Electrochemical and Electrochromic Behavior of Novel Poly(aniline-*co*-4,4′-diaminodiphenyl Sulfone)

P. Manisankar,*,† C. Vedhi,‡ G. Selvanathan,‡ and R. M. Somasundaram‡

Department of Chemistry, Periyar University, Salem-636 011, Tamil Nadu, India, and Department of Industrial Chemistry, Alagappa University, Karaikudi -630 003, Tamil Nadu, India

Received September 18, 2004. Revised Manuscript Received January 30, 2005

Electroactive conducting copolymers of aniline and 4,4′-diaminodiphenyl sulfone (DDS) were prepared electrochemically. The cyclic voltammetric studies were carried out with different feed concentration of DDS on a glassy carbon electrode surface. The voltammograms exhibited different behavior for different concentrations of DDS. The effect of scan rate and pH on the electroactive copolymer film was studied. The copolymer showed good adherence on the glassy carbon electrode surface and gave a response up to pH 7.0. Spectroelectrochemical analysis of copolymer film was carried out on an indium−tin oxide plate, and it showed multicolor electrochromic behavior when the applied potential was changed. The color of the copolymer was changed from neutral yellow (427 nm) to green (777 nm) and to blue (600 nm) at the concentration of 0.3 M aniline and 0.1 M DDS in 0.1 H_2SO_4 medium. When the DDS concentration changed to 0.5 M, the spectra exhibited the color change from neutral yellow (417 nm) to dark green (723 nm) and to dark blue (650 nm). The copolymer film was characterized by Fourier transform IR spectral data, and the surface morphology was studied using SEM analysis.

Introduction

Among the electroactive organic polymers, polyaniline has occupied prime position due to its high conductivity, good redox reversibility, swift change of color with potential, and stability in environment.[1] Polyaniline retains extensive interest because of the technological applications such as rechargeable batteries, devices, electrocatalysis, microelectronics, smart windows, electrochromic (EC) devices, sensors, electronics, etc.[2−6] ECs are materials which exhibit a different color as a function of applied potential. Both inorganic and organic materials have been used as EC materials. But there is still a lot of scope for further improvement in terms of switching speeds, stability, contrast, and ease of synthesis and processing. Conducting or conjugated polymers have been found to be more promising as EC materials because of their better stability, faster switching speeds, and easy processing compared to the inorganic EC materials.[7] EC materials are highly desirable, as they are the potential candidates for applications in display devices.[8] The conducting polymer films have shown promising applications in the field of biosensors and bioelectrochemistry by providing an active matrix with controlled morphology for immobilization of biological materials as well as transduction of the electrical signal.[9,10] One of the easiest ways to modify an electrode with conducting films is by electropolymerization of the monomer on the electrode surface.[11] Most of the attempts to get electroactive films of the homopolymers of the sulfonated polyelectrolytes by electrochemical polymerization were unsuccessful because both the monomers and the polymers were found to be soluble only in water.[12−14] However, the copolymerization with the unsulfonated monomers resulted in the function of electroactive films. But there is no direct evidence available in the literature to differentiate if the sulfonated monomers were covalently linked or were physically incorporated in the matrix of the unsubsituted homopolymers in these copolymers.[11] The utility of 4,4′-diaminodiphenyl sulfone in epoxy networks was already reported.[15] Poled polyureasulfone thin films having excellent transparency from near-UV to visible region have been prepared by carrying out additional polymerization of 1,4-phenylene diisocyanate and 4,4′-diaminodiphenyl sulfone

---

* To whom correspondence may be addressed. Phone: +91 427 2345766 ext. 218. Fax: +91 427 2345565. E-mail: pms11@rediffmail.com or pmsankarsiva@yahoo.com.

† Periyar University.

‡ Alagappa University.

(1) Oyama, N.; Tatsuma, T.; Sato, T.; Sotomura, T. *Nature* **1995**, *373*, 598.
(2) Gazotti, W. A.; Facz, R.; Depach, M. A. *J. Electroanal. Chem.* **1996**, *415*, 107.
(3) Jelle, B. P.; Hagen, G. *J. Electrochem. Soc.* **1993**, *140*, 3560.
(4) Batich, C. D.; Laitinen, H. A.; Zhou, H. C. *J. Electrochem. Soc.* **1990**, *137*, 883.
(5) Inzelt, G.; Csahok, E.; Kertesz, V. *Electrochim. Acta* **2001**, *46*, 3955.
(6) Inzelt, G.; Pineri, M.; Schultze, J. W.; Vorotyntsev, M. A. *Electrochim. Acta* **2000**, *45*, 2403.
(7) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism; Foundamentals and applications*; VCH: Weinheim, 1995.
(8) Krishnamoorthy, K.; Ambade, A. V.; Kanungo, M.; Contractor A. Q.; Kumar, A. *J. Mater. Chem.* **2001**, *11*, 1.
(9) *Handbook of conducting polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.
(10) Mcquade, D. T.; Pucllen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
(11) Krishnamoorthy, K.; Kanungo, M.; Ambade, A. V.; Contractor, A. Q.; Kumar, A. *Synth. Met.* **2001**, 125, 441.
(12) Zotti, Q.; Musiani, M.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater*. **1998**, *10*, 480.
(13) Zotti, Q.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A. *Chem. Mater.* **1997**, *9*, 2940.
(14) Sundoration, A. A.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *Chem. Comm.* **1987**, 621.
(15) Ritzenthaler, S.; Girard-Reydet, E.; Pascault, J. P. *Polymer.* **2000**, *41*, 6375.

10.1021/cm0483700 CCC: $30.25

simultaneously with poling. The polymerization process is monitored by in situ second harmonic generation.[16]

Copolymerization is a simple way of preparation of new polymers, and it greatly increases the scope of tailor-making materials with specifically desired properties.[17] In comparison with the chemical copolymerization, one of the advantages for the electrochemical copolymerization is that the effect of the applied potential and the monomer concentration ratio on the copolymerization rate and on the copolymerization behavior is readily observable. This is much more favorable for determining the optimum copolymerization conditions. In addition, the copolymerization potential of two different monomers plays an important role in the properties of a copolymer as well as the deposition potential of two different kinds of metallic ion for the electrochemical preparation of a metallic alloy. Changing the monomer concentration ratio[18] can readily control the copolymerization potential of two monomers.

This present work is a copolymerization of aniline with different concentrations of diaminodiphenyl sulfone (DDS) on glassy carbon electrode surface in aqueous medium. The EC behavior of the copolymers and the influence of pH and scan rate were studied. The developed copolymer film was characterized by Fourier transform (FT) IR and scanning electron microscopy (SEM).

Experimental Section

An EG&G M 273A electrochemical analyzer (Princeton Applied Research Corporation) was employed for all the electrochemical experiments. Electrochemical polymerization method was adopted using a three-electrode system. Glassy carbon (GCE) working electrode, Pt foil counter electrode, and saturated calomel (SCE) reference electrodes were used. The spectroelectrochemical studies were carried out in a quartz cuvette with a path length of 1 cm and with an optically transparent working electrode, indium−tin oxide (ITO) plate (10 ohm/cm^2), counter electrode Pt foil, and Ag/Ag$^+$ used as a reference electrode. The instrument employed was a computer-controlled JASCO V-530, UV−vis spectrophotometer. The prepared copolymer was characterized by FTIR spectra using KBr pellets recorded on a Perkin-Elmer 783 spectrophotometer. The polymer film surface morphology was studied by computer-controlled Hitachi S3000 H SEM. Double-distilled aniline (Merck) was used. DDS was prepared[19] by the action of thionyl chloride on acetanilide followed by the oxidation with CrO_3 to its sulfone. DDS was recrystallized from ethanol to white crystals (melting point 178−179 °C). The aqueous supporting electrolyte solutions of 0.1 M concentrated H_2SO_4 (pH 1.0), 0.01 M concentrated H_2SO_4 (pH 2.0), 0.001 M H_2SO_4 (pH 3.0), 0.04 M sodium acetate, and 0.16 M acetic acid (pH 4.0), 0.16 M sodium acetate and 0.14 M acetic acid (pH 5.0), 0.19 M sodium acetate and 0.01 M acetic acid (pH 6.0), and 0.1 M KCl (pH 7.0) were prepared and used. The required values of pH were obtained with the described solutions by mixing a few drops of 0.01 M KOH solution. The pH of the media was measured using a Cyberscan 500 pH meter. All chemicals were analar and purchased from Ranchem. All solutions were made with ultrapure water from TAK-LAB water system. Purging and blanketing of nitrogen were done for analyte solution placed in the electrochemical cell of 25-mL capacity for 20 min under stirred conditions. Then various voltammograms were recorded.

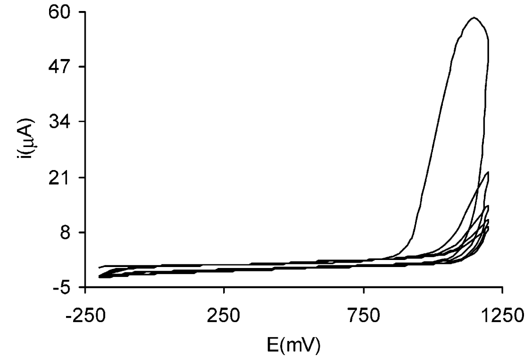

Figure 1. Cyclic voltammetric behavior of 0.5 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

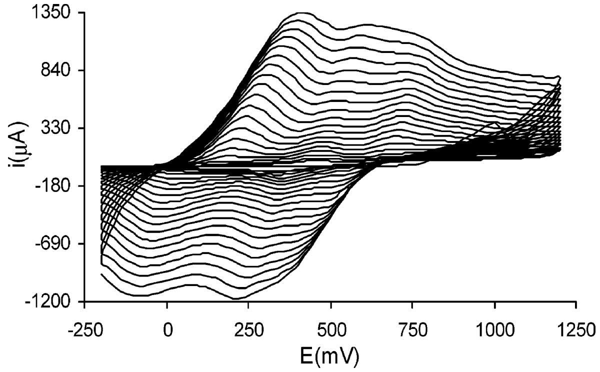

Figure 2. Cyclic voltammetric behavior of 0.3 M aniline on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

Results and Discussion

Copolymerization of Aniline and 4,4′-Diaminodiphenyle Sulfone (Poly(ani-*co*-DDS)). Figure 1 shows the cyclic voltammogram cycled between −0.2 and 1.2 V at the scan rate of 100 mV/sec for the electrochemical oxidation of 0.5 M DDS in 0.1 M H_2SO_4 medium on GCE. The voltammogram exhibited one broad oxidation peak at 1.160 V potential in first cycle. As the cycling process continued, the peak current reduced drastically. The anodic peak is caused by the oxidation of amino group in phenyl ring of DDS in 0.1 M H_2SO_4 medium. The Figure 1 shows that the oxidation current decreases apace with increases in the number of scanning cycles. After the completion of 10 cycles, the working electrode was washed with ultrapure water, and then a light brown film was seen on the surface of the working electrode. This film was thin, and the film growth was inhibited further because of lesser conductivity.

The cyclic voltammogram of 0.3 M aniline in 0.1 M H_2SO_4 medium was shown in Figure 2. The electro-oxidation was on a stationary glassy carbon electrode, the potential ranging from − 0.2 to 1.2 V at a scan rate of 100 mV/sec. The voltammogram showed an anodic peak at 1.0 V and a cathodic peak at 0.34 V in the first cycle.[20] Three anodic peaks at the potentials 0.18, 0.46, and 0.72 V and three

---

(16) Ye, C.; Yu, P.; Wong, G. K. L. *Proc. SPIE* **1996**, *2897*, 183.

(17) Bagheri, A.; Nateghi, M. R.; Massoumi, A. *Synth. Met.* **1998**, *97*, 85.

(18) Shaolin, M. *Synth. Met.* **2004**, *143*, 259.

(19) Manisankar, P.; Sarpudeen, A.; Viswanathan, S. *J. Pharm. Biomed. Anal.* **2001**, *26*, 873.

(20) Gao, M.; Huang, S.; Dai, L.; Wallace, G.; Gao, R.; Wang, Z. *Angew. Chem., Int. Ed.* **2000**, *39*, 3664.

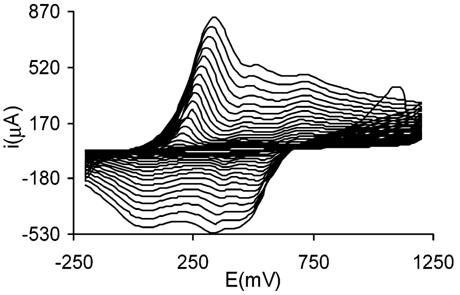

Figure 3. Cyclic voltammetric behavior of 0.3 M aniline and 0.03 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

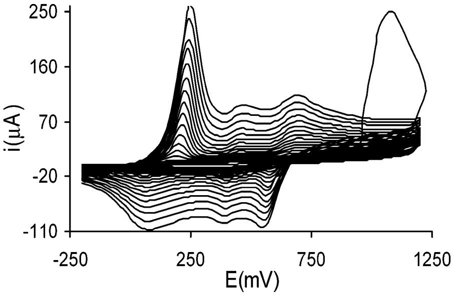

Figure 4. Cyclic voltammetric behavior of 0.3 M aniline and 0.05 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

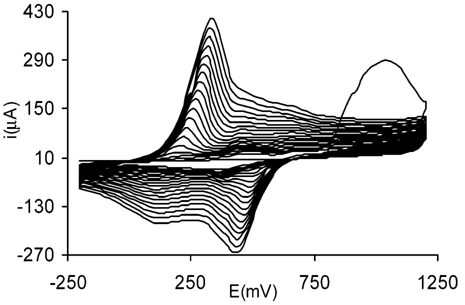

Figure 5. Cyclic voltammetric behavior of 0.3 M aniline and 0.1 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

cathodic peaks at 0.52, 0.34, and 0.02 V were observed. The peak current increased very quickly with increase in the number of cycles. This is probably due to autocatalytic polymerization, which causes quick polyaniline (PANI) film growths as the electrolysis proceeds.[21,22] After completion of the 20th cycle, a green-color polymer film on the working electrode was observed.

The monomers of 0.3 M aniline and 0.03 M DDS were electrolyzed on GCE in 0.1 M H_2SO_4 medium by repeated cycling between −0.2 and 1.2 V. The cyclic voltammogram (Figure 3) shows a broad anodic wave entered at a potential of 1.06 V in the first cycle. The broad oxidation wave indicates the oxidation of both aniline and DDS monomers. As the scanning cycle increased, new peaks on both anodic and cathodic sides were observed. The initial oxidation peak disappeared, and three oxidation peaks at 0.18, 0.46, and 0.66 V and three reduction peaks at 0.52, 0.38, and 0.04 V appeared. Though the peak potentials are closer to that of pure PANI formation, the peak currents and characteristics are different. When the cycling process continued, there was a gradual increase in the amine oxidation peak at potential 0.18 V and the peak became sharper compared to pure PANI formation, whereas the other two anodic peaks showed only small increase in the peak current. Such different type of behavior suggests the copolymerization of both aniline and DDS (ani-*co*-DDS). Since the radical cations of both monomers react with monomers, the chance for the second and third anodic oxidations became less, and hence lesser currents were observed. This type of incorporation of DDS monomer leads to the formation of a random copolymer on the working electrode. The bluish-green-color film seen on the working electrode indicates the difference in the color of the polymer formed.

The typical cyclic voltammogram of 0.3 M aniline and 0.05 M DDS in 0.1 M H_2SO_4 medium is presented in Figure 4. The cycling range and scan rate are the same as previously. The voltammogram exhibited one oxidation peak at 1.067 V in first cycle. When the cycle progressed, the first oxidation peak disappeared and three anodic and three cathodic peaks appeared at the potentials 0.2, 0.46, and 0.68 and 0.56, 0.40, and 0.04 V, respectively. Here also the voltammogram exhibited different behavior from polyaniline. During polymerization, the influence of DDS radical cation concentration changed the potential, current, and peak shape. The oxidation peak is at +0.25V and effectively its intensity increases, starting at the second cycle and growing more and more after with the cycle number. The peak sharpness of the peak also increased with the cycle number. These changes are similar to the previous one, but the overall decrease in peak currents is noticed. The color of the formed polymer exhibited bluer tint. These facts suggest that the incorporation of DDS during the formation of random copolymer cause reduction in conductivity of the polymer.

Figure 5 shows the cyclic voltammetric behavior of 0.3 M aniline and 0.1 M DDS in 0.1 M H_2SO_4 medium. The voltammogram exhibited one oxidation peak at 1.07 V in the first cycle. As the cycling continued, one new oxidation at 0.22 V and two reduction peaks at potentials 0.52 and 0.08 V were observed. The increase in the concentration of DDS monomer led to an overall decrease in the peak currents. The voltammetric behavior of the polymer formation was different from the previous cases. Only one oxidation was predominant, and the other two oxidations were almost unobserved. Increase in the number of cycles increased the oxidation peak current, and the peak became sharper. These behaviors indicate the incorporation of more DDS units compared to the previous concentration studies. The formed copolymer film color changed to peacock blue.

The oxidative copolymerization of 0.3 M aniline and 0.3 M DDS monomer in 0.1 M H_2SO_4 medium was carried out, and the resulted cyclic voltammogram is presented in Figure 6. The voltammogram showed an oxidation peak at 1.08 V in the first cycle, followed by the formation of new anodic peak at 0.2 V in the subsequent cycles. Two reduction peaks at 0.42 and 0.14 mV were also seen in the voltammogram from the second cycle. As previously, here also the oxidation peak current increased with an increase in the number of cycles. The ratio between the cathodic peak currents decreased from the previous cases. An overall decrease in the peak current was noticed. The peacock-blue color of the copolymer film was deepened.

---

(21) Stiwell, D. E.; Park, S. M. *J. Electrochem. Soc.* **1988**, *135*, 2254.
(22) Mu, S. L.; Kan, J. Q. *Electrochim. Acta* **1996**, *41*, 593.

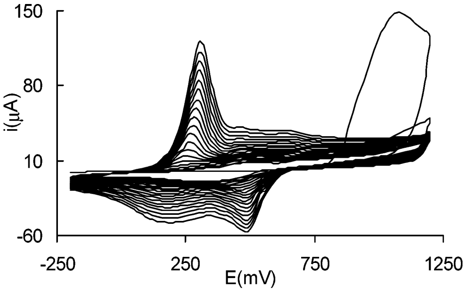

Figure 6. Cyclic voltammetric behavior of 0.3 M aniline and 0.3 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

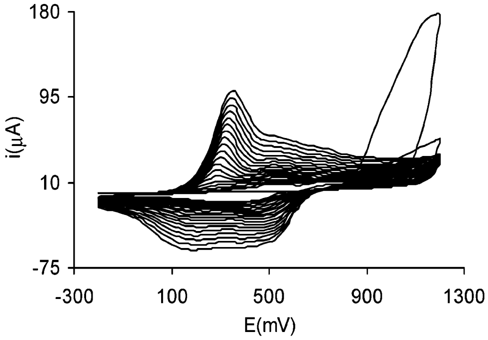

Figure 7. Cyclic voltammetric behavior of 0.3 M aniline and 0.5 M DDS on GCE in 0.1 M H_2SO_4 medium at scan rate 100 mV/s.

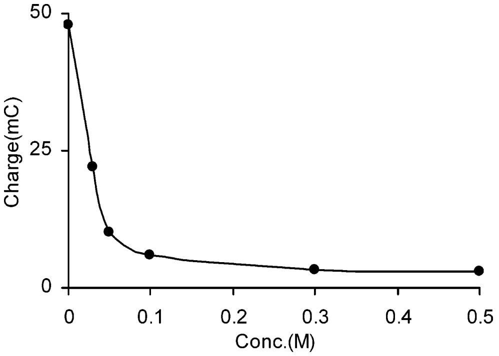

Figure 8. Plot of charge vs concentration.

The cyclic voltammetric behavior of copolymer formation from 0.3 M aniline and 0.5 M DDS in 0.1 M H_2SO_4 medium is shown in Figure 7. The voltammogram exhibited one oxidation peak at 1.160 V in first cycle. One oxidation around 0.26 V and one broad reduction peaks appeared from the second cycle onward. As the number of cycles increased, the polymer growth rate also increased, but the peak currents were considerably reduced. The voltammogram response indicates the influence of DDS cation radical incorporation during copolymerization with aniline. The copolymer film color was violet.

The cyclic voltammetric studies suggest the incorporation of DDS in the copolymer formed, and the copolymer is influenced by the concentration of DDS. The concentration of DDS monomer was plotted against the total charge of the formation of electroactive oxidative conducting copolymer films (Figure 8). The total charges decrease with increase in DDS monomer concentration. There was a sudden decrease in the total charge from PANI formation when 0.03 M DDS was employed. After this, increase in DDS concentration led to a slower decrease rate and at concentrations 0.3 and 0.5 M DDS only little change in total charge was observed. This indicates the incorporation of more and more DDS in the copolymer and decreases the electroactive behavior.

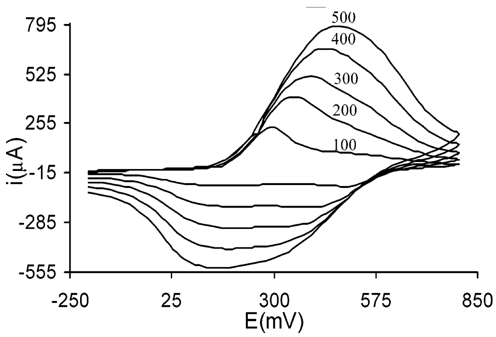

Figure 9. Effect of scan rate variation from 100 to 500 mV/s in 0.1 M H_2SO_4 medium.

Effect of pH. The formed copolymer film was washed with ultrapure water and monomer-free solution of pH 1.0. Then the film was scanned in monomer-free pH 1.0 solution between −0.2 and 0.8 mV. The cyclic voltammogram (Figure 9) resembles that of the electroactive polymer obtained previously. As the scan rate increased, the main oxidation peak current also increased linearly ($i_p = 1.374\nu + 106.8$; $R^2 = 0.9971$), indicating the adherent electroactive copolymer film. Similar studies were carried out at various pHs up to 13.0, but the film responded up to pH 7.0. From the voltammetric studies, it was observed that the peak current decreased with increase in pH, suggesting the involvement of H^+ ion. The effect of pH was studied for film at all concentrations, and similar results were observed.

Spectroelectrochemistry of Poly(ani-*co*-DDS). In situ UV−vis spectroelectrochemistry provides a useful tool for studying the electropolymerization and intermediate products analysis.[23] To study the spectroelectrochemical properties of the copolymer, the copolymer film was electrochemically deposited on an ITO glass plate at a constant potential of 1.2 V vs Ag/Ag^+. To ensure consistent content of electroactive polymer on the electrode surface between polymerizations, the same amount of charge was passed during copolymerization. After deposition, the blue color oxidized ITO adhered films were washed with monomer-free electrolyte solution, before recording the spectra at various applied potentials in 0.1 M H_2SO_4 medium. Since all of the copolymer films are blue in their oxidized state,[24] each was subsequently reduced to determine whether there was a direct correlation between monomer compositions and electrochromic response. As an illustration, the spectra of the copolymer films obtained from 0.3 M aniline and 0.1 M DDS at various applied potentials are presented in Figure 10. When the applied potentials changed from −0.2 to 1.2 V, the spectra exhibited absorption bands at 236 and 290 nm; the former one may be due to a $\pi-\pi^*$ transition, and the latter one may be a benzenoid band. As the applied potential increased to oxidation side, the film color changed from yellow to blue. Apart from these bands, an additional broad band was observed in the visible region. The wavelength maxima of this band depended on the applied potentials. When the

---

(23) Malinauskas, A.; Holze, R. *Electrochim. Acta* **1998**, *43*, 2413.

(24) Gaupp, C. L.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 6305.

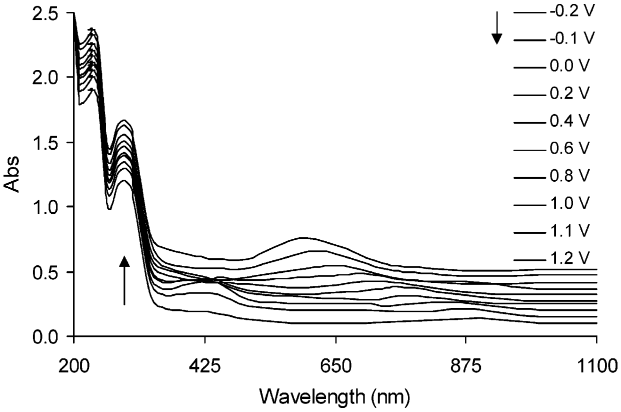

Figure 10. Spectroelectrochemical behavior of 0.3 M aniline and 0.1 M DDS deposited on ITO plate in 0.1 M H_2SO_4 medium with various applied potential.

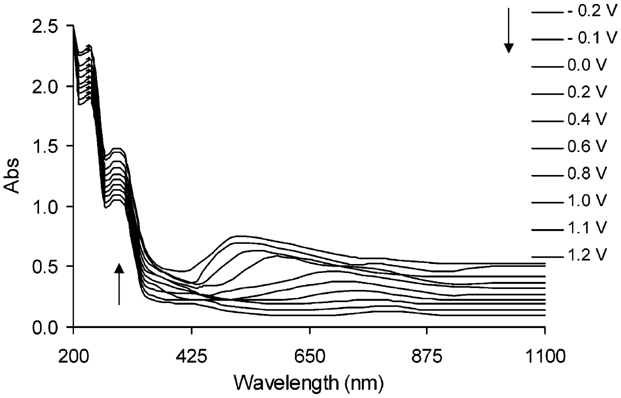

Figure 11. Spectroelectrochemical behavior of 0.3 M aniline and 0.5 M DDS deposited on ITO plate in 0.1 M H_2SO_4 medium with various applied potential.

applied potential changed from −0.2 to 0.0 V, an absorption band was obtained between 400 and 450 nm, exhibiting neutral yellow due to formation of cation radical (polaronic forms). As the potential varied from 0.1 to 0.8 V, the absorption band shifted to the lower-energy side, i.e., a bathochromic shift was observed. The absorption band between 777 and 850 nm may be due to the formation of bipolarons. The copolymer film was a conducting green color film. An absorption band appeared between 600 and 632 nm when the applied potential was varied from 1.0 to 1.2 V. The nonconducting blue film may be because of the fully oxidized copolymer.

The feed ratio of DDS monomer was increased to 0.5 M, and the film was coated as previously. After the deposition, the oxidation film was dark blue in color, indicating the incorporation higher amount of DDS in the copolymer. Here also the $\pi-\pi^*$ transition and benzenoid bands were observed. Figure 11 presents the spectra of the deposited copolymer film at various potentials. The applied potential was varied from −0.2 to 1.2 V. An absorption band between 400 and 450 nm exhibiting yellow color copolymer films was observed when the applied potential was varied between −0.2 to 0.0 V. When the potential changed from 0.2 to 0.6 V, the absorption band was shifted bathochromically to 685−723 nm. The film color was changed from yellow to dark green. An absorption band between 510 and 650 nm due to dark blue colored film was obtained when applied potential was changed from 0.8 to 1.2 V.

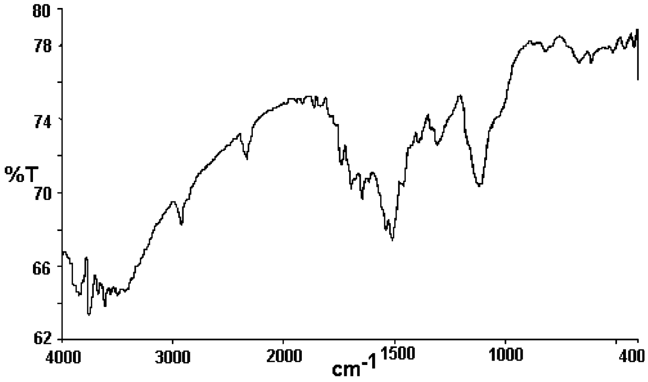

Figure 12. FTIR spectral behavior of poly(ani-*co*-DDS).

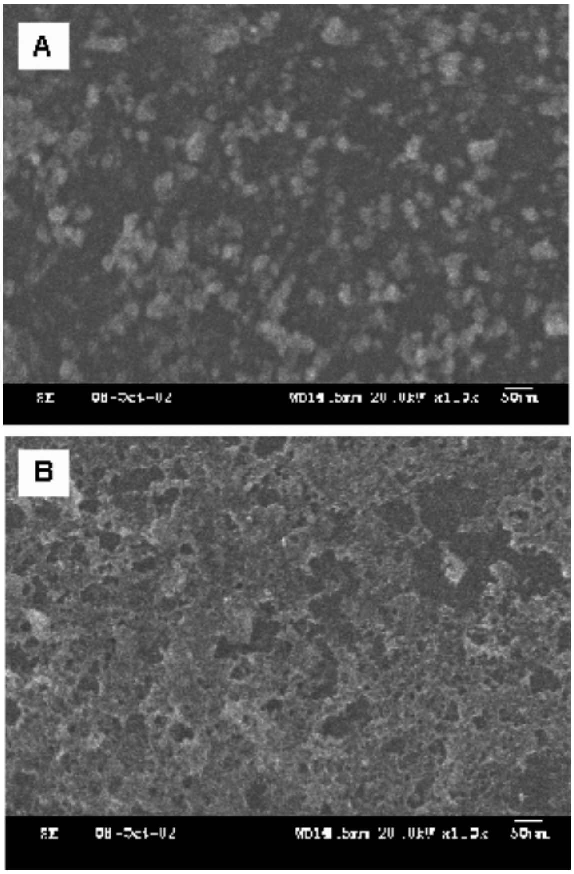

Figure 13. SEM photographs of (A) PANI surface (B) copolymer (ani-*co*-DDS) surface.

FTIR Spectrum and Scanning Electron Microscopy of Poly(ani-*co*-DDS). The FTIR spectrum of poly(ani-*co*-DDS) is shown in Figure 12. The copolymer was deposited on a Pt foil electrode surface by electrochemical oxidation. The peaks observed around 3420 cm^{-1} are attributed to the N—H stretching vibrations since both monomer units contain −NH groups. The copolymer showed peak characteristics of C—N stretching[25,26] in the range 1250−1300 cm^{-1}. The peak at 1311 cm^{-1} probably corresponds to aromatic C—N^+ stretching. Two peaks at 1511 and 1648 cm^{-1} are attributed to the C═C stretching vibrations of the benzene ring and quinone ring vibrations. The occurrence of these two bands clearly shows that these copolymers are composed

---

(25) Planes, G. A.; Morales, G. M.; Miras, M. C.; Barbero, C. *Synth. Met.* **1998**, *97*, 223.

(26) Wen, T. C.; Huang, L. M.; Gopalan, A. *Synth. Met.* **2001**, *123*, 451.

of amine and imine units. The spectra of sulfone S═O stretching vibrations shows a strong peak at 1121 cm^{-1}, and the peak at 2925 cm^{-1} is attributed to the C─H stretching vibrations. These interpretations are in accordance with the reported values for similar systems[25,26] and indicate the formation of copolymer.

Figure 13B shows a SEM photograph of copolymer formed from 0.3 M aniline and 0.1 M DDS monomers in 0.1 H_2SO_4 medium on glassy carbon surface. The poly(ani-*co*-DDS) exhibits a compact surface, and the structure looks more porous ridge morphology. The surface morphologies of the copolymer are different from the medium granular irregular surface structure of PANI (Figure 13A).

Conclusion

The copolymers of aniline and 4, 4′-diaminodiphenyl sulfone have been prepared electrochemically using continuous cycling method in a solution consisting of 0.3 M aniline, 0.1 M H_2SO_4, and different concentrations of 4,4′-DDS. The copolymers formed with different feed concentrations of 4,4′-DDS exhibited different cyclic voltammetric behavior, and various color changes were observed during the copolymerization. The synthesized poly(ani-*co*-DDS) films showed good adherent behavior and were found to be electroactive, but the total charge of poly(ani-*co*-DDS) was lower than that of PANI. The copolymer films responded up to pH 7.0. The multicolor electrochromic behavior of copolymer formed from 0. 3 M aniline and 0.1 M DDS exhibited neutral yellow, green, and blue colors when various potentials were applied. As the DDS feed concentration changed to 0.5 M, the color was changed from yellow to dark green and to dark blue while changing the applied potentials. The formation of copolymer, poly(ani-*co*-DDS), was ascertained from the FTIR and SEM data. These copolymers can be employed as potential candidates in the development of dynamic electrochromic devices and the conducting film can be used as a modified electrode in the development of sensors.

CM0483700