-doped polymer.[14] On the basis of their work and our studies involving the interaction between saccharides and PABA, we have been focusing on developing novel approaches for the chemical and electrochemical polymerization of PABA exploiting these interactions.

The complexation of saccharides (as well as alkyl and aromatic diols) with aromatic boronic acids produces a stable ester, where the association constant as well as the relative concentrations of the neutral trigonal ester and the tetrahedral boronate ester are dependent on the pH,[17] electrolyte concentration, and pK_a of the aromatic boronic acid among other factors.[18] Recent work from our laboratory has exploited this chemistry to allow, for the first time, the electropolymerization of a functionalized PANI under neutral conditions.[19] This was achieved through the formation of a self-doped polymer involving the anionic boronic ester complex between 3-aminophenylboronic acid and D-fructose in the presence of fluoride. Subsequently, we extended this chemistry to the chemical polymerization of a soluble, self-doped PABA.[20] In the current work we explore the electrochemical activity and spectroscopic properties of self-doped PABA in the presence of D-fructose and fluoride over a wide pH range (1−12) using various analytical tools.

Experimental Section

Material and Reagents. 3-Aminophenylboronic acid hydrochloride salt (3-APBA) and D-fructose were purchased from Aldrich Chemical Inc. Sodium fluoride and pH 7.4 phosphate-buffered saline stock solution (10×) were purchased from Fisher Scientific. Bulk distilled water was first filtered and ion-exchanged to yield 18.3 MΩ quality water using an EasyPure RF, Barnstead Thermolyne model 7031.

Electropolymerization of PABA. PABA was deposited electrochemically onto glassy carbon electrodes. The monomer solution was prepared in the phosphate-buffered saline stock solution (PBS). The potential was scanned between −0.1 and +1.0 V in an unstirred solution at a scan rate of 100 mV·s^{-1} until the charge under the cathodic peak reached ~0.9 mC·cm^{-2}. The final scan was stopped at a potential of +0.8 V and held at that potential for 10 s. For UV−vis and FTIR characterizations, films were deposited on optically transparent indium-doped tin oxide coated glass (Delta Technologies, Ltd.) in a similar manner.

Characterization. Cyclic voltammetric and potentiometric measurements were performed using a CH Instrument CHI-660 workstation. The first cycle involving PABA was typically variable, but stabilized and remained unchanged in subsequent cycles. A three-electrode cell was used and consisted of a glassy carbon disk (Bioanalytical Systems, 3.0-mm diameter) working electrode, a platinum coil auxiliary electrode, and a Ag/AgCl reference electrode. Open-circuit potential measurements were performed with a PABA modified glassy carbon electrode as a working electrode and Ag/AgCl reference electrode. UV−vis spectra were obtained using an Agilent 8453 spectrophotometer. Infrared spectra were obtained using a Bomem (Hartmann and Braun) FTIR spectrometer. Polymer samples were mixed with KBr powder to prepare pellets for IR measurements.^{11}B NMR and ^{19}F NMR studies were carried out using a Bruker AMX 500 NMR spectrometer. The samples were prepared using 10% D_2O in 10× PBS. Chemical shifts were determined relative to borontrifluoride etherate (^{11}B NMR reference) and hexafluorobenzene (^{19}F NMR reference).

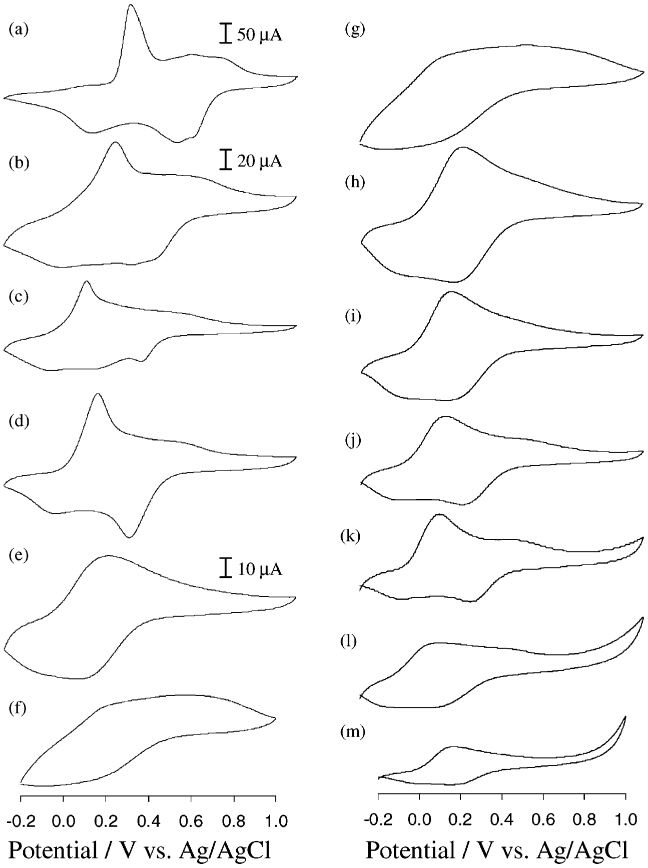

Figure 1. Cyclic voltammograms of PABA film in PBS with 10 M D-fructose and 40 mM NaF as a function of pH: (a) 1.0, (b) 2.5, (c) 3.5, (d) 4.2, (e) 5.5, (f) 6.4, (g) 7.0, (h) 8.0, (i) 9.0, (j) 10.0, (k) 11.0, (l) 12.0, and (m) 13.0.

Results and Discussion

Cyclic Voltammetry. The redox properties of PABA films were studied in electrolyte solution as a function of pH. Figure 1 shows cyclic voltammograms in the pH range of 1 to 13 indicating that PABA films are redox active throughout the entire pH range. At low pH values (1−4), cyclic voltammograms exhibit two sets of redox waves similar to PANI. These waves correspond to conversion of the nonconducting, reduced form into the conducting intermediate oxidized form (leucoemeraldine to emeraldine; $E_{1/2}$ = ~0.2 V vs Ag/AgCl) and subsequently to the nonconducting fully oxidized form (emeraldine to pernigraniline; $E_{1/2}$ = ~0.65 V vs Ag/

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AgCl).[2,21] The cyclic voltammograms are essentially identical to that of the parent PANI with the exception that the two sets of redox waves are more closely spaced as is observed with sulfonated PANI[22] and poly(*o*-toluidine).[23] At pH values greater than 4, only one set of peaks is observed until a neutral pH is reached. This result suggests that the emeraldine form is not stable in this pH range and PABA is converted directly from the leucoemeraldine to the pernigraniline form. In contrast to sulfonated PANI, with increasing pH the single set of waves split again and a well-behaved cyclic voltammogram similar to that obtained in acidic pH is observed in the pH range of 8−11. Interestingly, the magnitude of current observed changes significantly and reversibly as a function of pH. As seen in Figure 1, the current is maximum at pH 1, decreasing gradually with increasing pH up to 5. Above pH 5, the peak current values remain nearly constant.

According to MacDiarmid et al.,[2] the behavior of the redox waves as a function of pH is typical of the emeraldine salt form of PANI; at higher pH values, the individual oxidation and reduction peaks are merged into a single redox couple, this is indicative of emeraldine base form of PANI when little deprotonation and protonation occur during the redox process. In the case of PANI, complete loss of electroactivity is seen at basic pH. In contrast, self-doped forms of PANI are electroactive up to a pH of 12; however, they show only a single redox couple above pH 3.[8,24] The redox chemistry of self-doped PABA is clearly quite different from that of regular and previously reported forms of self-doped PANI, likely due to the pH-dependent nature of the boronic acid group of PABA.

Cyclic voltammograms of PABA films were obtained at various electrolyte solution conditions in PBS in order to determine the role of various species present in the solution and in the polymer on the observed behavior. As seen in Figure 2, at pH 2 the cyclic voltammograms of PABA in the absence and in the presence of fluoride (Figure 2A; i and ii, respectively) exhibit two sets of waves similar to PANI. In contrast, the PABA films are electrochemically inactive at a pH of 10.5 with or without fluoride (Figure 2B; i and ii, respectively). Further, the films are no longer redox active when returned to acidic solutions, suggesting irreversible degradation (over-oxidation) of PABA film in alkaline pH medium. Cyclic voltammograms of PABA film in PBS at a pH of 10.5 with or without fluoride show one broad anodic peak ~0 V which appeared only in the first anodic sweep. The disappearance of the peak in subsequent scans is typical voltammetric behavior of polymer on overoxidation in an aqueous alkaline solution. However, PABA films remain redox active at both pH values, with the addition of D-fructose both in the absence of fluoride (Figure 2A and 2B; iii) and in the presence of fluoride (Figure 2A and 2B; iv). To verify the reversibility and stability of PABA films in the presence of D-fructose and fluoride as a function of pH, cyclic voltammograms were obtained at the higher pH (10.5) followed by the lower (pH 2), and vice versa. The cyclic voltammograms obtained were identical to those obtained with freshly prepared PABA films at pH 2 and 10.5 (Figure 2A and 2B, respectively; iv) regardless of exposure and cycling at different pHs.

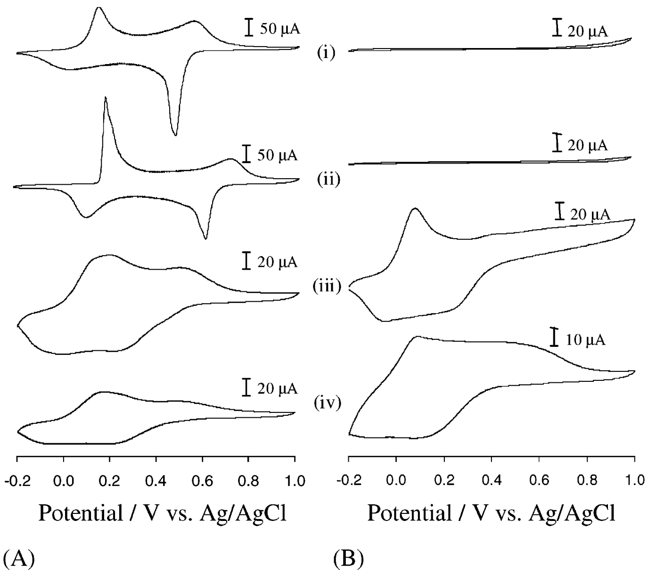

Figure 2. Cyclic voltammograms of PABA film in (i) PBS, (ii) PBS with 40 mM NaF, (iii) PBS with 10 M D-fructose, and (iv) PBS with 10 M D-fructose and 40 mM NaF, at pH (A) 2.0 and (B) 10.5.

NMR Spectroscopy. The above results suggest that the changes in redox mechanism of self-doped PABA as a function of pH and in different electrolyte solution are a result of structural changes in the complexation of boronic acid with D-fructose. To investigate the role of D-fructose, fluoride, and pH on the structure formed with boronic acid, NMR characterization of monomer solutions was carried out at different pH values in the presence of D-fructose, with and without fluoride. Specifically, ^{11}B and ^{19}F NMR were performed to determine the structure of the boron (neutral trigonal versus anionic tetrahedral) and the involvement of fluoride in the complex (free versus complexed fluoride). According to previous studies, the complexation of saccharide with aromatic boronic acid is pH dependent and can result in a neutral or anionic ester, depending on solution conditions.[18] Addition of fluoride can be used to enhance the complexation of saccharides under less basic conditions and facilitates the formation of an anionic ester.[25] Springsteen et al. have shown that the ^{11}B chemical shift of a tetrahedral boronate is approximately 20 ppm upfield from the trigonal boronic acid signal (borontrifluoride etherate reference in this case).[18] Because the rate of exchange between trigonal and tetrahedral boronate is fast on the NMR time-scale, a single resonance is observed with a chemical shift that is a function of the fraction of tetrahedral boron present. Similarly, ^{19}F is a sensitive nucleus which yields sharp signals and has a wide chemical shift range for the exchange reaction between boronic acid and fluoride.[26,27] Table 1 shows chemical shifts observed for ^{11}B and ^{19}F

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Table 1. ^{11}B and ^{19}F NMR Chemical Shifts of 3-Aminophenylboronicacid (3-APBA) Adducts

solution conditions	pH	chemical shift (ppm)[a] ^{11}B	chemical shift (ppm)[a] ^{19}F
40 mM 3-APBA + 40 mM NaF + 10 M fructose	1.4	3.7	−22.3
40 mM 3-APBA + 10 M fructose	1.4	29.2	
40 mM 3-APBA + 40 mM NaF + 10 M fructose	6.4	6.4	−20.3 −38.6
40 mM 3-APBA + 10 M fructose	6.4	6.4	
40 mM 3-APBA + 40 mM NaF + 10 M fructose	10.0	4.1	−40.1
40 mM 3-APBA + 10 M fructose	10.0	4.1	

[a] Shifts measured relative to reference borontrifluoride etherate and hexafluorobenzene.

under solution conditions similar to those in Figures 1 and 2 and similar to those used during the electrochemical polymerization of the monomer. Under acidic conditions in the presence of fluoride, boronic acid is tetrahedral. ^{19}F NMR of same solution suggests the involvement of fluoride in tetrahedral complex. In the absence of fluoride, a 25.5 ppm downfield shift in the boron resonance suggests a transition to the trigonal form of boronic acid, further supporting the involvement of fluoride in the complex. At near-neutral and alkaline pH solutions both with and without fluoride, the boron chemical shifts indicate that the monomer is converted to a tetrahedral form. ^{19}F NMR of the same solutions indicates the presence of both free and complexed fluoride near neutral pH suggesting partial involvement of fluoride in complexation at pH 6.4. However, at alkaline pH, the chemical shifts indicate that fluoride is not involved in complexation. Previous studies have shown that under basic conditions, the D-fructose complex with boronic acid involves three hydroxyl groups of β-D-fructofuranose moiety at C-2, C-3, and C-6 position.[28,29] These results suggest that the polymer is self-doped throughout this pH range and that: (i) under acidic conditions, the polymer is self-doped with the boronate anion present in (**1**); (ii) under neutral conditions there is a mixture of the anions present in (**1**) and(**2**); and (iii) under basic conditions, the polymer contains the anion present in (**2**).

In addition to the structural implications for the self-doped polymer as a function of pH, these results shed light on the structure of the monomer involved in the electropolymerization process at various pH conditions. According to the ^{11}B and ^{19}F NMR results, under the polymerization conditions used in this work (third entry in Table 1) the formation of tetrahedral boronate ester involves fluoride (**1**) as well as hydroxide (**2**) as shown in Scheme 1. Because polymerization does not occur at elevated pH where only **2** is present, nor does it occur at neutral pH in the absence of fluoride, **1** is most likely the species involved in polymerization under these conditions. Although the synthesis of the self-doped polymer occurs only through the formation of poly(**1**), once formed, the conversion of poly(**1**) to poly(**2**) extends the electroactivity of the polymer to neutral and alkaline pH conditions. The transition in the redox behavior of the polymer near neutral pH values (see Figure 1f and g) is in turn likely due to transition from poly(**1**) to poly(**2**) and the mixture of anionic species that result. The role of the mixed species present clearly impacts the charge compensation process that occurs during redox switching.

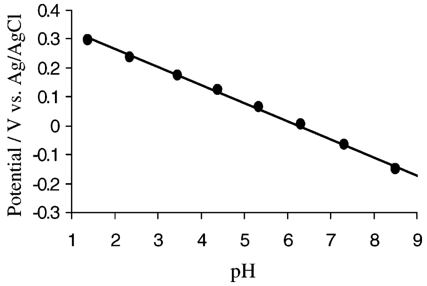
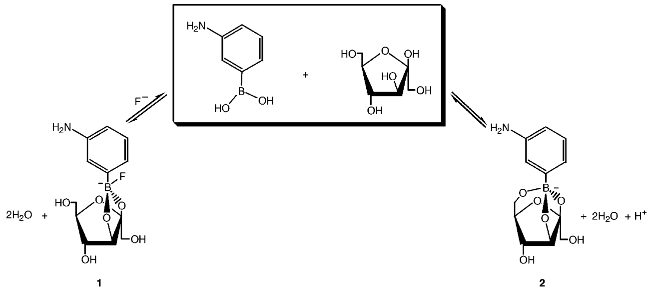


Figure 3. Potential of PABA film in PBS with 40 mM NaF and 10 M D-fructose as a function of pH. Slope = −58 mV·pH^{-1}.

Scheme 1



Open-Circuit Potential Measurement. Regardless of the nature of the anionic species involved in the doping process, the redox process is expected to remain coupled to proton transfer as is the case with the parent PANI. To verify the pH sensitivity, open-circuit potential measurements were made with PABA-modified glassy carbon electrodes. The pH dependence of the open-circuit potential is shown in Figure 3 to be linear throughout the entire pH range with a near Nernstian slope of 58 mV·pH^{-1}. This is identical to the behavior reported for PANI[30−32] where one proton per electron is transferred during the conversion of leucoemeraldine to pernigraniline.

Spectroelectrochemistry. To study the electrochromic behavior of the PABA film associated with the redox activity, in situ UV−vis measurements were made while the potential of a PABA film was stepped to potentials

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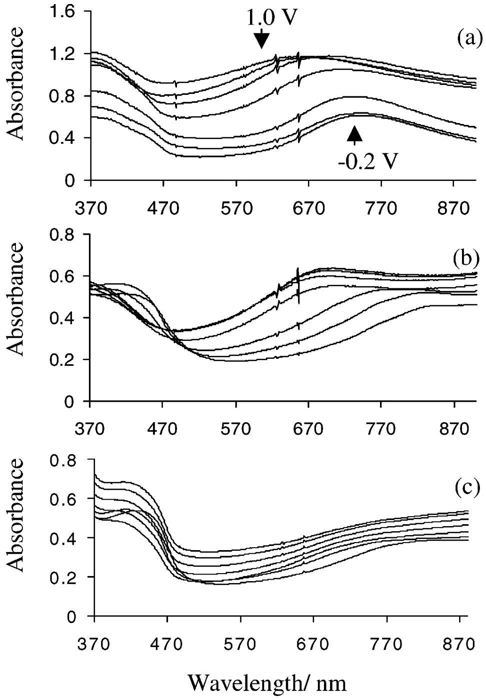

Figure 4. UV-vis spectra of PABA film in PBS with 10 M D-fructose and 40 mM NaF at potentials from −0.2 to 1.0 V with the difference of 0.2 V as a function of pH: (a) 1.3, (b) 6.4, and (c) 9.0.

between −0.2 to 1.0 V. The step technique was used to allow equilibrium to be established at each potential throughout the range of potentials. In acidic solution, potential steps of 60−120 s were sufficient to equilibrate (i.e., current to approach zero). However, at neutral pH, potential steps of ~400 s were required to reach equilibrium. This is likely due to an increase in resistance of PABA under these conditions, which has been confirmed with bulk resistance measurements and is consistent with the apparent ohmic induced broadening of the peaks in Figure 1f and 1g. After allowing equilibration, the spectra were obtained throughout the potential range and as a function of pH.

The spectral changes of PABA films as a function of potential are shown in Figure 4 and are consistent with previous studies of PANI in acidic solution.[33−36] In the potential window of −0.2 to 1.0 V, spectral changes in the range of 400−450 nm and 650−800 nm were observed. According to literature data, the absorptions of 400−450 and 750−800 nm are caused by localized and delocalized cation-radicals, respectively.[37] The presence of these polaron and bipolaron bands in Figure 4a−c confirms that PABA is in the self-doped state throughout the entire pH range. During oxidation, the band at 750−800 nm is displaced to 600−650 nm where the quinoneimine form of PANI absorbs, indicating that the transitions of leucoemeraldine to emeraldine and emeraldine to pernigraniline are observed spectroscopically in addition to electrochemically. In the case of PANI, the polaron band at ~400−450 nm is distinct only at low pH values. At pH < 1, the bipolaron band at 780−800 nm shows a strong blue shift with increasing potentials. However, with increasing pH, the extent of blue shift of the band at 780 nm decreased gradually and the band disappeared even at high oxidation potentials. A new band at ~600 nm begins to appear at pH > 4.[38] At higher pH values, the band near 600 nm shifts to shorter wavelengths, and an increase in absorption near 330 nm is observed.[33−36] The disappearance of the polaron and bipolaron bands and the evolution of a new band at ~600 nm with increasing pH are indicative of the existence of a quinoid structure. In contrast, the spectra in Figure 4 for all pH values are similar to that observed for PANI at low pHs with the exception of a decrease in the intensity observed for PABA. It should be noted that absorbance maxima at ~400 and 780 nm, which are characteristic of emeraldine salt form, are observed throughout the pH range at lower potentials. These results suggest that the emeraldine salt form of self-doped PABA is not very susceptible to pH changes.

The distinct decrease in intensity of absorption with increase in pH of solution may be due to a decrease in the number of redox centers, which is consistent with the change in the magnitude of current observed in cyclic voltammograms of PABA observed in Figure 1. This change in the magnitude of absorption and redox current is reversible when returned to acidic solution. The changes in the absorbance also correspond to the transitions between leucoemeraldine to emeraldine and emeraldine to pernigraniline form. It is clear that for a high degree of protonation the changes in the absorbance correspond to the charge transfer within the film for all transitions. At higher pH values, due to slower charge transfer, transition from leucoemeraldine to pernigraniline is suppressed to some extent according to both spectroscopic and electrochemical measurements.

FTIR Spectroscopy. To obtain additional information about the structural changes that occur in PABA films as a function of pH, FTIR spectra were obtained. The IR spectrum of PABA emeraldine salt shows the characteristic bands at 1597, 1462, 1353, 1230, 1140, 921, 812, and 780 cm^{-1} (figure not shown).[20] A band at 1063 cm^{-1} is attributed to C−O stretching and bending modes in the D-fructose moiety. These bands are all present in FTIR spectra of PABA films cycled in PBS with 40 mM NaF and 10 M D-fructose in the pH range of 1−9 (figure not shown). The ratio of the relative intensities of quinoid to benzenoid ring modes ($I_{\approx 1597}/I_{\approx 1462}$) is ~1.5 in the pH range of 1−9. These results clearly suggest that the percentage of imine units is higher than that of amine units, and the PABA is therefore in its conducting self-doped form throughout the pH range.

Conclusions

The studies described in this work demonstrate that the generation of self-doped PABA involves the formation of an anionic boronic ester complex with D-fructose extending the electroactivity of PABA to neutral and

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alkaline conditions. Unique changes in the redox behavior of PABA as a function of pH are due to a structure transition of the anionic complex covalently attached to the backbone of the polymer. Under acidic conditions fluoride is associated with the complex, whereas under basic conditions the anionic species is due to complexation with D-fructose only. The redox behavior observed for self-doped PABA is significantly different than that reported for other forms of self-doped PANI. For example, the emeraldine salt form of the polymer is stable to pH values approaching 12. Other properties characteristic of PANI such as the pH dependence of open-circuit potentiometric measurements and electrochromic behavior are maintained.

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