

Electrochemical Preparation of Soluble Sulfonated Polymers and Aniline Copolymers of Aniline Sulfonic Acids in Dimethylsulfoxide

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ABSTRACT: Fully sulfonated polyaniline was produced during the electrochemical polymerization of orthanilic, metanilic, and sulfanilic acids in dimethylsulfoxide (DMSO). The dry conductivity values of the polymers obtained from the above three isomers of aminobenzene sulfonic acids were found to be 0.052, 0.087, and 0.009 S/cm, respectively. Furthermore, partially sulfonated copolymers of these aniline sulfonic acids and aniline were also synthesized electrochemically in DMSO. The dry conductivity values of the copolymers obtained from these three acids were found to be 0.094, 0.26, and 0.033 S/cm, respectively. The polymers and copolymers are soluble in water, DMSO, and N-methyl-

2-pyrrolidone. The structure and properties of these polymers and copolymers were elucidated using cyclic voltammetry, scanning electron microscopy, Fourier transform infrared, elemental analysis, and ultraviolet-visible absorption spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2163–2169, 2003

Key words: self-doped polyaniline; orthanilic acid (*o*-aminobenzene sulfonic acid); metanilic acid (*m*-aminobenzene sulfonic acid); sulfanilic acid (*p*-aminobenzene sulfonic acid); aniline; copolymerization

INTRODUCTION

Sulfonated polyaniline (SPAN) is of interest because of its unusual physical properties, improved processability, and potential industrial applications.^{1–5} SPAN is the first reported self-doped water-soluble conducting polyaniline derivative and a prime model for dopant and secondary dopant-induced processability.^{6,7} The solubility of polyaniline in aqueous solutions and in most common organic solvents is greatly improved by the presence of $-\text{SO}_3^-$ groups.⁸ The environmental stability of the parent polyaniline is also further improved in SPAN. The conductivity of SPAN is independent of external protonation in a broad pH range. SPAN was found to have better thermal stability than its parent polyaniline.⁹

SPAN has been produced by treating chemically synthesized polyaniline with fuming H_2SO_4 .^{1,2} SPAN has also been prepared electrochemically through the copolymerization of aniline with metanilic or orthanilic acid. Lee et al.¹⁰ used a glassy carbon electrode for metanilic acid–aniline copolymer in HClO_4 , and obtained a copolymer with sulfonation of 40% of the aniline rings, using a platinum electrode¹¹ or a carbon electrode in H_2SO_4 .¹²

Wei et al. reported the synthesis and characterization of highly sulfonated polyaniline which had a sulfur-to-nitrogen ratio (S/N) of 0.75, using the reduced form of polyaniline, leucoemeraldine base, as the starting material.¹³ Polymerization of aniline sulfonic acid (ASA) as a monomer was used to produce fully sulfonated polyaniline. It was difficult to make polymers of ASAs alone with a high molecular weight since the reactivity of ASA as a monomer is low due to the presence of the electron attractive sulfonic acid group. It was found that metanilic acid did not polymerize itself and orthanilic acid polymerized with a low yield. The electrooxidation of these acids produced only dense purple oligomers near the electrode. Kitani et al. reported the electropolymerization of metanilic, orthanilic, and sulfanilic acid in H_2SO_4 solution. Deposition of polymeric product onto the Pt electrode surface was not observed during electrolysis. The polymers were obtained by evaporation of the solvent from the polymer dissolved in solution. These polymers were found to dissolve in water and partly dissolve in dimethylsulfoxide (DMSO) and in N-methyl-2-pyrrolidone (NMP).¹⁴ Kilmartin and Wright also electrochemically produced the copolymers of orthanilic acid and aniline¹⁵ and *m*-toluidine¹⁶ in aqueous medium, and found that the electrodeposited films were partly soluble in this medium.

There were some attempts to obtain fully sulfonated polyaniline by using as monomer metanilic acid,^{8,14}

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orthanilic acid,^{10,14} sulfanilic acid,¹⁴ 2,5-diaminobenzene sulfonic acid,¹⁷ 2-methoxyaniline-5-sulfonic acid,⁸ and 2- and 3-cyanoaniline¹⁸ in aqueous media, but no solid films were obtained on the electrode surface.

In this study, fully sulfonated polyaniline was prepared in DMSO by electrochemical polymerization of orthanilic, metanilic and sulfanilic acids. Electrochemical copolymerization of these aniline sulfonic acids with aniline was also achieved in DMSO. The structural and properties of these conducting polymers and copolymers were studied using Fourier transform infrared (FTIR), elemental analysis, and ultraviolet-visible (UV-Vis) methods.

EXPERIMENTAL

Orthanilic acid, metanilic acid, and sulfanilic acid (Aldrich, Milwaukee, WI) were of reagent grade, and were used without further purification. Aniline (Merck, Germany) was vacuum distilled (67°C). Aniline was kept under nitrogen atmosphere. DMSO (Aldrich) was used without any purification and was kept under nitrogen atmosphere. Tetrabutylammonium perchlorate (TBAP) was prepared by reacting concentrated perchloric acid solution (AnalaR, Germany) with a 40% aqueous solution of tetrabutylammonium hydroxide (TBAOH) (Aldrich). It was recrystallized from ethanol several times and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120°C. All electrochemical experiments were carried out under nitrogen atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode [Ag/AgCl sat. (saturated)] and the counterelectrode (Pt spiral). The working electrode for the cyclic voltammetric studies was a Pt disk (area, 0.0132 cm²). The macro-samples of polyaniline films were prepared on a Pt macroelectrode (area, 1.0 cm²). The working microelectrode was cleaned by polishing with Al₂O₃ slurry. The macroelectrode was cleaned by holding it in a flame for a few minutes.

The polymer and copolymer films were prepared by potential scanning electrolysis of anilinesulfonic acid solutions between -0.30 and +1.30 V vs Ag/AgCl (sat.) in DMSO solutions. The bulk solution was poured into a petri glass and then vacuum dried at

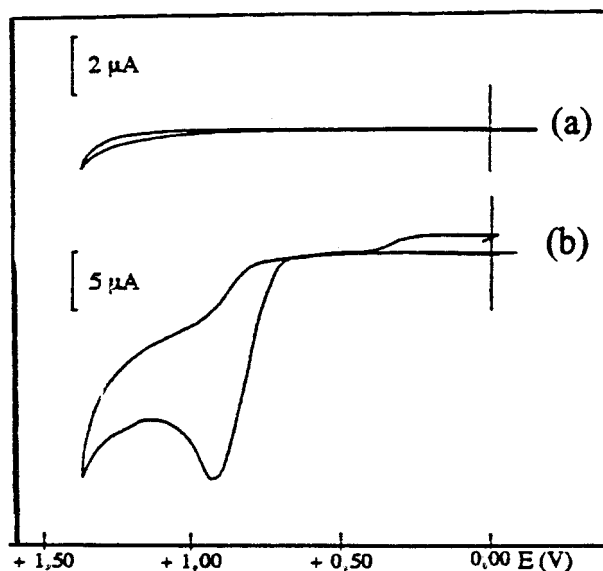


Figure 1 The electrooxidation behavior of (a) 0.1M TBAP and (b) 10 mM ASA + 0.1M TBAP in DMSO on a Pt disk electrode. Scan rate: 100 mV/s.

70°C for 24 h was applied to obtain the solid polymer. All the polymers and copolymers were shiny and dark purple.

The dry conductivity values were measured using a four-point 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 173 Potentiostat coupled to a PAR model 175 Universal Programmer and a PAR model 179 digital coulometer. The current-voltage curves were recorded using a BBC Metrawatt Goerzt X-Y recorder. The structure of the polymers and copolymers were determined by FTIR spectroscopy using a Jasco FTIR 400E and KBr pellets of solid samples. UV-Vis spectra of the copolymer solutions in NMP and DMSO were recorded on a Shimadzu UV-2101 PC spectrophotometer. Elemental composition of the copolymers was determined by Carlo Erba EA1108 Elemental Analysis. Scanning electron microscopy (SEM) pictures of the polymer and copolymer samples were taken using Cam Scan 3.

TABLE I
Solubility and Intrinsic Viscosity Values of the Cast Poly(ASA) Samples in Different Media

	Solubility of the cast film in DMSO (mg/mL)	Solubility of the cast film in NMP (mg/mL)	Solubility of the cast film in 0.1N KOH (mg/mL)	Intrinsic viscosity in DMSO (dL/g)
Poly(<i>o</i> -ASA)	32	26	36	0.139
Poly(<i>m</i> -ASA)	35	28	38	0.129
Poly(<i>p</i> -ASA)	30	22	31	0.069

TABLE II
The S/N Ratio and Dry Conductivity Values of Polymetanilic, Polyorthanilic, and Polysulfanilic Acids Obtained After Oxidative Electrolysis at +1.20 V (vs Ag/AgCl) of 0.1M ASAs in 0.1M TBAP/DMSO

	Sulfur to nitrogen (S/N) ratio	Dry conductivity of the cast film (S/cm)
Poly(<i>o</i> -ASA)	0.96	0.052
Poly(<i>m</i> -ASA)	1.11	0.087
Poly(<i>p</i> -ASA)	0.84	0.009

TABLE 4
The S/N Ratio and Dry Conductivity Values of Poly(aniline-co-ASA) Samples Obtained After Oxidative Electrolysis at +1.20 V (vs Ag/AgCl) of 0.1M ASAs + 0.1M Aniline in 0.1M TBAP/DMSO

	Sulfur to nitrogen (S/N) ratio	Dry conductivity of the cast film (S/cm)
Poly(aniline-co- <i>o</i> -ASA)	0.51	0.094
Poly(aniline-co- <i>m</i> -ASA)	0.39	0.26
Poly(aniline-co- <i>p</i> -ASA)	0.60	0.033

RESULTS AND DISCUSSION

The electrooxidation behavior of metanilic, orthanilic, and sulfanilic acids were first investigated in 0.1M TBAP solution in DMSO using potential cycling between 0.0 and +1.30 V (vs Ag/AgCl). Each of these aniline sulfonic acids gave one oxidation peak at +0.90 V (vs Ag/AgCl) with no corresponding reverse cathodic peak (Fig. 1). The oxidation peak potentials and currents of the monomers did not change upon addition of increasing amounts (up to 20 mM) of HClO₄ to 10 mM monomer solutions in 0.1M TBAP/DMSO medium. The possibility of the formation of inter- and/or intramolecular hydrogen bonding between the sulfonic acid group and the aniline group apparently prevents the interaction between the amine group and the external proton. The hydrogen bonding is thus responsible for the electrooxidation behavior of the monomers in acidic DMSO solution.

During the electrooxidation of aniline sulfonic acids in 0.1M TBAP/DMSO, which was carried out by either a potential cycling between -0.30 and +1.30 V (vs Ag/AgCl) or at a constant applied potential of +1.20 V (vs Ag/AgCl), no polymer film was found to adhere to the electrode surface. Instead, the generation of purple-colored material was observed near the electrode, which diffused away from the surface into the bulk solution, indicating the formation of soluble oligomers or low molecular weight polymers. The bulk solution was then poured into a petri glass after electrolysis and vacuum dried at 70°C for 24 h. Shiny and dark purple solid polymers that dissolved in NMP and water and partially dissolved in tetrahydrofuran was obtained. The solubilities of the samples are given in Table I. The elemental analysis of these poly(aniline

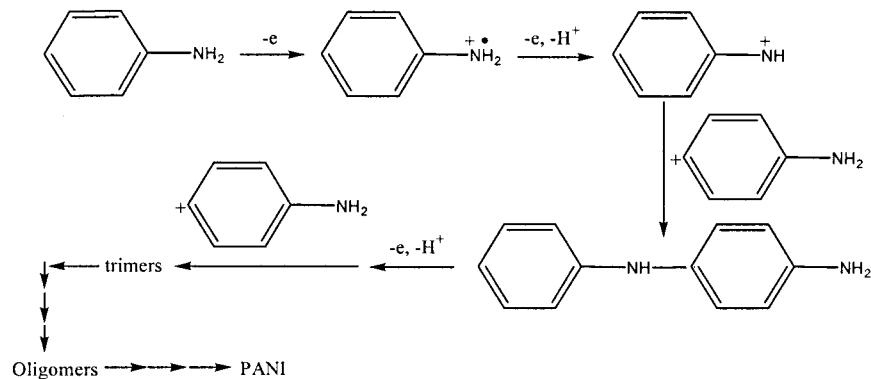
sulfonic acid) samples [poly(ASA)] revealed the S/N ratios, which are tabulated in Table II together with the dry conductivity values. As seen from this table, fully sulfonated polyaniline films were obtained as expected. Lower dry conductivity values compared to those obtained previously in acetonitrile solution containing FSO₃H¹⁹ reflects the fact that much lower molecular weight polymers are produced in DMSO. The intrinsic viscosities of the polymers and copolymers are listed in Tables I and III. These values were measured in DMSO at 25°C. The comparison of our measured intrinsic viscosity values with those reported by Yang et al.²⁰ for polyanilines and by Mav et al.²¹ and Shimizu et al. for sulfonated polyanilines⁸ indicate that the approximate range of weight average molecular weights of our polymers and copolymers are between 6×10³ and 14×10³ g/mol.

Electrolysis of equimolar mixture of aniline and ASAs in 0.1M TBAP/DMSO were also carried out under the same experimental conditions to obtain copolymers of aniline and ASAs. Again, no polymer films were deposited on the electrode surface during electrolyses. The sulfur-to-nitrogen ratios, dry conductivity values, and solubilities of these copolymers are given in Tables III and IV. The sulfur-to-nitrogen ratios of the copolymers are around 0.5, as expected. The dry conductivity values are again low with the exception of the copolymer of aniline with metanilic acid.

As pointed out by Roy et al.,²² the steric effect of SO₃⁻ groups changes the torsional angle between adjacent phenyl rings, thus disturbing the overlapping of orbitals between phenyl π electrons and the nitrogen lone-pair electrons, resulting lower degree of conjugation. The strong electron withdrawing effect of the

TABLE III
Solubility and Intrinsic Viscosity Values of the Cast Poly(aniline-co-ASA) Samples in Different Media

	Solubility of the cast film in DMSO (mg/mL)	Solubility of the cast film in NMP (mg/mL)	Solubility of the cast film in 0.1N KOH (mg/mL)	Intrinsic viscosity in DMSO (dL/g)
Poly(aniline-co- <i>o</i> -ASA)	29	22	33	0.131
Poly(aniline-co- <i>m</i> -ASA)	32	25	35	0.164
Poly(aniline-co- <i>p</i> -ASA)	25	17	27	0.144



Scheme 1

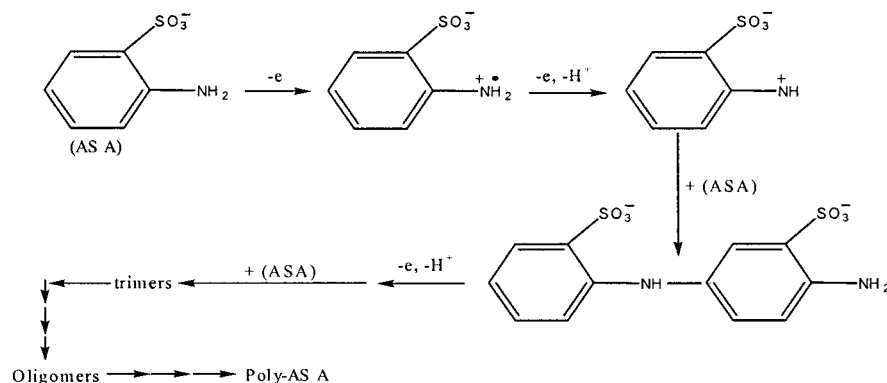
SO_3^- group also causes an additional decrease in conductivity. Furthermore, the large density of SO_3^- groups leading to increased interchange separation and twist of the phenyl rings may lead to stronger interaction between chains, causing disturbance within the charge transport within a single chain.²³

In the accepted mechanism of polyaniline formation, the cation radical, which is primarily formed as the product of the electrooxidation, loses a proton forming a neutral species. The latter dimerizes with another cation radical. As a result of further electrooxidations and proton losses followed by the attacks of the cation radicals, trimers, oligomers, and eventually polyaniline are formed.^{12,24} (See Scheme 1.) During the formation of poly(ASA), the primary species is the cation radical of ASA formed during the electrolysis. (See Scheme 2.) The copolymers of aniline and aniline sulfonic acids are produced with the attack of either the aniline cation radical or the cation radical of aniline sulfonic acids on the intermediate neutral species. Incorporation of aniline sulfonic acid units into the polymer chain prevents the autocatalytic growth of polyaniline, producing less conductive lower molecular weight polymers.

Figure 2 shows the SEM pictures of the cast poly(*m*-ASA) [Fig. 2(a)] and poly(aniline-co-*m*-ASA) [Fig. 2(b)]; the highest conductivity is understandable from

these pictures. As is evident from these pictures, poly(aniline-co-*m*-ASA) is much less porous than poly(*m*-ASA), giving rise to a higher conductivity value. The difference in morphology between these two films stems from the fact that the cast poly(*m*-ASA) has an S/N ratio of about 1.0, which causes inhibition of fibrillar structure forming colloidal aggregates,²⁵ whereas the cast poly(aniline-co-*m*-ASA) has an S/N ratio of about 0.4, forming preferably a fibrillar structure.

The FTIR spectra of poly(ASA) and poly(aniline-co-ASA) powders in KBr tablet form were measured and are seen Figure 3 and Figure 4, respectively. The peaks at 1170 cm^{-1} are due to CH in-plane deformation.²⁶ The peaks at 1580 and 1400 cm^{-1} correspond to the stretching of the benzenoid and quinoid units in a polyaniline (PANI)-like structure.²⁷ The absorption bands at 1400 and 1200 cm^{-1} are characteristic of the aromatic CN stretching.²⁸ The peak at 1040 cm^{-1} , which is due to $\text{S}=\text{O}$ stretching confirms the presence of sulfonate group in the polymers.²⁹ The $\text{S}-\text{O}$ stretching bands are seen at 700 cm^{-1} , and the peaks at 630 cm^{-1} are responsible for the $\text{C}-\text{S}$ stretching vibrational mode. These absorptions of maxima at 1170 , 1040 , 700 , and 630 cm^{-1} are consistent with the presence of SO_3^- groups attached to the aromatic rings.³⁰



Scheme 2

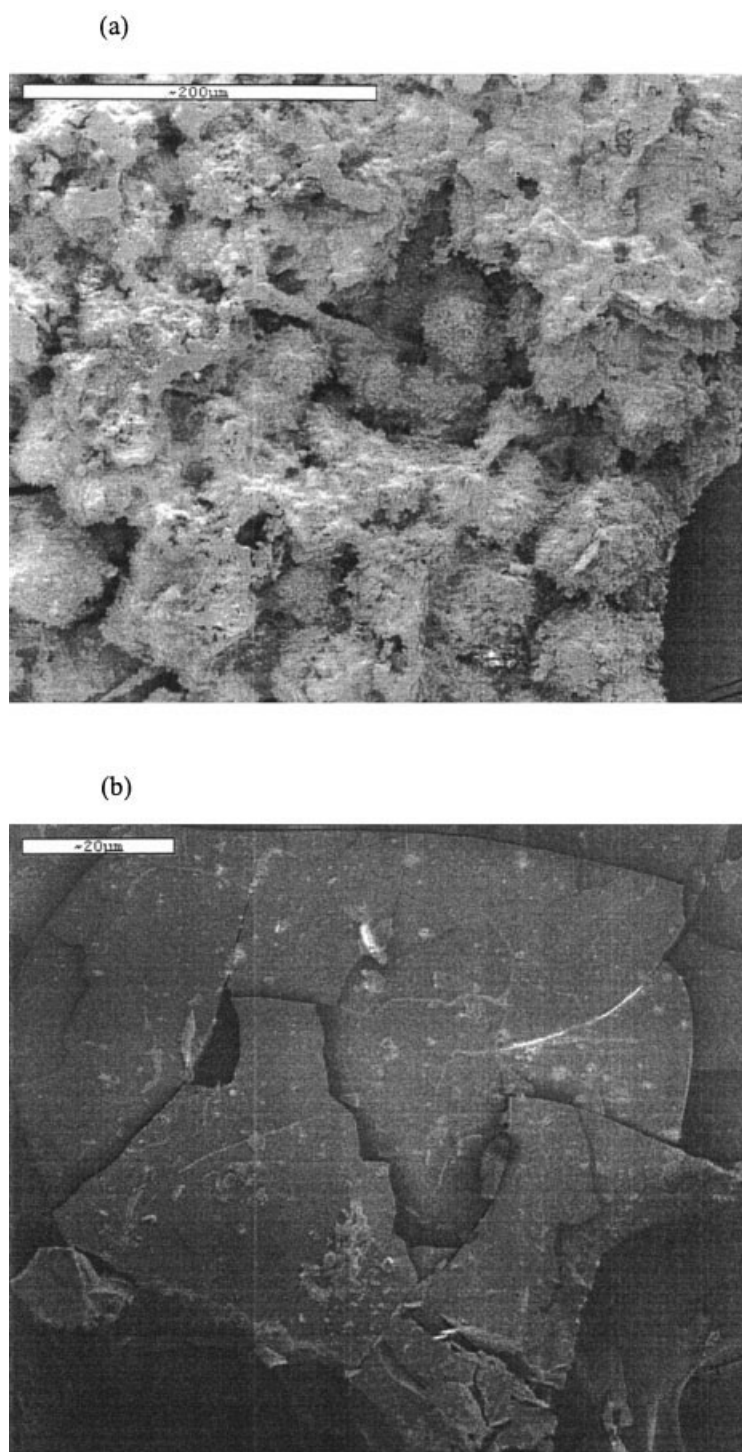


Figure 2 SEM pictures of the cast (a) poly(*m*-ASA) and (b) poly(aniline-co-*m*-ASA).

The UV-vis spectra of poly(ASA) and poly(aniline-co-*m*-ASA) solutions in DMSO are shown in Figure 5(a) and Figure 5(b), respectively. The spectra are dominated by two broad absorption bands at 300–350 nm (peak 1) and at 580–650 nm (peak 2) in DMSO solution. According to the general practice of peak assignment, peak 1 is attributed to the π - π^* transition of the benzenoid moieties in the polymer linear struc-

ture or simply to the bandgap of the polymer.³¹ The broad band around 580–650 nm could be attributed to the intramolecular π - π^* transition of benzenoid to quinoid units in the polymer structure.³² All of the polymers and copolymers show the same characteristic spectrum. The wavelengths of the absorption band maxima of copolymers are longer than those of poly(ASA), possibly because of the changes in the degrees of sulfon-

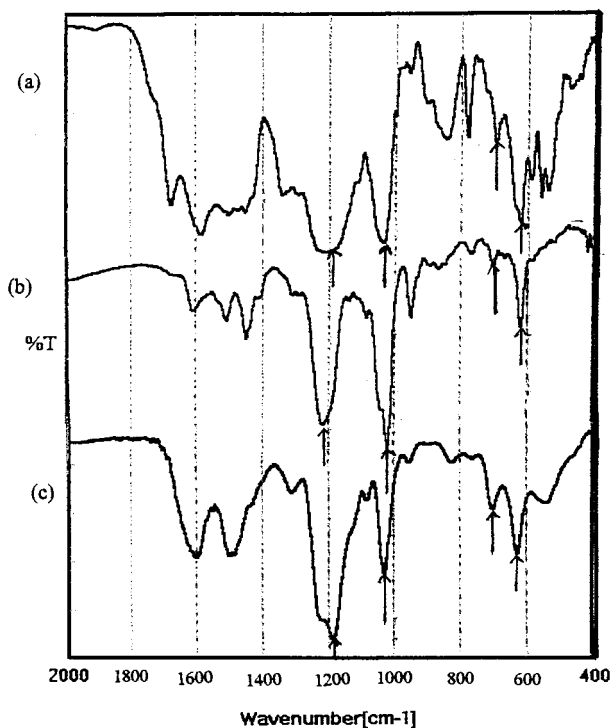


Figure 3 Baseline-corrected FTIR spectra, showing 2000–400 cm^{-1} region, of the (a) poly(*o*-ASA), (b) poly(*m*-ASA), and (c) poly(*p*-ASA).

ation. The steric effect of the SO_3^- groups which changes the torsional angles between the adjacent phenyl groups lowering the degree of conjugation and thus decreasing the conductivity value also controls the position of the band maxima. The band maxima show a blue shift with the increase in S/N ratio value for poly(*m*-ASA) [Fig. (5a)]. The decrease in S/N ratio to about 0.4 in poly(aniline co-*m*-ASA) results a red shift [Fig. 5(b)].

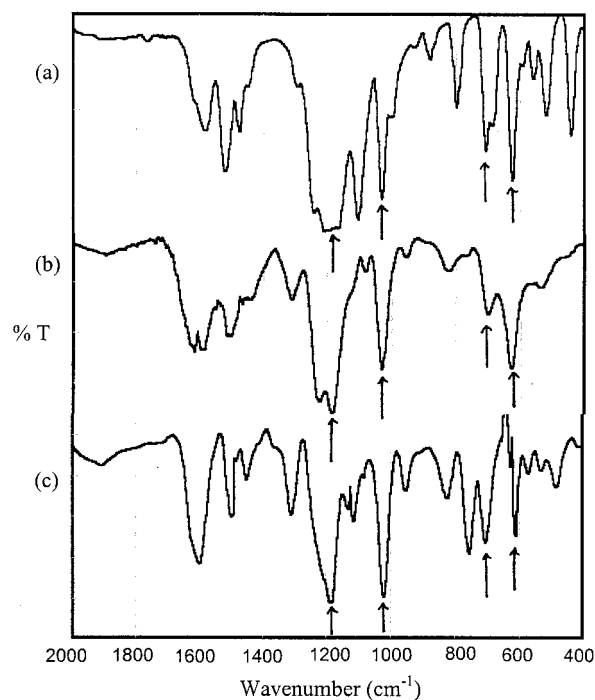


Figure 4 Baseline-corrected FTIR spectra, showing 2000–400 cm^{-1} region, of the (a) poly(aniline-co-*o*-ASA), (b) poly(aniline-co-*m*-ASA), and (c) poly(aniline-co-*p*-ASA).

CONCLUSION

It can be concluded that soluble polymers of ASAs and copolymers of aniline and ASAs can be obtained during the electrooxidative polymerization of the corresponding monomers or monomer mixtures. No electrodeposition of the corresponding polymers and copolymers occurs in the 0.1M TBAP/DMSO medium during electropolymerization. The use of strong acid such as FSO_3H is not required when DMSO is used as a solvent, as was the case in acetonitrile.¹⁹

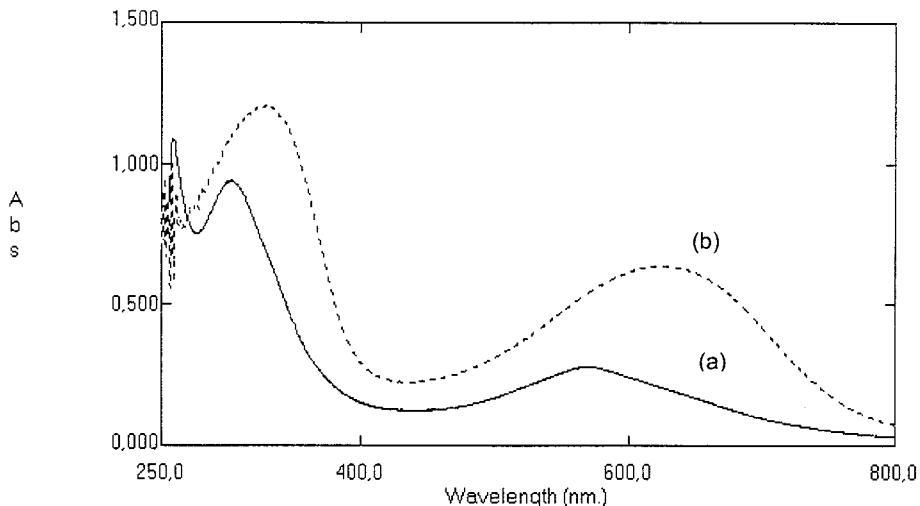


Figure 5 UV-Vis absorption spectra of the cast (a) poly(*m*-ASA) and (b) poly(aniline-co-*m*-ASA) in DMSO.

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References

1. Yue, J.; Epstein, A. J. *J Am Chem Soc* 1990, 112, 2800.
2. Yue, J.; Wang, A. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J Am Chem Soc* 1991, 113, 2665.
3. Yue, J.; Gordon, G.; Epstein, A. J. *Polymer* 1992, 33, 4409.
4. Barbero, C.; Miras, M. C.; Koetz, R.; Haas, O. *Synth Met* 1993, 55, 1539.
5. Ferreira, M.; Rubner, M. F. *Macromolecules* 1995, 281, 7107.
6. MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1994, 65, 103.
7. Cao, Y.; Heeger, A. J. *Synth Met* 1993, 52, 193.
8. Shimizu, S.; Saitoh, T.; Uzawa, M.; Yuasa, M.; Yano, K.; Maruyama, T.; Watanabe, K. *Synth Met* 1997, 85, 1337.
9. Yue, J.; Epstein, A. J.; Zhong, Z.; Gallogher, P. K.; MacDiarmid, A. G. *Synth Met* 1991, 41, 765.
10. Lee, J. Y.; Cui, C. Q.; Su, X. H.; Zhou, M. S. *J Electroanal Chem* 1993, 360, 177.
11. Lee, J. Y.; Su, X. H.; Cui, C. Q. *J Electroanal Chem* 1994, 367, 71.
12. Lee, J. Y.; Cui, C. Q. *J Electroanal Chem* 1996, 403, 109.
13. Wei, X. L.; Wang, Y. Z.; Long, S. M.; Bobeczko, C.; Epstein, A. J. *J Am Chem Soc* 1996, 118, 2545.
14. Kitani, A.; Satoguchi, K.; Tang, H. Q.; Ito, S.; Sasaki, K. *Synth Met* 1995, 69, 129.
15. Kilmartin, P. A.; Wright, G. A. *Synth Met* 1999, 88, 153.
16. Kilmartin, P. A.; Wright, G. A. *Synth Met* 1999, 88, 163.
17. Tang, H.; Kitani, A.; Yamashita, T.; Ito, S. *Synth Met* 1998, 96, 43.
18. Ranger, M.; Leclere, M. *Synth. Met* 1997, 84, 85.
19. Şahin, Y.; Pekmez, K.; Yildiz, A. *Synth Met* 2002, 129, 107.
20. Yang, D.; Adams, P. N.; Mattes, B. R. *Synth Met* 2001, 119, 301.
21. Mav, I.; Zigon, M.; Sebenik, A. *Synth Met* 1999, 101, 717.
22. Roy, B. C.; Gupta, M. D.; Bhoumik, L.; Ray, J. K. *Synth Met* 2002, 130, 27.
23. Lee, W.; Du, G.; Long, S. M.; Epstein, A. J.; Shimuzu, S.; Saitoh, T.; Uzawa, M. *Synth Met* 1997, 84, 807.
24. Tang, H.; Kitani, A.; Ito, S. *Electrochim Acta* 1997, 42, 3421.
25. Wu, Q.; Wu, L.; Qi, Z.; Wang, F. *Synth Met* 1999, 105, 13.
26. Chiang, J. C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
27. Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth Met* 1986, 16, 305.
28. Tang, H.; Jing, X.; Wang, B.; Wang, F. *Synth Met* 1988, 24, 231.
29. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991.
30. Yue, J.; Epstein, A. J.; MacDiarmid, A. G. *Mol Cryst Liq Cryst* 1990, 189, 255.
31. Lee, J. Y.; Cui, C. Q. *J Electroanal Chem* 1996, 403, 109.
32. McCall, R. P.; Ginder, J. M.; Leng, J. M.; Ye, H. Y.; Manohar, S. K.; Astruias, G. E.; MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1997, 84, 97.