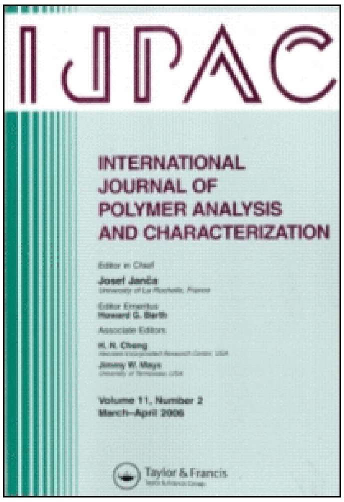

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Investigation of the Dopant Exchange Behavior of Polyaniline Hydrochloride Films upon Addition of Sulfuric Acid

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Abstract: The effect of sulfuric acid and its concentration on polyaniline (PANI) hydrochloride film was studied. The PANI hydrochloride film was prepared using the chemical oxidation of aniline and was monitored using the quartz crystal microbalance (QCM) technique. QCM was also used to determine the dopant weight fraction (DWF) and the exchange behavior of PANI films. Upon the addition of sulfuric acid, exchange of the chloride ion dopants from the polymer chains with the sulfate dopants was observed. The extent of doping was found to depend on the concentration of sulfuric acid. The UV-vis absorption spectra and the conductivity of the in situ PANI films deposited onto glass supports immersed in the polymerization medium were measured.

Keywords: Conducting polymer; Dopant exchange; Polyaniline film; Quartz crystal microbalance

INTRODUCTION

The phenomenal growth in the applications of polymers has resulted in the synthesis of myriad macromolecules with various properties. These macromolecules may be classified as ion-exchange polymers, redox polymers, inert neutral polymers, and electrically conducting polymers.

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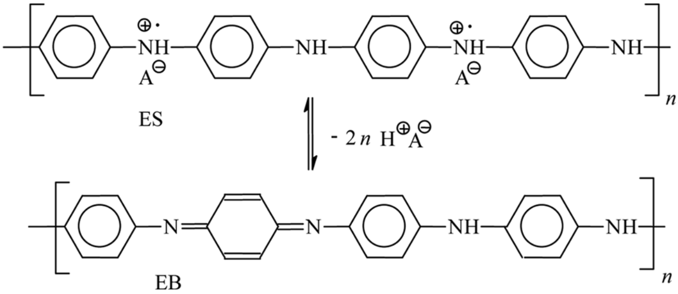
In the past few years there has been a growing awareness of the need to produce polymers with new properties.[1]

Polyaniline (PANI) is a conducting polymer whose properties are not only dependent on its oxidation state but also on its protonation state.[2] It exhibits conductivity switching during acid-base treatment. The pristine PANI doped with hydrochloride is de-doped by stirring in aqueous ammonia solution to produce the emeraldine base form (EB) of PANI (Scheme 1).[3] The EB form is doped again by reacting with protic acid to produce the doped conductive PANI, emeraldine salt (ES), with a concomitant increase in conductivity.[4] This way of producing conducting PANI by doping EB with protic acid provided PANI having more uniform protonation.

PANI films can be fabricated using EB solution and converted into conducting ES by contacting vapor of acids or immersing into solution of various acids,[5–7] although difficulties in penetration of acids inside films or coatings may result in inhomogeneous distribution of dopants in the film[8] or incomplete doping. Stejskal et al.[9] have reported that the solid-state doping of EB powder could be achieved by direct blending of EB powder with solid organic acids. These kinds of protonic acid doping reactions of EB are basically simple acid-base reactions as the most basic imine nitrogens in EB are protonated first and ES, the conductive PANI, is produced after internal redox reaction and charge separation process (Scheme 1).[4] ES is a salt with the positive charges delocalized over the polymer chain balanced with negative charges coming from counter-ions. Hence, the polymer may behave as an ion-exchange material. This indeed has been demonstrated in detail for polypyrrole by Burgmayer and Murray.[10,11] A similar behavior can be expected for PANI.[12] Studies of PANI films using voltammetric, quartz crystal microbalance (QCM), and probe beam deflection techniques revealed that protons and anions are exchanged during the oxidation process.[13–16]



Scheme 1. Protonated (doped) PANI, emeraldine salt (ES), is deprotonated (de-doped) by treatment with an alkali to PANI, emeraldine base (EB).

De-doping and re-doping processes have been assumed to accompany ion migration out of or into the polymer film. Therefore, the mass changes in PANI films resulting from these processes provide direct information concerning the dopant weight fraction (DWF). Piezoelectric QCM was applied to determine the DWF of PANI film deposited onto the surface of the quartz crystal.[17] This method also has provided the possibility to follow in situ small mass changes induced by the interaction between a dopant solution and PANI.[18,19]

Rao et al.[20] have studied the effect of sulfuric acid on the properties of PANI hydrochloride and its base powders. These powders were treated with different sulfuric acid concentrations. They stated that the sulfate anions were incorporated into the PANI chains. However, it has not been mentioned whether (1) that incorporation takes place in addition to the initially present chloride dopants or (2) the incorporation involved the exchange of chloride dopants with sulfate dopant. Therefore, the present study aims at differentiation between these two possibilities using the QCM technique. The effect of sulfuric acid on PANI hydrochloride films prepared by the chemical oxidation of aniline was studied. Also, this work aims at the investigation of the effect of sulfuric acid on the UV-vis absorption spectra and the conductivity of the PANI hydrochloride and EB films.

EXPERIMENTAL SECTION

Chemicals

Aniline (Adwic, Egypt) was freshly distilled twice under atmospheric pressure. Ammonium peroxydisulfate, APS (Winlab, Market Harborough, UK), was used without further purification. Hydrochloric and sulfuric acids were from Adwic (Egypt) and were used as received. Freshly distilled water was used to prepare all aqueous solutions.

Experimental Procedures and Arrangement

The experimental arrangement has been described elsewhere.[21–23] A 5 MHz cut quartz crystal was used. The resonance frequency of the crystal was determined by using the crystal as the frequency-determining element of an electronic oscillator, the measurements being taken using a GW frequency counter, model GFC-8055 G. The mass per unit area of PANI film, m' (g/cm^2), grown onto the gold electrode on the crystal surface was determined from the change in its resonance frequency. The frequency decreased linearly with increasing mass deposited on the electrode. The relation between the frequency change Δf (Hz) and m' is well established from the work of Sauerbrey[24] and is given by

$$\Delta f = -(2f_o^2/\sqrt{\rho_Q \mu_Q})m' \qquad (1)$$

where f_o (Hz) is the natural frequency of the quartz crystal (unloaded resonator frequency), ρ_Q is the quartz density with the value 2.649 g/cm^3, and μ_Q is the shear modulus with the value 2.947×10^{11} dyne/cm^2.

In a typical example of solution preparation for PANI film, 0.1 M APS solution in 50 mL of 0.1 M HCl was added to 0.08 M aniline in 50 mL of 0.1 M HCl. The APS/aniline molar ratio after mixing was 1.25. The ES film formed during the polymerization was rinsed with 0.1 M HCl. Then it was exposed to 0.1 M H_2SO_4 for approximately 15 min. The de-doping process was made by exposure of the ES film to 0.1 M ammonia solution to give the EB film. The EB film was then re-doped by exposing the film to 0.1 M H_2SO_4 to produce another ES film. The mass loss or gain due to the de-doping and re-doping processes was determined by calculating the increase or decrease, respectively, in the frequency of the PANI-coated quartz crystal.

The above experiment was repeated for different films obtained from the solutions of 0.1 M APS in 50 mL of 0.1 M HCl and 0.08 M aniline in 50 mL of 0.1 M HCl. The mass changes due to the exposures of the ES films to different sulfuric acid concentrations (0.3, 0.5, 0.7, 1, 2, 3, and 4 M), the de-doping processes using 0.1 M ammonia solution, and the re-doping processes by 0.3, 0.5, 0.7, 1, 2, 3, and 4 M H_2SO_4 were determined by calculating the change in the frequency of the PANI-coated quartz crystal as described before. The time dependence of frequency was recorded at 26°±1°C.

In situ PANI films were also obtained during the polymerization of aniline on rectangular glass supports. These supports were stuck onto adhesive tape and introduced into the reaction vessel before the polymerization started. Once the reactants were introduced to the vessel, the film grew simultaneously onto both the gold electrode of the QCM and the glass support. After the polymerization, these supports were removed from the reaction mixture and rinsed with 0.1 M HCl and finally dried in an oven at 60°C for 3 h. After that, they were dipped in a specific sulfuric acid solution. Then they were immersed in 0.1 M ammonia solution to prepare EB films. Finally, EB films were dipped in the previously used sulfuric acid solution. The time of exposure was approximately 15 min. The concentrations of sulfuric acid solutions were similar to those used in the QCM experiments. The ES or EB powders at all stages were collected from the reaction media by filtration and rinsed with sulfuric acid or ammonia, respectively, and finally dried.

Conductivity Measurement of PANI Films

The glass supports coated with PANI films were used to measure conductivity. A Simpson 260 VOM multimeter and a Keithley 617 Programmable Electrometer were used in the four-probe circuit. The contacts in the sample holder were made of gold. The conductivity of the samples was measured at room temperature. The film thickness can be determined from the optical absorption at 345 nm according to an earlier work.[25]

UV-Vis Absorption Measurement

The UV-vis absorption spectra for the PANI films deposited onto glass supports were measured using a Shimadzu UV-2101 DC Spectrophotometer. Uncoated glass supports were used as a reference.

RESULTS AND DISCUSSION

QCM Investigation for Dopant Exchange in PANI Films

Ayad et al.[17] have recently used the QCM technique to determine the DWF of PANI film deposited onto the surface of the quartz crystal during the de-doping and re-doping processes for PANI film prepared in 1 M sulfuric acid solution.

The plot of the frequency changes due to PANI film deposition onto the gold electrode of the QCM as a function of polymerization time is shown in Figure 1. This is for a solution of 0.1 M APS in 50 mL of 0.1 M HCl and 0.08 M aniline in 50 mL of 0.1 M HCl. The APS/aniline molar ratio after mixing was 1.25. It is expected that there are three regions. Initially, the first deposits of PANI must nucleate on the gold surface and give rise to a rather slow deposition rate. Following this induction period, the rate of deposition is observed to increase, as evidenced by the increasing magnitude of the slope, and then attains a steady state as the deposition finishes. This is due to the depletion of the monomer.

The polymerization in the depletion periods ends with the formation of in situ PANI hydrochloride film, which is denoted as ES(1). These films are in situ doped with chloride anions due to the presence of hydrochloric acid in the polymerization medium. Also, there is a small contribution from the sulfate dopant, which arises from the reduction of APS. Based on the knowledge that the molecular formula for 50% intrinsically oxidized ES film after protonation in HCl is $C_{24}H_{18}N_4(HCl)_2$,[26] the chloride dopant content would be 16.7 wt.%.

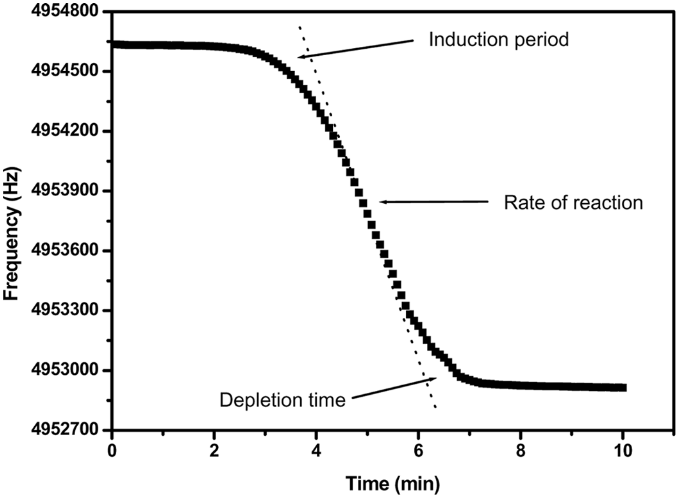


Figure 1. Time dependence of quartz oscillation frequency during PANI film formation for the oxidation of 0.08 M aniline with 0.1 M APS in 1.0 M H_2SO_4.

It can be seen from Figure 2 that if the initial frequency at zero time of polymerization is f_o and the final frequency at the end of polymerization is $f_{ES(1)}$, then the frequency change corresponding to the deposition

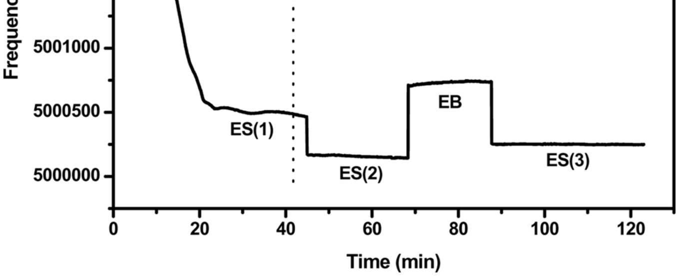


Figure 2. Time dependence of quartz oscillation frequency during PANI film formation, the exposure to 0.1 M H_2SO_4, and the successive de-doping and re-doping of PANI film by successive additions of 0.1 M ammonia solution and 0.1 M H_2SO_4, respectively.

of PANI hydrochloride film would be $\Delta f_{(1)} = f_o - f_{ES(1)}$. The frequency difference $\Delta f_{(1)}$ was calculated as 2263 Hz.

Figure 2 (stage II) shows the frequency changes due to the successive exposure of the ES(1) film to 0.1 M H_2SO_4, 0.1 M ammonia, and 0.1 M H_2SO_4. First, the ES(1) film was exposed to 0.1 M H_2SO_4 to give ES(2) film. The mass of the film increased as evidenced from the decrease in frequency. The frequency change due to this mass gain would be $\Delta f_{(2)} = f_{ES(1)} - f_{ES(2)}$, and it equals 337 Hz. The frequency change at the end of this latter process, $\Delta f_{(3)} = f_o - f_{ES(2)}$, was calculated, and it corresponds to the mass of ES(2) film (2600 Hz). Second, the ES(2) film was de-doped using 0.1 M ammonia to give EB film. Since we are dealing with PANI film of relatively small thickness of tens or hundreds of nanometers the de-doping process occurs immediately, and the weight loss was recorded by measuring the decrease in the frequency of the quartz crystal. The protons and the dopant counter-ions, i.e., the acid molecules, were completely removed during the de-doping process. As can be seen, there is a steady state of frequency after the de-doping with ammonia solution, indicating the completion of the de-doping process. The frequency change due to the mass loss would be $\Delta f_{(4)} = f_{EB} - f_{ES(2)}$, and it equals 569 Hz. The percentage of the DWF during the de-doping process can be calculated from the ratio of the frequency change due to de-doping process to the frequency change due to ES(2) film formation $= (f_{EB} - f_{ES(2)})/\Delta f_{(3)} \times 100 = 569/2600 \times 100 = 21.88$ wt.%.

Third, the re-doping of the EB film to give PANI sulfate film (ES(3)) was made by exposing the EB film to 0.1 M H_2SO_4 solution. With $f_{ES(3)}$ as the frequency of ES(3) film, the frequency change, $\Delta f_{(5)} = f_o - f_{ES(3)}$, at the end of the re-doping process was calculated, and it corresponds to the mass of ES(3) film (2522 Hz). The frequency change due to the re-doping (mass gain) is $\Delta f_{(6)} = f_{EB} - f_{ES(3)}$ and it equals 491 Hz. Consequently, the percentage of the DWF during the re-doping process is $491/2522 \times 100 = 19.47$ wt.%.

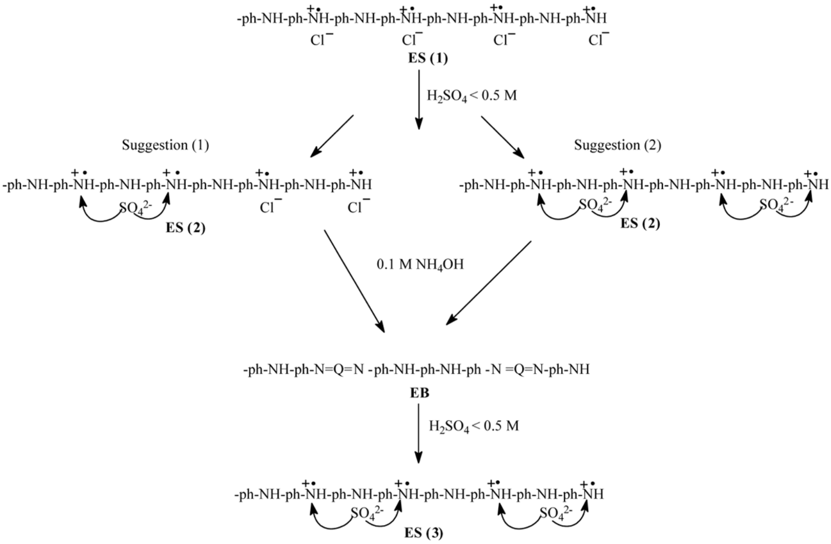
The above experiment was repeated and the initial PANI hydrochloride films (ES(1)) were exposed to 0.3, 0.5, 0.7, 1, 2, 3, or 4 M H_2SO_4 solutions instead of 0.1 M H_2SO_4 to give ES(2) films. This was followed by de-doping the ES(2) films with 0.1 M ammonia solution to obtain the corresponding EB films. The latter films were re-doped with 0.3, 0.5, 0.7, 1, 2, 3, or 4 M H_2SO_4 to give the corresponding ES(3) films. The mass gains and losses were calculated in a way similar to the previous experiments in which 0.1 M H_2SO_4 was used. These calculations are given in Table I.

The QCM is a useful tool for determining the direction and magnitude of mass changes in polymer films. The frequency change allows identification of the mass changes on the PANI film; see Figure 2 (stage II). It can be seen that there are three separate processes occurring during

Table I. Percentage of the DWF due to the exposure of the ES film to 0.1, 0.3, 0.5, 0.7, 1, 2, 3, and 4 M H_2SO_4, de-doping with 0.1 M ammonia solution, and re-doping with 0.1, 0.3, 0.5, 0.7, 1, 2, 3, and 4 M H_2SO_4

Re-doping $DWF = \frac{\Delta f_{(6)}}{\Delta f_{(5)}} \times 100\%$	De-doping $DWF = \frac{\Delta f_{(4)}}{\Delta f_{(3)}} \times 100\%$	$[H_2SO_4]$ mol/L
19.47	21.88	0.1
19.24	21.10	0.3
28.99	27.29	0.5
30.33	27.89	0.7
34.48	34.48	1
35.94	33.77	2
35.37	32.48	3
35.67	34.28	4

the film exposure to 0.1 M H_2SO_4, 0.1 M ammonia, and 0.1 M H_2SO_4 solutions, respectively. The first process involved a mass gain. We suppose that this mass gain is due to either (1) the incorporation of sulfate anions into the PANI chains during the dipping of ES(1) film in 0.1 M H_2SO_4, in addition to the initial chloride and sulfate dopant anions obtained during the polymerization (suggestion (1) in Scheme 2), or (2) the exchange of the initial chloride-anion dopant with the sulfate-anions obtained from the dipping of ES(1) film in 0.1 M H_2SO_4, (suggestion (2)



Scheme 2. Effect of sulfuric acid <0.5 M on ES(1) and EB films.

in Scheme 2). To differentiate between these two suggestions, the ES(1) film was subjected to the second process (de-doping) and the third process (re-doping). The percentage of DWF determined from the de-doping and re-doping processes could indicate the possibility of only one of the previous two suggestions. The DWF percentages of the de-doping and re-doping processes were calculated and they equal 21.88 wt.% and 19.47 wt.%, respectively. These values are approximately close. A similar observation can be seen from Table I at different concentrations of sulfuric acid. It can be concluded that the exposure of the ES(1) film (PANI hydrochloride) to sulfuric acid involved chloride anion migrations and their substitution with sulfate anions to produce ES(2) film (PANI sulfate) according to suggestion (2) in Scheme 2. This is in contrast to the conclusion obtained by Rao et al.[20] who mentioned that when PANI hydrochloride powder was dipped in sulfuric acid solution the sulfate anions as dopants were incorporated into the PANI hydrochloride chains (suggestion (1) in Scheme 2). Also, they stated that 0.1 M H_2SO_4 does not cause any doping for the EB powder. In contrast, our results showed that the treatment of the EB film with 0.1 M H_2SO_4 increases the mass of the film, which indicates that doping occurred. This is possibly because of the high sensitivity of the QCM technique to record any small mass changes.

It can be seen from Table I that when the ES(1) film is treated with 0.1 and 0.3 M H_2SO_4, the values of DWF obtained from the de-doping and re-doping processes are in the range 19.24–21.88 wt.%. These values are consistent with those obtained in our previous studies, 20–22 wt.%.[17] It can be concluded that the sulfate counter-anions using sulfuric acid solutions <0.5 M are present in the PANI films as $\frac{1}{2}SO_4^{2-}$ (Scheme 1, $A^- = \frac{1}{2}SO_4^{2-}$ and Scheme 2). When the concentration of sulfuric acid increases, i.e., >0.5 up to 4 M, the percentage of the DWF obtained from the de-doping and re-doping processes increases and the sulfate counter-anions ($\frac{1}{2}SO_4^{2-}$) present in PANI film change to hydrogen sulfate anions (Scheme 1, $A^- = HSO_4^-$). This is consistent with previous results.[27,28] In this latter case, suggestion (2) is also valid.

Conductivity Measurement

Conductivity was measured for in situ PANI films deposited onto glass supports (Table II). It can be seen that all the ES(1) films that represent PANI hydrochloride have average conductivity equal to $1.20 \pm 0.15\ S\,cm^{-1}$. However, ES(2) films, which were produced on dipping the ES(1) films in different concentrations of sulfuric acid, have a conductivity similar to that of ES(1) films except the films dipped in sulfuric acid of concentrations of 3 and 4 M. At these latter concentrations, a higher conductivity

Table II. Conductivity of PANI films

σ ES(3) (S cm^{-1})	σ ES(2) (S cm^{-1})	σ ES(1) (S cm^{-1})	[H_2SO_4] mol/L
0.62	1.27	1.08	0.1
0.71	1.00	0.98	0.3
0.88	1.31	1.181	0.5
0.68	1.07	0.99	0.7
3.36	0.73	1.51	1
2.29	1.77	1.2	2
9.1	5.454	1.42	3
12.4	6.73	1.27	4

was obtained, 5.5–6.7 S cm^{-1}. In addition, the conductivity of ES(3) films produced from re-doping of the EB films with different concentrations of sulfuric acid is shown in Figure 3. The films have conductivity approximately similar to that of ES(1) and ES(2) films at concentrations of sulfuric acid <1 M. At higher concentrations of sulfuric acid, higher conductivities (3.3–12.4 S cm^{-1}) were obtained. The increase of conductivity is due to the conformational changes in the PANI chains during the protonation-deprotonation cycle. Previous work has described the conformation of PANI chains as either tight coils or expanded coils.[29] It has been found that the conductivity of doped PANI in an expanded

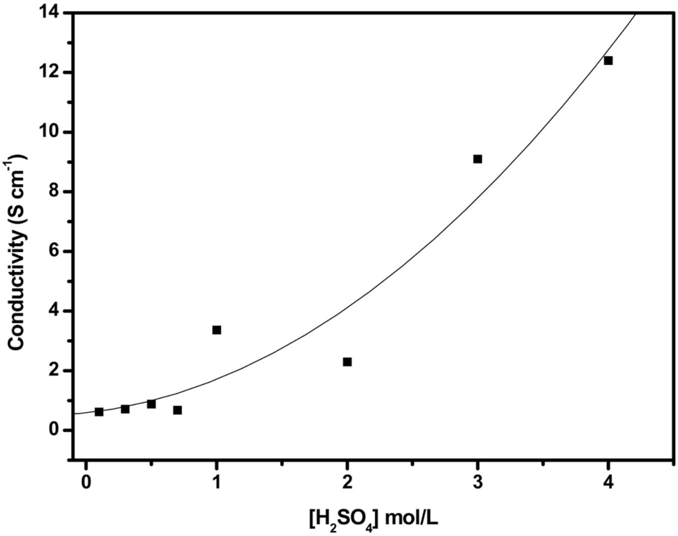


Figure 3. Conductivity of ES(3) films at different concentrations of sulfuric acid.

coil conformation is higher than that of doped PANI in a tight coil conformation.[30,31]

It can be concluded that PANI salt films prepared by re-doping EB film with sulfuric acid >1 M give higher conductivity than the pristine PANI hydrochloride films (ES(1)) and also higher than the PANI salt films treated with sulfuric acid (ES(2)).

UV-Vis Absorption Spectra Measurement

The in situ PANI films deposited onto glass support were treated with ammonium sulfate and sulfuric acid solutions to obtain ES(1), ES(2), and ES(3) films by procedures similar to those for the in situ PANI films deposited onto the gold electrode of the quartz crystals. The UV-vis absorption spectra of these films were measured and are shown in Figure 4. The spectra of EB film exhibit the presence of two absorptions at 320 and 615 nm. The absorption at 320 nm corresponds to the π-π^* transition of the benzenoid rings, while the absorption at 615 nm can be assigned to the molecular exciton associated with the quinone diimine structure.[32] The ES(1), ES(2), and ES(3) films' spectra have nearly the same absorptions with a similar absorbance (except for marginal

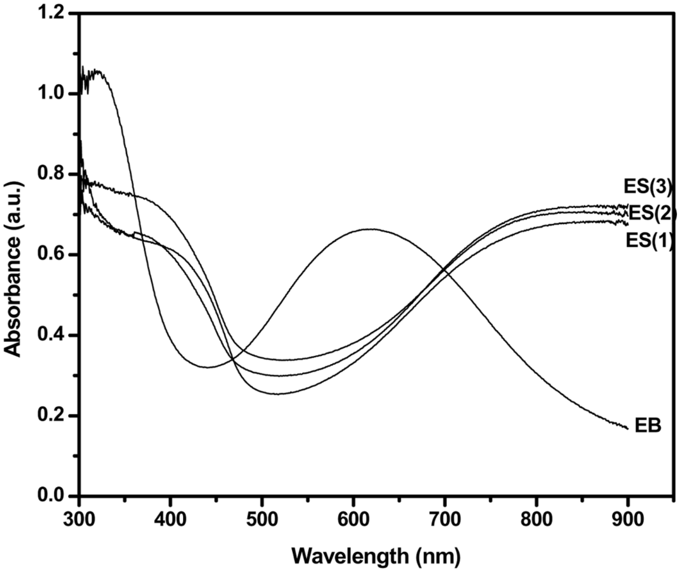


Figure 4. UV-vis absorption spectra for PANI films deposited onto glass supports: ES(1), ES(2), EB, and ES(3).

differences). There are three absorptions bands at 320 nm, 400 nm (390 nm in the curve of ES(2)), and an extended absorption tail after 800 nm. The absorption at 320 nm corresponds to the π-π^* transition of the benzenoid rings, while the absorption at 400 nm (or 390 nm in the curve of ES(2)) can be assigned to the localized polarons that are characteristic of the protonated PANI. The extended absorption tail after 800 nm represents the conducting ES phase of the polymer.[33] It can be concluded that PANI hydrochloride film treated with different concentrations of sulfuric acid shows UV-vis spectral behavior similar to that of the EB with sulfuric acid treatment.

CONCLUSIONS

The QCM technique has successfully been used to monitor the dopant exchange behavior of PANI hydrochloride films upon the addition of sulfuric acid. Whenever the PANI hydrochloride films were treated with different concentrations of sulfuric acid, the chloride anions were substituted with sulfate anions. The values of DWF obtained from the de-doping are in close agreement with the values of DWF obtained from the re-doping of the EB films. In the protonation in PANI in sulfuric acid <0.5 M, one molecule of acid is associated with two imine sites in PANI, and PANI thus has sulfate counter-ions. In more concentrated (0.5–1.0 M) sulfuric acid, each of the imine nitrogens in PANI is protonated with a single molecule of sulfuric acid and the counter-ions are hydrogen sulfate anions.

The PANI salt films prepared by re-doping of EB films with sulfuric acid give higher conductivity than the pristine PANI hydrochloride films. However, the UV-vis spectra show that the structures of PANI hydrochloride, PANI sulfate, and EB treated with sulfuric acid are similar.

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