Electrochemical Copolymerization of Aniline and Anilinesulfonic Acids in FSO$_3$H/Acetonitrile Solution

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ABSTRACT: The effects of 2-aminobenzenesulfonic acid (orthanilic acid), 3-aminobenzenesulfonic acid (metanilic acid), and 4-aminobenzenesulfonic acid (sulfanilic acid) on the electropreparation and properties of polyaniline (PANI) were investigated in acetonitrile containing 200 mM fluorosulfonic acid. The cyclic voltammetric studies of the products showed characteristics similar to those of conventional PANI in neutral solution, but there was a significant difference between the electrochemical behavior of the polymer films in basic solution. The sulfur-to-nitrogen ratios were found to be about 0.50, which indicated that copolymers were formed. The copolymers were soluble in a basic aqueous solution and in 1-methyl-2-pyrrolidinone and dimethyl sulfoxide solvents. The dry electrical conductivity values of the copolymers were measured. The structure and properties of these conducting copolymers in acetonitrile were elucidated with cyclic voltammetry, Fourier transform infrared spectroscopy, and ultraviolet–visible absorption spectroscopy. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1227–1235, 2002

Key words: copolymerization; conducting polymers; electrochemistry; self-doped polyaniline; heteroatom-containing polymers

INTRODUCTION

Polyaniline (PANI) is the first conducting polymer whose electronic properties can be reversibly controlled by protonation.[1] PANI can be obtained by the chemical[2] or electrochemical oxidation of aniline.[3] The electrochemical process occurs readily in acidic aqueous media[4] and nonaqueous media.[5] Because of the probability of degradation and deactivation of the polymers in aqueous media, nonaqueous media is preferred.[6] Pekmez and Yildiz studied the catalytic effect of Cu$^+$ ions on the electrolytic formation of PANI in the presence of dissolved H$_2$ gas in acetonitrile.[7] Electropolymerization of aniline derivatives has been widely investigated for the improvement of processability and other properties of conductive PANI because the applications of PANI are limited because of its poor processability. The use of some aniline derivatives causes improvements in some of the physical and chemical characteristics, such as stability and solubility, of the conducting polymers. The aim is to obtain polymer films that are electroactive in a wider range of solvents.[8]

The first chemical synthesis of self-doped conducting PANI was produced as a sulfonated polyaniline (SPAN) by chemical treatment of synthesized PANI with fuming H$_2$SO$_4$.[9] Electrochemical polymerization of aniline derivatives containing a sulfonic acid group, which lead to self-doped PANI, has

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also been reported.[8,10–18] SPAN had about zero orders of magnitude lower electric conductivity than PANI.[9] In a self-doped conjugated polymer, the counter ions are not necessarily supplied by the medium in which the polymer is immersed; rather, they originate from moieties covalently bound to the polymer. Thus, only protons need move.[10]

Sulfonic acid ring-substituted PANI differs from the parent PANI. It is generally accepted that PANI is insoluble in aqueous solution and most common organic solvents. The solubility of PANI is greatly improved by the presence of —SO_3^- groups. Specifically, SPAN dissolves in basic aqueous solutions, in contrast to PANI.[19] Applications of PANI in bioelectrochemistry are limited because of the complete loss of electrochemical activity in neutral aqueous solutions.[20] A conducting PANI film that is electroactive in neutral aqueous solutions is needed for the immobilization of enzymes as required in biosensors.[8] The conductivity of SPAN is independent of external protonation in a broad pH range. The good environmental stability of the parent PANI is further improved by the presence of the —SO_3^- group on the phenyl rings due to its strong electron-withdrawing properties.[19] It has also been shown that SPAN has better thermal stability than its parent PANI doped with HCl.[21] In previous studies from our research group, *in situ* sulfonation during the polymerization of aniline in acetonitrile mixtures was achieved.[22]

A different approach to obtain SPAN has been the copolymerization of aniline with its sulfonated derivatives. Lee and colleagues copolymerized aniline and metanilic acid (*m*-ASA) on various electrodes.[11–13] SPAN formed by copolymerization of aniline with *m*-ASA also proved to be thermally more stable than PANI itself.[8] In another study, SPAN was prepared by the copolymerization of aniline with 2,5-diaminobenzene-sulfonic acid on an IrO_2-coated titanium electrode,[14] which produced a SPAN with a lower conductivity, perhaps due to a more highly crosslinked and branched structure. SPAN was prepared by the copolymerization of orthanilic acid (*o*-ASA) with aniline on a platinum electrode in H_2SO_4 solution by Kilmartin and Wright.[8] In another study by Kilmartin and Wright, SPAN was prepared by the copolymerization of *o*-ASA with *m*-methyl aniline on a platinum electrode.[15] The chemical oxidative copolymerization of aniline with 1-(*o*-amino)-propane-3-sulfonic acid and 1-(*o*-amino)-butane-3-sulfonic acid was reported by Pla and colleagues.[16]

It is reasonable to expect that the synthesis of self-doped PANI would be possible during the polymerization of monomers such as *o*-ASA, *m*-ASA, sulfanilic acid (*p*-ASA),[17] or aniline-2,5-disulfonic acid (ADSA).[10] However, attempts to polymerize these monomers chemically or electrochemically have not been successful. It is known that *m*-ASA cannot polymerize by itself and that electrooxidation of *m*-ASA produces only dense purple oligomers near the electrode surface in aqueous media.[18] When a pure *o*-ASA solution was used, the results for attempted electropolymerizations were very similar to those reported for *m*-ASA in aqueous media.[18] In the polymerization of ADSA, no solid film was obtained in an acidic aqueous solution.[10]

In this study, the synthesis of SPAN was attempted via electrochemical copolymerization of the aniline and *m*-ASA, *o*-ASA, and *p*-ASA in a nonaqueous fluorosulfonic acid (FSO_3H)/acetonitrile solution. The electrochemical behaviors of the copolymer films thus obtained were investigated in neutral and basic media. The structure and properties of these copolymers were elucidated with cyclic voltammetry, Fourier transform infrared spectroscopy (FTIR), elemental analysis, and ultraviolet–visible (UV–Vis) methods.

EXPERIMENTAL

o-ASA (Aldrich, Germany), *m*-ASA (Aldrich), and *p*-ASA (Aldrich) were reagent grade and were used without further purification. Aniline (Merck, Germany) was vacuum distilled (67°C). The procedure used to purify acetonitrile (Merck) was described elsewhere.[23,24] Aniline and acetonitrile were kept under a nitrogen atmosphere. Anhydrous FSO_3H (Aldrich, triple distilled) was used as a supporting electrolyte without further purification. All electrochemical experiments were carried out under nitrogen (Birlesik Oksijen Sanayii) atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl, saturated) and the counter electrode (Pt spiral). The working electrode for the cyclic voltammetric studies was a Pt disk (area = 0.0132 cm^2). The macro samples of the copolymer films were prepared on a Pt macroelectrode (area = 1.0 cm^2). We cleaned the working microelectrode by polishing it with Al_2O_3 slurry. We cleaned the macroelectrode by holding it in a flame for a few minutes. The microelectrode and macroelectrode were rinsed with acetonitrile and dried before

use. The films prepared electrochemically were immersed in acetonitrile to remove FSO_3H and the soluble oligomers formed during electropreparation of the copolymer films and were then vacuum dried. Electrodeposition was performed by cyclic potential sweeping in the potential range of -0.30 V to 2.30 V (vs. Ag/AgCl) at a scan rate of 100 mV/s.

The copolymers were first dissolved in dimethyl sulfoxide (DMSO), and then, the bulk solution was filtered and poured onto a clean glass plate under a nitrogen atmosphere to obtain a cast film. Finally, the copolymer film was dried in a vacuum furnace for at least 48 h.

The dry conductivity values were measured with a four-probe technique at room temperature. Gold-plated probes were used to avoid any errors that might arise from ohmic contacts. At least 10 different current values were used in the measurement of the potential drop.

Electrochemical instrumentation consisted of a PAR model l73 potentiostat coupled to a PAR model l75 universal programmer and a PAR model l79 digital coulometer (Princeton Applied Research, U.S.A.). The current–voltage curves were recorded with a BBC Metrawatt Goerzt X-Y recorder (Germany).

UV–Vis spectra of the copolymer solutions in 1-methyl-2-pyrrolidinone (NMP) and DMSO were recorded on a Shimadzu UV-2101 PC spectrophotometer (Japan). The copolymer structure was determined by FTIR spectroscopy with a Jasco FTIR 400E (Japan) and KBr pellets of solid samples. Elemental composition of the copolymers were determined by elemental analysis with a Carlo Erba EA1108 (Italy) machine. *In situ* spectroelectrochemical studies were made with a combination of a Wenking POS 88 model potentiostat (Bank, Germany) and a Shimadzu UV-2101 PC spectrophotometer.

RESULTS AND DISCUSSION

The solubilities of anilinesulfonic acids (ASAs; *o*-ASA, *m*-ASA, and *p*-ASA) were very low in acetonitrile. To improve the solubilities, FSO_3H was added to the acetonitrile solutions. ASA (100 m*M*) dissolved completely in acetonitrile containing 200 m*M* FSO_3H. ASA cannot polymerize electrochemically without the presence of aniline in solution, and electrooxidation leads only to the formation of soluble oligomers or low-molecular-weight polymers near the electrode surface. The
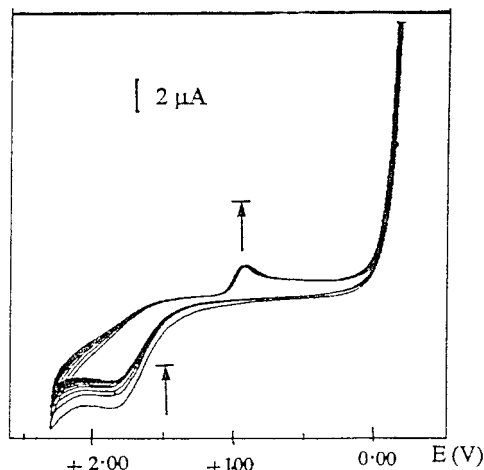

Figure 1 Multisweep cyclic voltammograms of 100 m*M* *o*-ASA in 200 m*M* FSO_3H/acetonitrile solution.

electrochemistry of the three ASAs were quite similar, so only the results related to the *o*-ASA are discussed next.

The oxidation of *o*-ASA was recorded at the peak potential of 1.78 V (0.90 V for *m*-ASA and 1.40 V for *p*-ASA; vs. Ag/AgCl) in an acetonitrile/ 200 m*M* FSO_3H medium. If the potential scan was reversed toward the cathodic direction, a reduction peak appeared at 0.90 V (0.60 V for *m*-ASA and 0.80 V for *p*-ASA). Figure 1 shows the multisweep cyclic voltammograms of 100 m*M* *o*-ASA in 200 m*M* FSO_3H/acetonitrile solution. Neither any polymeric film deposited on the electrode nor any colored soluble products were generated near the electrode surface. The electron-withdrawing effect of the pendant sulfonate group apparently caused the radical cation intermediate formed on the oxidation of monomer to be unstable. Polymerization could not proceed easily for this reason.

A polymeric film was deposited onto the electrode surface when aniline was added to the previous solution during electrooxidation. The films were grown in solutions of varying aniline concentrations in the range of 25–400 m*M* by the cycling of the potential between -0.30 and 2.30 V for the same period of time at a scan rate of 100 mV/s (30 min). Specific color changes of the SPAN film were also seen during these sweeps.[22] When the potential was scanned between -0.30 and 2.30 V, the color of the copolymer changed from yellow at 0.00 V (reduced state, polyleucoemeraldine) to green at 0.80 V (partially oxidized state, polyemeraldine) and blue at 1.30 V (fully oxidized state, polypernigraline). The charge passed during the
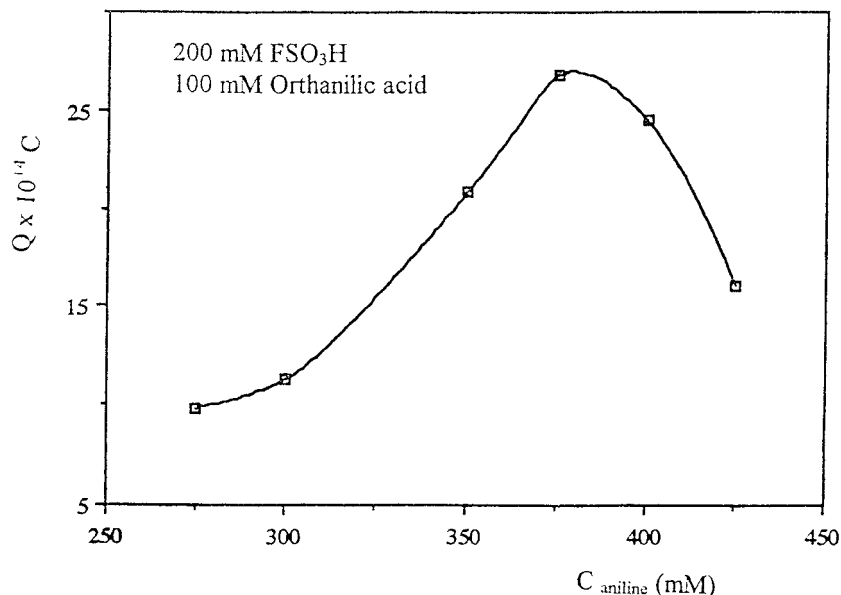
Figure 2   Plot of the charge passed during the electrooxidation of the aniline– *o*-ASA copolymer films in (0.1*M* pyridine + 0.1*M* FSO$_3$H)/ acetonitrile solution. The concentrations of *o*-ASA and FSO$_3$H were held constant at 100 and 200 m*M*, respectively.

electrooxidation of these films in the neutral blank solution (0.1*M* FSO$_3$H + 0.1*M* pyridine) was measured. The oxidation charge was also measured in basic and acidic solutions and was found to be similar to that measured in neutral solution. The charge was measured during the first oxidative cycle of the cyclic voltammograms of the film in the blank solution. The anodic charge, which should have been proportional to the thickness of the deposit, was found to increase with increasing aniline concentration. Figure 2 shows the results of these measurements. It can be concluded that the optimum aniline concentration under these conditions was about 375 m*M*. There was a considerable decrease in the yield of copolymer formation below and above this aniline concentration. Because the solubilities of ASAs were very low in acetonitrile, 200 m*M* FSO$_3$H had to be added into the acetonitrile solution to dissolve 100 m*M* ASA completely. On the other hand, polymerization of aniline could not occur in the presence of excess FSO$_3$H in acetonitrile. By the addition of increasing amounts of ASAs into the solution containing 100 m*M* aniline and 200 m*M* FSO$_3$H, no growth of the copolymer was observed. Therefore, no study of the oxidation charge as a function of ASA concentration in a solution of fixed amounts of aniline and FSO$_3$H was carried out.

Figure 3(a) illustrates the first six cyclic voltammetric sweeps taken during the oxidation in

FSO$_3$H/acetonitrile solution containing aniline and *o*-ASA. The peak due to the oxidation of aniline disappeared in the second cycle. This behavior demonstrated that there was a thin insulating film formed on the electrode surface. After a few cycles, the peak due to the oxidation and reduction of the product appeared as the film grew. The
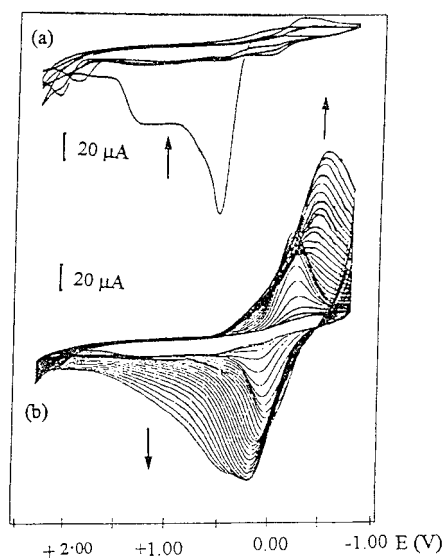
Figure 3   Cyclic voltammograms of the acetonitrile solution containing (375 m*M* aniline + 100 m*M* *o*-ASA)/ 200 m*M* FSO$_3$H: (a) initial sweeps and (b) successive cyclic voltammograms. Scan rate = 100 mV/s.
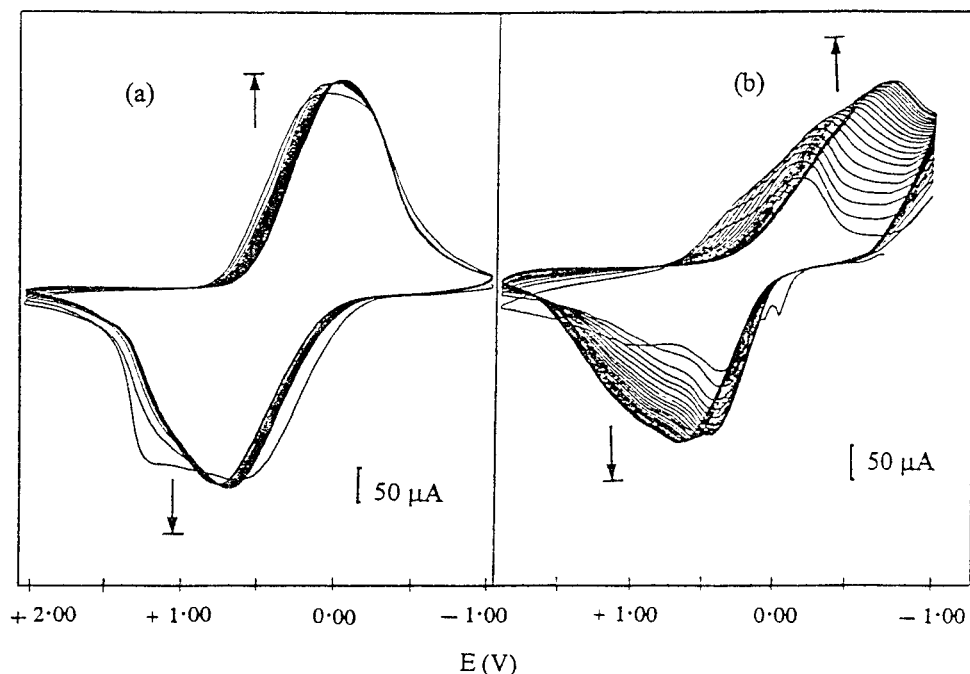
Figure 4 Electrochemical behavior of the copolymer film synthesized from the acetonitrile solution containing 375 mM aniline + 100 mM o-ASA + 200 mM FSO$_3$H, in (a) neutral blank solution (0.1M FSO$_3$H + 0.1M pyridine) and (b) basic blank solution (50 mM pyridine + the neutral blank solution) acetonitrile solution. Scan rate = 100 mV/s.

formation and the growth of the film could easily be seen during the following sweeps [Fig. 3(b)].

In the simultaneous electrooxidation of ASA and aniline, copolymerization can be initiated by the generation of radical cations of aniline molecules followed by a propagation based on the attack of these radical cations on aniline and o-ASA molecules.[12] Incorporation of ASA units into the polymer interrupts the autocatalytic growth of PANI, especially when the o-ASA/aniline ratio in the solution is high.[13,25] Because of the unfavorable combination of inductive and steric effects of the o-ASA unit in the polymer, the growth of the copolymer was not detected when the aniline concentration was below 150 mM. When the aniline addition was continued, the deposition rate of the polymer became higher. Maximum copolymer growth was observed with the polymerization solution containing 375 mM aniline. The amount of copolymer deposit decreased with aniline concentrations exceeding this value.

It is known that the self-doped PANI shows resistance against degradation in weak basic solutions. Figure 4 shows the electrochemical behavior of the copolymer film in neutral blank solution [0.1M FSO$_3$H + 0.1M pyridine in acetoni-

trile; Fig. 4(a)] and in basic blank solution [when 50 mM pyridine was added to the previous solution; Figure 4(b)]. Electroactivity of the film did not change in neutral solution. There was one broad oxidation and one broad reduction peak at the potentials of 0.70 and 0.00 V, respectively. As seen in Figure 4(b), the o-ASA –aniline copolymer was very stable in basic solutions as well. PANI itself loses its electroactivity completely after a few cycles on the addition of even small amounts of pyridine into tetrabutylammoniumperchlorate/acetonitrile solution.[26] This shows that the electrochemical characteristics of PANI and aniline–ASA copolymer are similar in neutral solution but are quite different in basic solution.

The degree of sulfonation and the dry conductivity values of the copolymers obtained from 375 mM aniline + 200 mM FSO$_3$H + 100 mM ASA in acetonitrile solution are listed in Table I. This table also includes the conductivity values of the cast copolymers. The copolymers dissolved in aqueous KOH to form a colorless solution. The copolymers also dissolved in NMP to form a dark blue solution and in DMSO to form a blue-violet solution. The solubility values of the copolymers

Table I Dry Conductivity Values of the Deposited Copolymer Films Obtained from the Acetonitrile Solution Containing 375 mM Aniline + 100 mM ASA + 200 mM FSO$_3$H and the Cast Films

Composition of the Electropolymerization Solution (mM)	Sulfonation Degree (S/N)	Conductivity of the Deposited Film (S/cm)	Conductivity of the Cast Film (S/cm)
100 o-ASA + 200 FSO$_3$H + 375 aniline	0.50	3.16	6.20
100 m-ASA + 200 FSO$_3$H + 375 aniline	0.41	7.0	8.3
100 p-ASA + 200 FSO$_3$H + 375 aniline	0.52	2.76	3.80

with various degrees of sulfonation in the three media are listed in Table II.

The elemental composition of the copolymers were also determined. The mole numbers of the elements (S and N) were found with their atomic weights and weight percentage ratio. The sulfonation ratio (S/N ratio) of the copolymers was then calculated with these mole numbers. Table I shows the calculated degrees of sulfonation. S/N ratios were calculated to be about 0.50 for the copolymers. These results suggest that approximately one ASA group was substituted for every two phenyl rings in these copolymers. This means that the aniline rings were not sulfonated during the electropolymerization process and incorporated to the polymeric chain without sulfonation.

The FTIR spectra of the copolymer powders were also obtained, especially to ascertain the presence of —SO$_3^-$ groups in the copolymer [Fig. 5(a–c)]. The peak at 1170 cm^{-1} was due to CH in-plane deformation. The peaks at 1580 and 1460 cm^{-1} corresponded to the stretching of the benzenoid and quinoid units, respectively.[27] Aromatic C—N stretching was responsible for the clustering of peaks between 1400 and 1200 cm^{-1}.[28] Symmetric O=S=O stretching vibrations appeared at 1040 cm^{-1}. The S—O stretching band was seen at 700 cm^{-1}, and the peak at 630 cm^{-1} was for the C—S stretching vibrational mode.[29] These absorptions of maxima at 1040, 700, and 630 cm^{-1} were consistent with the presence of —SO$_3^-$ groups attached to the aromatic rings.[30] The fundamental IR bands of the copolymers were similar to those of the IR bands of the polymers that were obtained from aniline in FSO$_3$H/acetonitrile solution.[22]

Figure 6 shows the UV–Vis spectra of the copolymer (deposited from a solution that contained 375 mM aniline + 100 mM o-ASA + 200 mM FSO$_3$H) solutions in DMSO and in NMP solutions, respectively. The spectrum was dominated by three absorption bands at 300 nm (Peak 1), 450 nm (Peak 2) and 600 nm (Peak 3) in DMSO solution [Fig. 6(a)]. Peak 1 was attributed to the π–π^* transition of the benzenoid moieties in the copolymer structure.[13] Peak 2 was assigned to the optical absorption of the metallic polaron band of the conducting form.[31,32] Peak 3 was rather broad and closely resembled the interchain benzenoid–quinoid π–π^* transition in the copolymer structure. Peak 1 and Peak 3 were also observed for the polymers that were deposited from 100 mM FSO$_3$H in acetonitrile with varying amounts of aniline.[22] In the spectrum of the copolymer in NMP, there were two broad absorption bands at 350 nm (Peak 4) and 620 nm [Peak 5; Fig. 6(b)]. The wavelengths of the absorption band in Figure 6(a) were shorter than (hypsochromic shift) those in Figure 6(b), as was the case for SPAN solution obtained from aniline electrooxidation in FSO$_3$H/acetonitrile media. The absorption band at 450 nm was not observed in NMP solution [Fig. 6(b)].

Table II Solubility Values of the Copolymers Obtained from the Acetonitrile Solution Containing 375 mM Aniline + 100 mM ASA + 200 mM FSO$_3$H in Basic Aqueous Solution and in DMSO and NMP

| Composition of the Electropolymerization Solution (mM)	Solubility of the Deposited Film in DMSO (mg/mL)	Solubility of the Deposited Film in NMP (mg/mL)	Solubility of the Deposited Film in 0.1N KOH (mg/mL)
100 o-ASA + 200 FSO$_3$H + 375 aniline	16	15	19
100 m-ASA + 200 FSO$_3$H + 375 aniline	18	16	19
100 p-ASA + 200 FSO$_3$H + 375 aniline	12	10	15
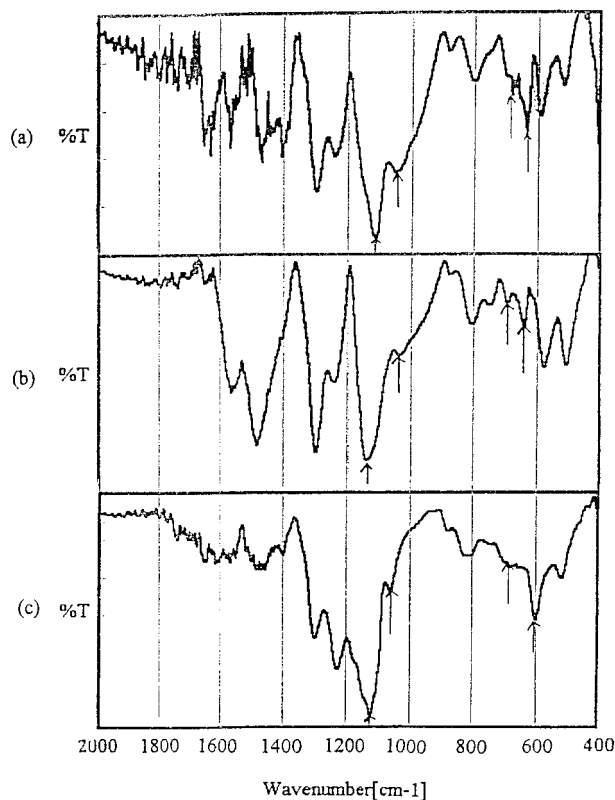
Figure 5 Baseline-corrected FTIR spectra, showing the $2000-400$ cm^{-1} region, of the copolymer obtained from acetonitrile solutions containing (a) 375 mM aniline + 100 mM o-ASA + 200 mM FSO$_3$H, (b) 375 mM aniline + 100 mM m-ASA + 200 mM FSO$_3$H, and (c) 375 mM aniline + 100 mM p-ASA + 200 mM FSO$_3$H.

NMP caused dedoping when the copolymer was dissolved in this solvent, whereas a self-doped structure was present in DMSO solvent.[33]

In situ UV–Vis spectra of the copolymers were also taken with an indium tin oxide (ITO) glass electrode during the oxidation and reduction of the copolymers at different applied potentials. The copolymers were first coated on the ITO electrode with potential cycling from -0.30 to 2.30 V (vs. Ag/AgCl) at a rate of 20 mV/s three times in a solution that contained 100 mM o-ASA + 200 mM FSO$_3$H + 375 mM aniline. The copolymers obtained were then immersed in 2 mM FSO$_3$H/acetonitrile (weak acidic) solution, and different electrode potentials were applied under a nitrogen atmosphere. First, the potential was scanned from -0.25 V to anodic potentials at 1.90 V, and the spectra were taken at each applied potential [-0.25, 0.00, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 1.90 V; Fig. 7(a)]. Second, the applied potential was then changed from the highest anodic potential (1.90 V) to the cathodic potential (-0.25 V) step by step, and the spectra were taken to show whether a degradation occurred in the copolymer film in a previous anodic applied potentials [Fig. 7(b)].

At -0.25, 0.00, 0.25, and 0.50 V, the copolymer films showed the same absorption spectra [Fig. 7(a)]. There were two absorption bands at about 800 and 420 nm in the UV–Vis spectra. These
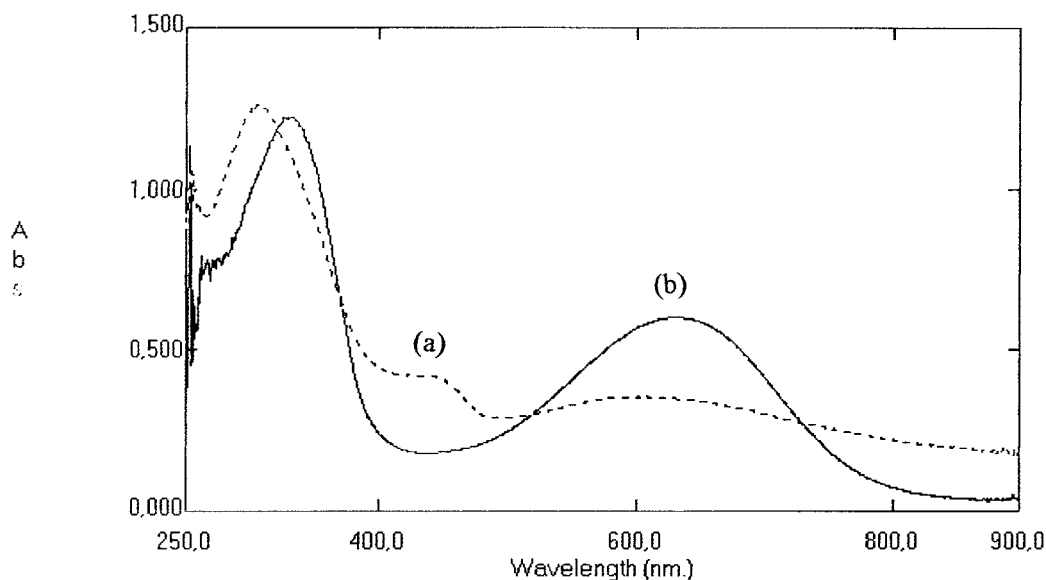
Figure 6 UV–Vis absorption spectra of the copolymer obtained from the acetonitrile solution containing 375 mM aniline + 100 mM o-ASA + 200 mM FSO$_3$H in (a) DMSO and (b) NMP.
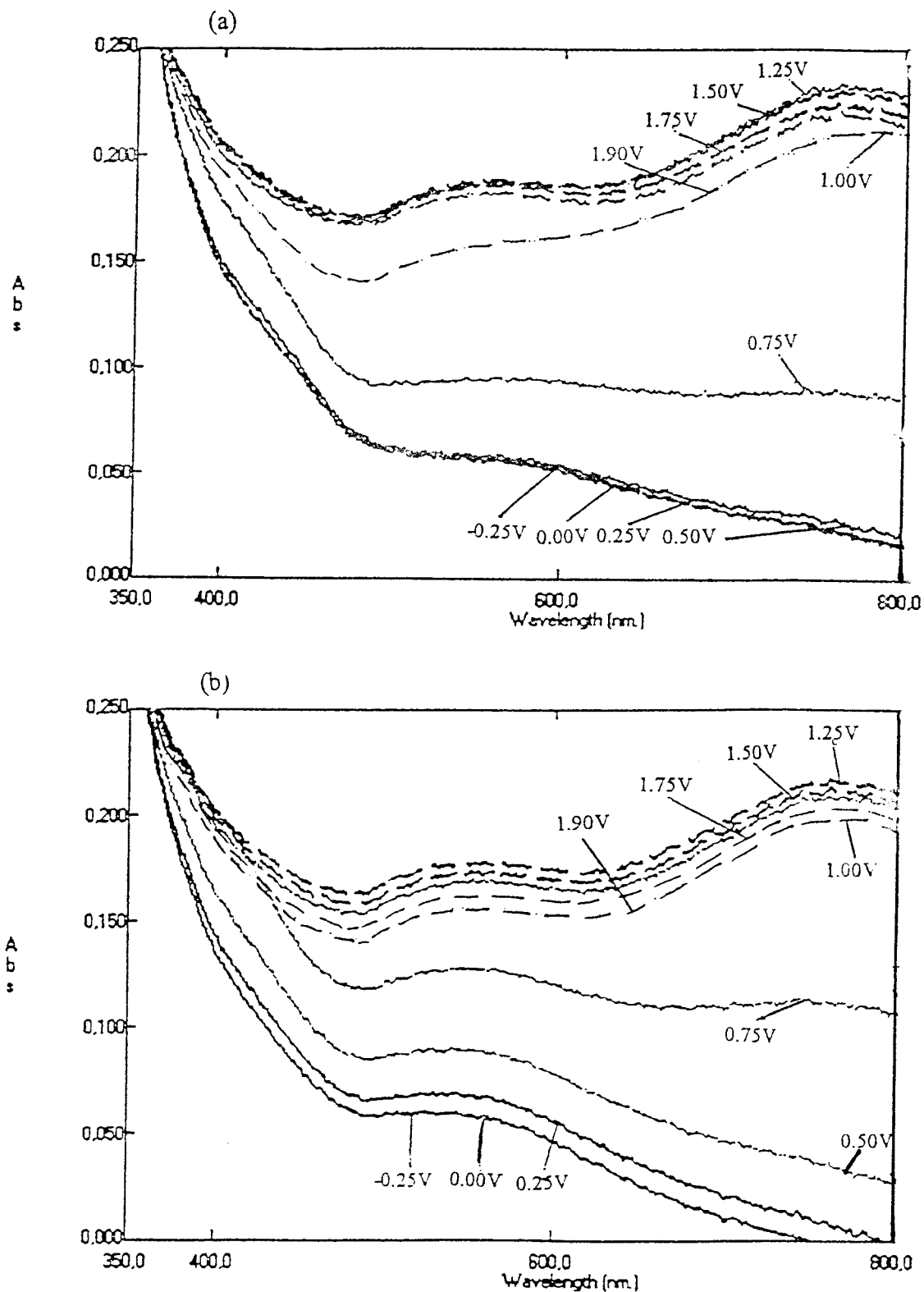
Figure 7 *In situ* UV–Vis spectra of the copolymer coated from the acetonitrile solution containing 375 m*M* aniline + 100 m*M* *o*-ASA + 200 m*M* FSO$_3$H on ITO glass in 2 m*M* FSO$_3$H + 0.1*M* FSO$_3$H + 0.1*M* pyridine (weak acidic) acetonitrile solution at various applied potentials from (a) −0.25 to 1.90 V and (b) 1.90 to −0.25 V (vs. Ag/AgCl).

bands were assigned to the optical absorption of the metallic polaron band of conducting form.[31,32] The broad band at about 800 nm was shifted to smaller wavelengths when increasing amounts of aniline were used in the electropolymerization solution. This means that the sulfonation degree of the copolymer increased with increasing amounts of aniline. When the applied potential was increased to 0.50–1.00 V, an absorption band appeared at about 550–600 nm. This absorption band closely resembled the benzenoid–quinoid π–π^* transition in the emeraldine form of the copolymer. At higher applied potentials (1.25–1.90 V), the copolymer became blue, and a significant hypsochromic shift of the absorption band at about 800 nm occurred.

When the applied potential was decreased in reverse order from 1.90 to −0.25 V, approximately the same spectroscopic behavior of the copolymer film was observed [Fig. 7(b)]. This means that a complete reduction of the oxidized film occurred, and there was no degradation in the structure of the copolymer film in weak acidic acetonitrile solution during electrooxidation, even at potentials as high as 1.90 V.

CONCLUSIONS

The copolymers of aniline with *m*-ASA, *o*-ASA, and *p*-ASA were prepared electrochemically in acetonitrile solutions containing FSO_3H and investigated with cyclic voltammetry. All the copolymers showed the same electrochemical behavior in neutral and basic solutions. The copolymers prepared contained one sulfonate group per two benzene rings (S/N = 0.5), which was equivalent to 50% doping. The electrodeposited copolymers were soluble in basic aqueous solution and in NMP and DMSO solvents. The dry conductivity values were measured for the copolymers of aniline with *o*-ASA, *m*-ASA, and *p*-ASA.

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