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Water-Soluble Poly(aniline-*co*-*o*-anthranilic acid) Copolymers

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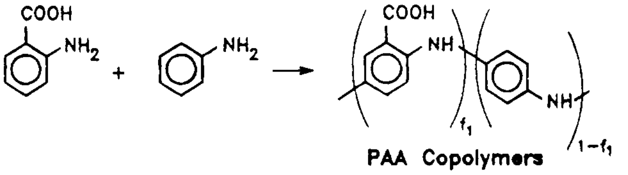
ABSTRACT: Poly(aniline-*co*-*o*-anthranilic acid (PAA) copolymers which are soluble in aqueous alkaline solutions and in some organic solvents were obtained from the chemical polymerization of aniline and *o*-anthranilic acid. The copolymers have MWs ranging from 84K to 126K depending on the composition. The copolymers are recovered in the oxidized state and have a strong EPR signal. The FTIR and UV−visible spectra indicated that the anthranilic acid groups restrict the π-conjugation along the polymer chain. The electrical conductivity of the PAA copolymers decreases dramatically along the series from the polyaniline value of 5.2 S/cm to the poly(*o*-anthranilic acid) value of 10^{-8} S/cm. Films of the PAA copolymers on a platinum foil can be oxidized and reduced at potentials between 0.0 and 1.0 V vs the Ag/AgCl reference electrode when immersed in 1.2 M HCl. The waves in the voltammogram for the stepwise oxidation of the polymer which are normally observed with polyaniline become merged into a single broad wave with the incorporation of the anthranilic acid. The films exhibited multiple color changes from clear yellow to green to dark brown during the redox process. Poly(*o*-anthranilic acid) itself is fairly inactive, revealing little or no electrical conductivity and electroactivity.

Introduction

Conducting polymers with a polyaromatic backbone have received a great deal of research attention in the last 15 years, e.g., polypyrrole,[1] polythiophene,[2] polyphenylene,[3] polyaniline,[4] etc. In particular, polyaniline has been extensively studied for the possible use in commercial applications related to rechargeable batteries,[5] electrochromic windows,[6] biosensors,[7] and antistatic materials,[8] but like the other polymers in this class, it is severely limited by its intractable and nonprocessable nature. The nonconductive form of substituted polyanilines (with alkyl, alkoxy, and halide substituents) which is soluble in several common aprotic organic solvents has been used to circumvent this limitation.[9,11] These materials can be processed in the nonconducting form and then converted to the conducting form when in their final physical configuration. These substituted polymers retain the electrochemical and electrochromic properties but have much lower electrical conductivities (10^{-3}−10^{-7} S/cm) than the parent polyaniline polymer.

From a practical standpoint, polyanilines which are soluble in aqueous solutions are particularly attractive because they can be processed in water, thus avoiding the environmental concerns associated with the use of organic solvents. It has been shown that polyanilines with sulfonic acid groups on the benzene rings[12] or on the nitrogen atoms[13−18] are soluble in water and have conductivities between 0.1 and 10^{-9} S/cm depending on the level of substitution. Polyanilines with carboxy groups are also expected to be soluble in aqueous alkaline solutions. Poly(*o*-anthranilic acid), which is effectively nonconducting, is reported to be soluble in aqueous alkaline solutions.[19] The copolymers of aniline and *o*-anthranilic acid are reported to be soluble in *N*-methylpyrrolidone and dimethyl sulfoxide when in the base form, but no mention is made of their solubility in aqueous solutions.[19] These copolymers are produced in low yields, mostly reflecting the yield characteristics of the anthranilic acid polymerization reaction. From the surface data (XPS analysis), one estimates 42−60% anthranilic acid in the copolymers, which is close to the 33−66% content expected from the monomer ratios used in the reaction. The conductivities of the copolymer decrease along the series from 24 S/cm for polyaniline to 10^{-8} S/cm for poly(*o*-anthranilic acid). This decrease is not due to changes in the oxidation level of the copolymers because it was estimated to remain at 20−25% from the XPS analysis. Instead, the decrease was attributed to "self-doping" and a decrease in the degree of conjugation along the polymer chain. In this paper, we report some additional characterization of these poly(aniline-*co*-*o*-anthranilic acid (PAA) copolymers plus the electrochemical and spectroelectrochemical characteristics. We find that the copolymers are soluble in aqueous alkaline solutions and these solutions can be used to prepare films.



PAA Copolymers

Experimental Section

Aniline, *o*-anthranilic acid, ammonium persulfate, and hydrochloric acid were purchased from Aldrich Chemical Co., Inc., and used without further purification. Methyl sulfoxide, *N,N*-dimethylformamide, *N*-methyl-2-pyrrolidinone, and tetrahydrofuran were obtained from Fisher and used as received.

Aniline and *o*-anthranilic acid were polymerized in a 1.2 M HCl aqueous solution using $NH_4S_2O_8$ as the oxidizing agent. The molar fraction of *o*-anthranilic acid in the reaction mixture (f_1) was varied from 0.25 to 0.75, and the resulting copolymers are referred to as PAA(f_1). The oxidant/monomer ratio was 1.5 in every preparation. A typical polymerization of PAA-(0.5) copolymer is as follows: To a 50 mL solution of 1.2 M HCl containing aniline (0.93 g) and *o*-anthranilic acid (1.37 g) was slowly added 50 mL of a 1.2 M HCl solution containing 6.8 g of ammonium persulfate with constant stirring at room temperature. A dark green color developed immediately and the polymeric product precipitates from the solution. The reaction mixture was stirred at room temperature for 20 h. The polymer was collected by filtration, washed with 1.2 M HCl until the filtrate was colorless, and then dried in vacuum at 20 °C to constant weight. Poly(*o*-anthranilic acid) was prepared in the same manner and using a 48 h reaction time. This material was recovered in 22% yield as a brown powder.

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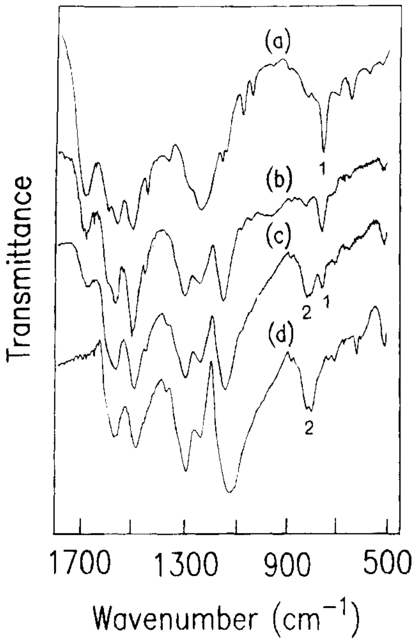

Figure 1. FTIR spectra in KBR pellets of poly(aniline-*co-o*-anthranilic acid) with different molar ratios of anthranilic acid in the reaction mixture: f_1 = (a) 1.00, (b) 0.60, (c) 0.50, and (d) 0.25.

The average molecular weights (M_w) of the polymers were determined by steric exclusion chromatography (SEC) and monodisperse polystyrene standards. The room temperature electrical conductivity of the polymers as films or pressed pellets was measured by the conventional collinear four-probe technique using a Keithley 177 amperometer and a HP 3478A multimeter. The FTIR spectra of the PAA copolymers and homopolymers in KBr pellets were recorded using the IBM IR44 spectrometer. The ^{1}H NMR spectra of the polymers in DMSO-d_6 were obtained on a Bruker 250 MHz spectrometer. The EPR spectra were measured using dispersions of the copolymers in ZnS (5% w/w) and were recorded at room temperature using a Bruker ER080. The number of spins/gram was estimated comparing the size of the EPR signals with the signal for the 2,2-diphenyl-1-picrylhydrazyl hydrate standard. The UV–visible spectra were recorded using a HP 8452A diode array spectrometer. For the in-situ UV–visible spectra, the polymer films were coated on NESA glass electrodes. The films were kept at the desired potential for at least 2 min before each measurement. The electrochemical properties of the polymer films on platinum foil electrode were studied in a one-compartment cell equipped with a gold wire counter electrode and an Ag/AgCl (3.8 N KCl) reference electrode. The cyclic voltammograms were recorded using an EG&G PAR potentiostat/galvanostat (Model 273) connected to an IBM $x-y-t$ plotter (Model 7424-MT).

Results and Discussion

The preparation procedure used in our studies is similar to the one described by Chan et al.[19] The differences are a monomer/oxidant ratio of 1.5 instead of 1.0, 1.2 M HCl instead of 1.0 M, and extensive washing of the product instead of "washed with a small amount of HCl". The poly(*o*-anthranilic acid) is recovered as a brown powder which is soluble in aqueous solutions of NH_4OH and NaOH. It is also soluble in acetone, *N*-methylpyrrolidinone, dimethyl sulfoxide, and dimethylformamide. It is not soluble in tetrahydrofuran; therefore the M_w of the polymer was not determined. The FTIR spectrum for poly(*o*-anthranilic acid) in Figure 1 shows strong bands for the C=O stretching at 1694 cm^{-1} and C–N stretching at 1205 cm^{-1}. The vibration modes of the benzene rings appear between 1600 and 1450 cm^{-1}. In addition, the band appearing at 758 cm^{-1} (label 1) probably corresponds to the C–H out-of-plane bending vibration of the 1,2,3-trisubstituted benzene rings.[20] This result suggests that the poly(*o*-anthranilic acid) may not have a conjugated quinoid backbone as the general polymer structure as proposed by Chan and co-workers.[19] The ^{1}H NMR spectrum for poly(*o*-anthranilic acid) is shown in Figure 2a. Unlike the monomer (not shown), the homopolymer displays several broad peaks for the aromatic protons between 6.0 and 8.5 ppm. The resonance of the carboxylic acid group appears at 10.7 ppm.

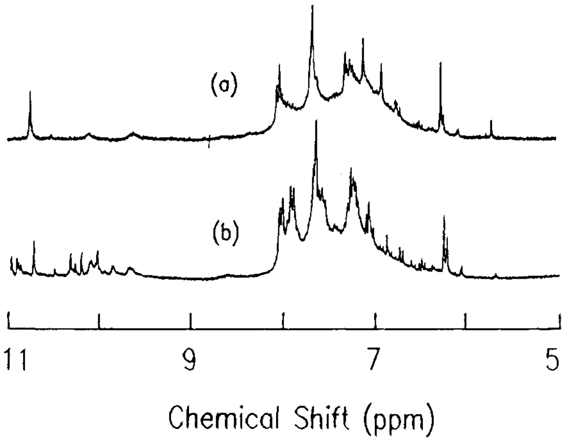

Figure 2. ^{1}H NMR spectra in DMSO-d_6 of (a) poly(*o*-anthranilic acid) and (b) PAA(0.5).

The UV–visible spectra of polyaniline and poly(*o*-anthranilic acid) homopolymers dissolved in 0.1 M NH_4OH/NMP solution are shown in Figure 3a. In this solution, polyaniline is in the emeraldine base form (blue), and its spectrum shows an absorption band at 320 nm for the $\pi-\pi^*$ transition of the benzoid rings and at 640 nm for the exiton transition from the benzoid to the quinoid segments.[21] The solution spectrum of the poly(*o*-anthranilic acid) shows the $\pi-\pi^*$ transition band at 290 nm, indicating a substantial reduction in the level of conjugation along the polymer backbone. There is no exiton band, indicating little or no intra- or interchain charge transfer. Thus, both the FTIR and the UV–visible results suggest little or no conjugation along the poly(*o*-anthranilic acid) polymer backbone. No EPR signal is observed for poly(*o*-anthranilic acid) (Figure 4). This is surprising since Chan et al.[19] report that this material is ca. 20% oxidized. This oxidation level was based on the assignment of the 401 and 402 eV peaks in the XPS spectrum to the C–N$^+$ and C=N$^+$ groups and using it as a measure of the degree of oxidation of the copolymers. Therefore, the cationic nature of the polymer does not include free spins.

The poly(aniline-*co-o*-anthranilic acid) copolymers were recovered in 28–68% yield depending on the *o*-anthranilic acid content as previously reported.[19] This is seen in Table 1. The copolymers are partially soluble in the above-mentioned solvents, and the solubility increases with the *o*-anthranilic acid content in the copolymers. They are also partially soluble in tetrahydrofuran but show decreasing solubility as the *o*-anthranilic content in the copolymer increases. SEC of the soluble portion shows one broad peak for the copolymers and the M_w decreases from 126 000 to 84 000 as the *o*-anthranilic acid content in the polymer increases. The copolymers do not have a bimodal molecular weight distribution like the parent and substituted polyaniline.[10] Since the PAA copolymer

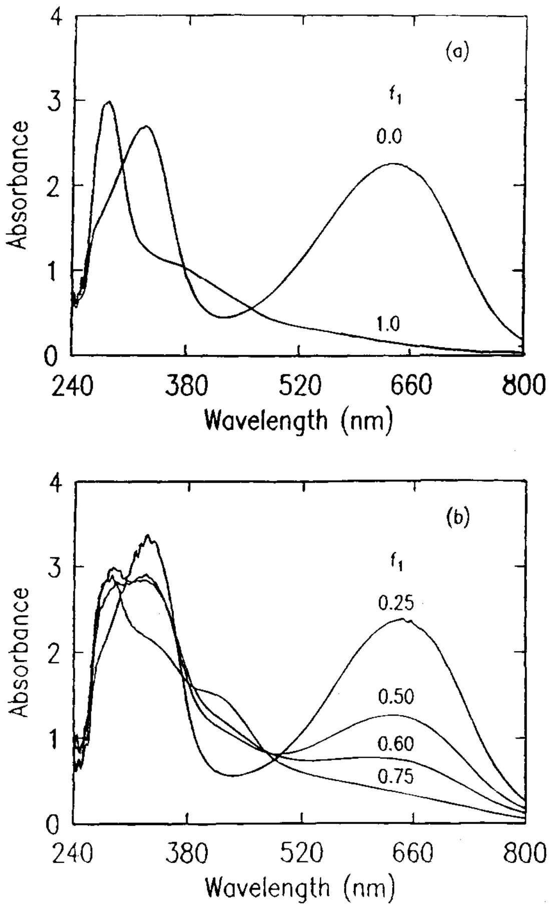

Figure 3. UV–visible spectra of (a) polyaniline and poly(*o*-anthranilic acid) and (b) poly(aniline-*co*-anthranilic acid) copolymers dissolved in 0.1 M NH_4OH/*N*-methylpyrrolidone solution.

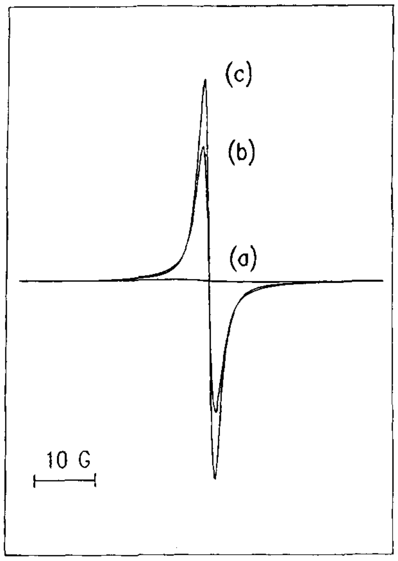

Figure 4. EPR spectra of poly(aniline-*co*-*o*-anthranilic acid) powder in ZnS (5% by weight); f_1 = (a) 1.0, (b) 0.6, and (c) 0.5.

Table 1. Polymerization Yields, Electrical Conductivities, and Oxidation Peak Potentials for the Poly(aniline-*co*-anthranilic acid) Copolymers

f_1[a]	yield, %	σ, S/cm	$E_{pa1}/E_{pa2}/E_{p3}$,[b] V
0.00	84	5.2	0.24/0.55/0.84
0.25	68	1.2×10^{-2}	0.25/0.55/0.78
0.50	57	4.5×10^{-5}	0.33/0.55/0.75
0.60	34	6.1×10^{-7}	0.39/0.55/—
0.75	28	1.0×10^{-8}	—/0.53/—
1.00	22	1.0×10^{-8} 3.0×10^{-8} [c]	—/—/—

[a] Mole fraction of *o*-anthranilic acid in copolymer. [b] Films on Pt immersed in 1.2 M HCl solution using a 100 mV/s scan rate. [c] Reference 19.

chains are more rigid and quite different from those of polystyrene standards, the actual molecular weights of the copolymers must be lower than the values estimated from the polystyrene calibration. The FTIR spectra of the PAA copolymers show the C–H out-of-plane bending vibration of the 1,4-disubstituted benzene rings at around 814 cm^{-1} (label 2).[20] This band confirms the presence of the polyaniline segment in the copolymer backbone. As expected, the intensity of the C=O bands at 1694 cm^{-1} and the C–H out-of-plane bending vibration of the 1,2,3-trisubstituted benzene rings at 758 cm^{-1} decrease as the *o*-anthranilic acid content in the PAA copolymer decreases.

The ^1H NMR spectra for all the PAA copolymers dissolved in DMSO-d_6 are all quite similar and resemble the spectra for PAA(0.5) shown in Figure 2b. The signal for the carboxylic proton appears at 9.6–10.9 ppm. The ^{13}C NMR spectra of the copolymers and of poly(anthranilic acid) in DMSO-d_6 show several peaks between 90 and 180 ppm; however, the poor resolution of the spectra did not provide structural information.

The UV–visible spectra of the PAA copolymers in 1.0 M NH_4OH/NMP solution (Figure 3b) spectra show the bands at 290 and 320 nm in varying intensities depending on the copolymer composition. The copolymers are probably a mixture of copolymer chains with different monomer contents and with variations in the monomer content along a given chain. The copolymers probably have a significant number of block segments resulting from the reactivity difference between the two monomers and the complexity of the polymerization. Considering the unconjugated nature of the anthranilic units, the block copolymer must be poorly conjugated because the anthranilic acid units (blocks) will isolate the aniline blocks. The random copolymer, whether or not it is present in the product, would also have poor conjugation because the anthranilic units isolate the aniline units along the chain. This probably results from the molecular interactions between the COOH group and the polaronic nitrogen atoms.[19] The band at 640 nm is probably related to the aniline segments in the chain. The PAA copolymers are in the oxidized form as evident by their color and as reported by Chan et al.[19]. Unlike the *o*-anthranilic acid homopolymer, the EPR spectra of the copolymers show a strong Lorentzian peak (Figure 4). The copolymers show a decrease in the level of paramagnetism and the number of spins/gram as the *o*-anthranilic acid content in the copolymer increases. The copolymers with more than ca. 0.5 mole fraction aniline (1 f_1) have a high number of spins/gram like polyaniline, and a dramatic decrease in the number of spins is observed with 0.2–0.4 mole fraction aniline. This response is seen in the plot in Figure 5. This behavior was previously observed with the copolymers of aniline and diphenylamine-4-sulfonic acid and was shown to correlate with the degree of protonation in the copolymers.[18]

The electrical conductivities (σ) of the copolymers decrease monotonically from 5.2 S/cm for polyaniline to 1.0×10^{-8} S/cm as the anthranilic acid content in the copolymer increases. The values are listed in Table 1. We measure σ values which are 3–4 times smaller for the homopolymers and ca. 100 times smaller for the

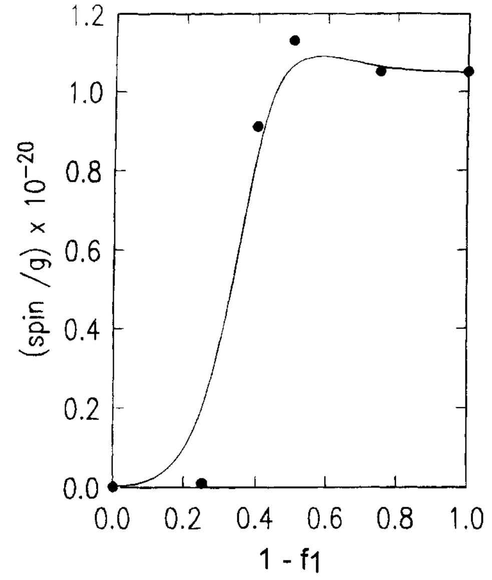

Figure 5. Plot of the spins/gram of the poly(aniline-*co*-*o*-anthranilic acid) copolymers vs the mole fraction of aniline (1 − f_1).

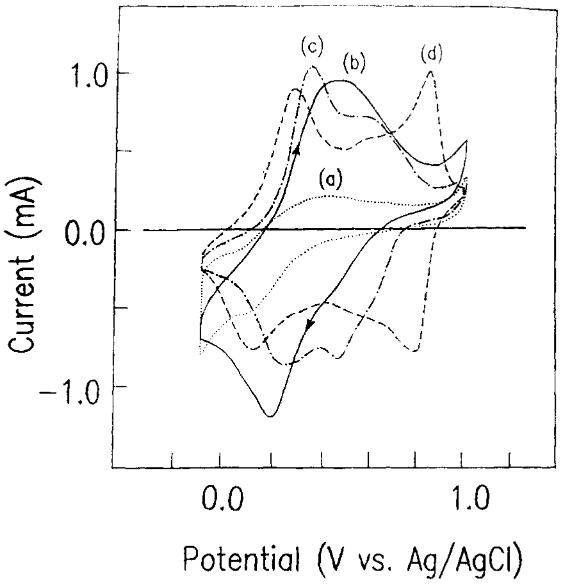

Figure 6. Cyclic voltammograms of poly(aniline-*co*-*o*-anthranilic acid) films immersed in 1.2 M HCl solution (a 100 mV/s can rate was used); f_1 = (a) 1.00, (b) 9.75, (c) 0.5, and (d) 0.25.

copolymers than those reported by Chan et al.[19] This difference may result from differences in the purity of the samples, since the polymeric product was washed differently in the two procedures. The presence of ionic impurities will give high conductivity values. The log(σ) values for polyaniline and the copolymers plot linearly against f_1, and the slope of the line is −11 with a 2% fit. The value for poly(*o*-anthranilic acid) is obviously off the line and was not included. This fit is not expected for samples consisting of a mixture of two polymers with different conductivities. The decrease in the conductivity probably reflects the decrease in the number of carriers and the conjugation lengths along the polymer backbone as discussed above, and not the oxidation level of the copolymers which remains fairly constant at 20−25%.[19]

The copolymers are soluble in aqueous alkaline solutions and the solutions can be used to prepare adherent film coatings on various substrates, such as Pt, Au, NESA glass, etc. Thin films of poly(*o*-anthranilic acid) and PAA copolymers spin coated onto Pt foil were used for electrochemical analysis. Figure 6 shows the cyclic voltammograms of these films immersed in 1.2 M HCl solution. The films are stable to the electrochemical conditions, and the voltammograms could be reproduced for 20 or more cycles. Unlike polyaniline and many of its substituted forms, the poly(*o*-anthranilic acid) film does not show well-defined oxidation or reduction peaks in the potential region between −0.1 and 1.0 V (curve a) and may not be electroactive. On the other hand, the copolymers are electroactive and show wide variations in their redox properties as can be seen in Figure 6 and the oxidation peak voltages listed in Table 1. With 25% anthranilic acid in the copolymer the voltammogram shows the general characteristics of the polyaniline voltammogram although the waves are broader (curve d). As the anthranilic acid content in the copolymer increases, the three oxidation peaks in the voltammogram for polyaniline transform into a voltammogram having one broad peak centered at 0.53 V. In this changeover, the more anodic peak (0.82 V) for the oxidation of the radical cation to the dication is affected first. With PAA(0.5) the peak at 0.82 V becomes a small shoulder to the large center peak (curve c). This suggests that the restrictions to π-conjugation in the copolymer backbone have a greater effect on the formation of the pernigraniline structure (C_6H_4-$NH{=}C_6H_4{=}NHC_6H_4N{=}C_6H_4{=}N$, base form). The less anodic peak at 0.24 V for the oxidation of the neutral nitrogen atoms to the radical cation[21] is also affected. It shifts anodically and merges into the broad peak with the higher anthranilic acid content. The relative sensitivities of the two oxidation steps to the incorporation of the anthranilic acid suggest that the restrictions to the conjugation are less important for the oxidation to the emeraldine structure ($C_6H_4NHC_6H_4NHC_6H_4N{=}C_6H_4{=}N$, base form). Finally, the PAA(0.75) film produces only a broad oxidation peak centered at ca. 0.53 V, which is probably due to the short aniline segments in the polymer backbone (curve b). Similar observations have been reported for other substituted polyaniline.[9,10,22,23]

The oxidation/reduction process of the PAA copolymers is accompanied by a color change in the film. Figure 7 shows the in-situ UV−visible spectra of the PAA(0.25) film on the NESA glass which was immersed in a 1.2 M HCl solution. At an applied voltage of −0.1 V, this film has a clear yellow color and displays only one absorption band around 300 nm. When the voltage is increased to 0.4 V, the PAA(0.25) film turns green and two new absorption bands appear at ca. 415 and 820 nm. These absorption bands resemble those observed for the parent and other substituted polyaniline films[9,10] and are assigned to the electronic transitions of the radical cations. Increasing the potential to 0.8 V changes the color of the film to dark green, and the absorption band at 820 nm increases in intensity and shifts to shorter wavelength, which indicates the formation of the dication state. Similar electrochromic properties are observed for the other PAA copolymer films. However, those with a higher anthranilic acid content become dark brown at 0.8 V, and a broad absorption band appears which covers most of the UV−visible region.

Conclusion

Poly(aniline-*co*-anthranilic acid) was synthesized by the oxidative polymerization of aniline and *o*-anthranilic

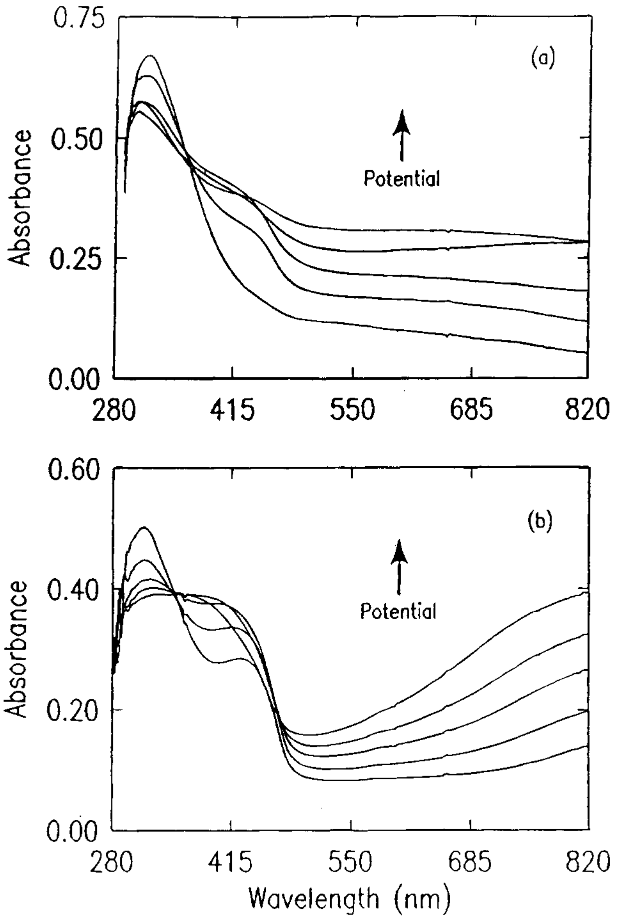

Figure 7. UV–visible spectra of poly(aniline-*co*-*o*-anthranilic acid) films on the NESA glass electrode immersed in 1.2 M HCl solution and with different applied potentials; f_1 = (a) 0.5 and (b) 0.25, and the potentials are 0.0, 0.4, 0.6, 0.8, and 1.0 V.

acid in 1.2 M HCl aqueous solution using $(NH_4)_2S_2O_8$ as the oxidizing agent. These copolymers are soluble in aqueous alkaline solutions and in some organic solvents. The FTIR and UV–visible spectra indicated that the anthranilic acid segments in the copolymers do not have a conjugated structure. The EPR spectra for the copolymers indicate a decrease in the number of spins/gram with increasing *o*-anthranilic acid content. Poly(*o*-anthranilic acid) itself shows no EPR signal. The data also suggest that the samples may be a mixture of two homopolymers or copolymers with extended block characteristics. The reduced conjugation lengths in the copolymers strongly affect the electrical conductivity. The log(σ) for the copolymers decreases linearly with the mole fraction of *o*-anthranilic acid in the copolymer. The *o*-anthranilic acid homopolymer conductivity is off this line. The copolymers are electroactive. Films of the copolymers can be oxidized and reduced when immersed in aqueous media, and the reactions proceed with visible color changes. The *o*-anthranilic acid homopolymer is not electroactive.

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