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A new self-doped copolymer consisting of 3-methyl thiophene and aniline units

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Abstract The copolymer films of sulfonated aniline and sulfonated 3-methyl thiophene were synthesized by electrochemical polymerization. The sulfonated copolymer films have better solubility in DMSO and KOH than the corresponding homopolymers. The conductivity of the copolymer films increase with the increase in the number of thiophene rings in the polymeric backbone. Copolymer films synthesized were investigated by cyclic voltammetry, UV-visible and FT-IR spectroscopy, dry conductivity and intrinsic viscosity measurements and elemental analysis. The elemental analysis and UV-visible spectroscopic results show that copolymer films have properties intermediate between the two homopolymers.

Keywords Copolymerization · Conducting polymers · Polyaromatics · Self-doped polymer · Solubility

Introduction

The discovery of electronically conducting polymers offers a promise to open many new applications for polymeric materials. In particular, polythiophene, polyaniline and polypyrrole have attracted attention. But all of these conducting polymers are insoluble and infusible which makes practical applications rather difficult. Recently, two chemical approaches have been considered to overcome this problem. First, soluble conducting polymers having long alkyl hydrocarbon chains at a β -position of the heterocycle rings or self-doped polymer films have been prepared. Secondly, soluble conducting copolymers of two different heterocycles have been obtained.

Elsenbaumer and co-workers reported the synthesis of the first class of soluble conjugated polymers in 1986, which can be rendered conductive upon chemical or electrochemical doping [1]. These soluble polymers were poly(3-alkylthiophenes), which were obtained by derivatization of the β -position of the thiophene ring with alkane substituents. Analogous soluble polyaniline derivatives have been more elusive, although several organic solvent soluble alkyl ring- and *N*-substituted-poly(anilines) have been prepared [2]. Contrary to alkyl ring-substituted polyanilines which are limited to low molecular mass polymers ($< 10,000$), [3], high molecular weight ($> 100,000$) polymers that are soluble in common solvents can be chemically synthesized with *N*-alkyl substituents [4].

The good solubility of the poly(3-alkylthiophenes) is contrasted with polythiophene and poly(3-methyl thiophene), which are not soluble at all [5]. Although incorporation of the side-groups on conjugated polymer chains increases their processability, it was anticipated that derivatization of the polymer backbone would affect conductivity by modifying the planarity of the backbone, thus interfering with electron transport along, and between, polymer chains [6]. Recently, scientists were able to enhance the processability of conducting polymers without using substituted alkyl groups. Since the dopant (sulfonate groups) is covalently bonded to the chain, such conjugated systems were named as self-doped conducting polymers [7–9]. The self-doping mechanism of these polymers was simply explained in terms of the potential counterions being covalently bound to the polymer chain and the charge injected into the π -electron system of the polymer being compensated by H^+ (or Na^+ , Bu_4N^+) ions migration, leaving behind the oppositely charged counterion [10, 11].

First soluble ring sulfonated polyaniline (SPAN) was obtained by McDiarmid and co-workers via chemical synthesis [12, 13]. This polymer had a wide range of solubility values which improved the processability of the polymer. Elemental analysis and spectroscopic data showed that approximately half of the phenyl rings in

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the polymer were monosubstituted by $-\text{SO}_3^-$ groups. DC conductivity of highly sulfonated polyaniline was found to be unaffected by the pH over the range 0–14 [14]. Water soluble polyaniline (N-propyl-sulfonic acid) was also synthesized by derivatization of polyaniline and multiple and reversible color changes were observed for the polymer film on ITO electrode dipped in acetonitrile solution [2].

Copolymerisation has received extensive interest because of its high potential for modifying the physical properties of these polymers, providing materials with intermediate properties between two polymer systems, and creating soluble copolymers of heterocycles. The polymers with better film-forming properties (molecular weight ca. 35,000) and higher conductivities ($1\text{--}5\text{ ohm}^{-1}\text{ cm}^{-1}$) were produced by random copolymerisation of 3-methyl thiophene and 3-*n*-butylthiophene [15]. Solubility at room temperature decreased and the glass transition temperature increased as the content of 3-methylthiophene in the copolymer. Conducting copolymer of 3-methyl thiophene and methyl methacrylate exhibiting good solubility and thermal stability were prepared by Nalwa [16]. Copolymerization of 3-methyl thiophene and methyl methacrylate through two different reaction sequences generated two processible conductive copolymers which exhibited different optical, electrical and electrochemical properties [17].

In this paper, we present results that are related to the electrochemically synthesized self-doped (3-methyl thiophene–aniline) copolymer films. The cyclic voltammograms, conductivity values, thermal analysis results, and spectroscopic results of these copolymers are reported. Elemental analysis and solubility data confirm that sulfonated copolymer films were obtained by electrochemical oxidative synthesis.

Materials and methods

Thiophene and aniline were vacuum-distilled and was kept under nitrogen atmosphere. Anhydrous fluoro-sulfonic acid (FSO_3H , triple-distilled, Aldrich) was used as sulfonation reagent. The procedure used to purify acetonitrile (Merck) has been described elsewhere [18, 19]. Acetonitrile, concentrated monomer solutions and anhydrous acid were kept in darkness under a nitrogen atmosphere. Tetrabutylammoniumperchlorate (TBAP) was prepared by reacting a 30% aqueous solution of perchloric acid (Analar) with a 40% aqueous solution of tetrabutylammoniumhydroxide (Aldrich). It was recrystallized from ethanol–water mixture and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120 °C. Electrochemical measurements were carried out under a nitrogen (BOS) atmosphere in a three-electrode type cell with separate compartments for the reference electrode (Ag, AgCl(sat) in acetonitrile) and the counter electrode (Pt spiral). The acetonitrile/0.1 M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode which was

cleaned by polishing with Al_2O_3 slurry for the cyclic voltammetric studies was a Pt disc (area, 0.0132 cm^2). The macrosamples of copolymer films were prepared on a Pt macroelectrode (area, 1.0 cm^2), which was cleaned 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 TBAP and soluble oligomers and vacuum dried. The pellets from the films were obtained under a pressure of 3 ton cm^{-2} . The dry conductivity values were measured using a four-probe technique at room temperature. Gold-plated probes were used to avoid any errors that might arise from the ohmic contacts. At least, ten different current values were used in the measurement of the potential drop.

The electrochemical instrumentation consisted of a PAR model 273 potentiostat–galvanostat. The current–voltage curves were recorded using a BBC Metrawatt Goertz X–Y recorder. UV-visible spectra of the polymer solution in dimethyl sulfoxide (DMSO) was recorded on Jasco V-530 UV-VIS spectrophotometer. The FT-IR spectra of the polymer was taken using Mattson 1000 FT-IR spectrophotometer. Elemental composition of the polymers were determined by LECO CHNS-932 elemental analyzer. Scanning electron microscopy (SEM) photograph of the films were taken by JMS 6400 Scanning Electron Microscopy. The nuclear magnetic resonance (NMR) spectra were measured in $\text{DMSO-}d_6$ on a Bruker 400 MHz spectrometer.

Results and discussion

Cyclic voltammetric behavior of 100 mM FSO_3H in acetonitrile/0.1 M TBAP solution was investigated in a previous study [8, 9]. The anodic limit of that solution was found to be +2.50 V vs. Ag/AgCl. This limit is quite suitable for the electrooxidation of 3-methyl thiophene (oxidation peak potential is at +1.60 V vs. Ag/AgCl) and that of aniline (oxidation peak potential is at +0.96 V vs. Ag/AgCl).

An amount of 100 mM aniline and 25 mM FSO_3H was added to acetonitrile solution containing 0.1 M TBAP. The sulfonated polyaniline film was synthesized in this solution at a constant applied potential of +1.4 V vs. Ag/AgCl. The cyclic voltammetric response of polymer film obtained is given in Fig. 1a. As seen from this figure, polyaniline has an oxidation peak potential of +0.3 V vs. Ag/AgCl. Using acetonitrile solution containing 200 mM 3-methyl thiophene, 25 mM FSO_3H and 0.1 M TBAP the sulfonated poly(3-methyl thiophene) film was synthesized at a constant applied potential of +1.4 V vs. Ag/AgCl. Sulfonated poly(3-methyl thiophene) has an oxidation peak potential of +0.8 V vs. Ag/AgCl as seen in Fig. 1b. After the charges consumed during the deposition of the sulfonated polyaniline and sulfonated poly(3-methyl thiophene) films reached the value of 15 mC the electropolymer-

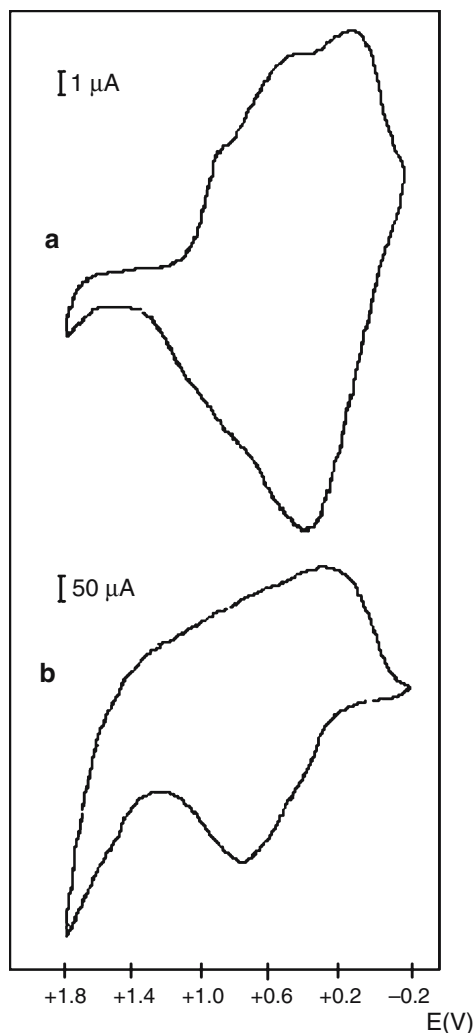


Fig. 1 The blank solution (acetonitrile/0.1 M TBAP) cyclic voltammometric response of the polymer film obtained in an acetonitrile solution containing **a** 100 mM aniline, 25 mM FSO_3H /0.1 M TBAP, **b** 200 mM 3-methyl thiophene, 25 mM FSO_3H /0.1 M TBAP

izations were terminated. In order to obtain 3-methyl thiophene/aniline copolymer, varying amounts of thiophene were added to acetonitrile solution containing 100 mM aniline, 25 mM FSO_3H and 0.1 M TBAP. The

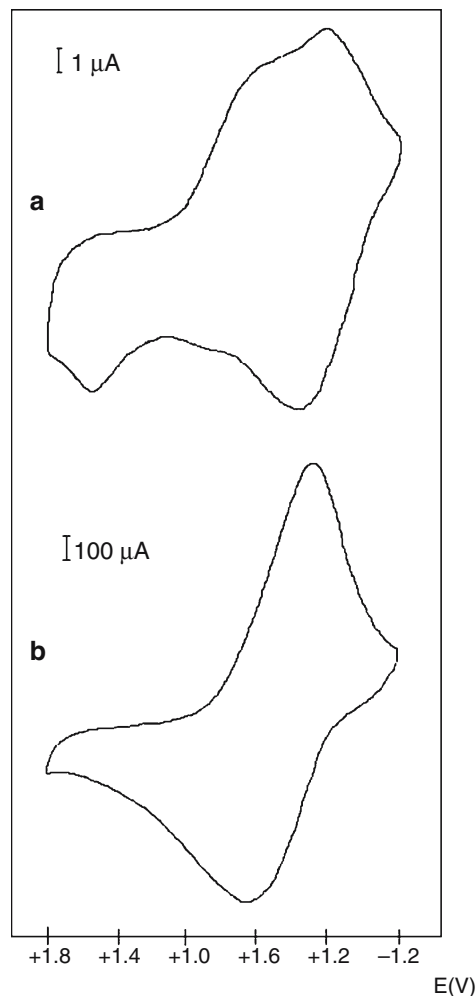


Fig. 2 The blank solution (acetonitrile/0.1 M TBAP) cyclic voltammometric response of the polymer film obtained in an acetonitrile solution containing **a** 100 mM aniline, 25 mM FSO_3H and 150 mM 3-methyl thiophene/0.1 M TBAP, **b** 100 mM aniline, 25 mM FSO_3H and 250 mM 3-methyl thiophene /0.1 M TBAP. Scan rate: 100 mV/s

electropolymerization was carried out at a constant potential of +1.4 V vs. Ag/AgCl until 15 mC charge was consumed during the polymerization. Figure 2a shows the electrochemical behavior of a polymer film obtained from acetonitrile solution containing 100 mM

Table 1 The S/N ratios and the dry conductivity values of the polymer films obtained from the acetonitrile/0.1 M LiClO_4 solutions containing 100 mM aniline, 25 mM and different concentrations of 3-methyl thiophene

Polymer	Signal to noise ratio		Conductivity (S cm^{-1}), freshly prepared film
	Freshly prepared film	Reduced film	
100 mM An	–	–	0.034
100 mM An + 25 mM HSO_3F	0.20	0.25	1.4
100 mM An + 25 mM HSO_3F + 100 mM 3-MTy	4.9	5.1	2.3
100 mM An + 25 mM HSO_3F + 150 mM 3-MTy	5.8	5.9	3.3
100 mM An + 25 mM HSO_3F + 200 mM 3-MTy	6.2	6.8	5.4
100 mM An + 25 mM HSO_3F + 250 mM 3-MTy	6.7	7.1	8.5
100 mM An + 25 mM HSO_3F + 300 mM 3-MTy	10	11	12
200 mM 3-MTy + 25 mM HSO_3F	–	–	56
200 mM 3-MTy	–	–	72

aniline, 25 mM FSO_3H and 150 mM 3-methyl thiophene. The electrochemical behavior of this electrodeposited film was studied by potential cycling between -0.20 V and $+1.80$ V vs. Ag/AgCl in 0.1 M acetonitrile solution of TBAP (blank solution). It is clearly seen that there are two oxidation peaks of $+0.4$ and $+1.5$ V vs. Ag/AgCl. The polymer film obtained using 250 mM 3-methyl thiophene, 100 mM aniline and 25 mM FSO_3H in acetonitrile/0.1 M TBAP solution, showed only one oxidation peak with a peak potential of $+0.6$ V vs. Ag/AgCl as seen in Fig. 2b. The integrated oxidation charges obtained from blank solution cyclic voltammograms are also calculated. For the homopolymers of aniline and 3-methyl thiophene 0.056 C and 1.3 mC were measured from Figs. 1a and 1b as oxidation charges, respectively. From the cyclic voltammogram of the copolymers (Figs. 2a, 2b) 0.046 C and 4.5 mC were obtained as oxidation charges. The copolymer in Fig. 2a did not produce significantly different electroactivity as the aniline homopolymer in Fig. 1a. This copolymer consists of more aniline units than the copolymer in Fig. 2b as seen from the S/N ratios in Table 1. On the other hand, the oxidation charge value of the copolymer in Fig. 2b is about two orders of the magnitude greater than that of the aniline homopolymer and the copolymer in Fig. 2a. The oxidation charge value of this latter copolymer is about three times greater than that of 3-methyl thiophene homopolymer.

In addition to this significant increase in electroactivity, the copolymer in Fig. 2b is more reversible than the 3-methyl thiophene copolymer in Fig. 1b. Furthermore, the 3-methyl thiophene homopolymer starts to be overoxidized beyond $+1.4$ V vs. Ag/AgCl whereas there is no over oxidation current for the copolymer in Fig. 2b up to $+1.8$ V vs. Ag/AgCl.

Elemental analyses of the 3-methyl thiophene/aniline copolymer films obtained from 0.1 M acetonitrile solutions of 100 mM aniline and 25 mM FSO_3H containing different concentrations of thiophene (25–300 mM) were carried out. Since the $-\text{SO}_3^-$ groups can also be present as counter anions in the positively charged self-doped copolymer the S/N ratios of the freshly prepared form and electroreduced form of the copolymer films are listed in Table 1. As is evident from these ratios, increasing number of 3-methyl thiophene units are incorporated in the polymeric structure with increasing 3-methyl thiophene concentration in electropolymerization solution.

It is known from the previous results that sulfonation of poly(3-methyl thiophene) and polyaniline backbone causes a decrease in dry conductivity values and an increase in the solubilities in organic solvents [7, 9]. The dry conductivity values of sulfonated polyaniline vary between 14.6 S cm^{-1} and 1.2 S cm^{-1} , sulfonated poly(3-methyl thiophene) 56 and 19 S cm^{-1} depending on the S/N ratio (degree of sulfonation).

Dry conductivity values of the copolymer films were also measured. Table 1 lists the changes in dry conductivity values with increasing 3-methyl thiophene con-

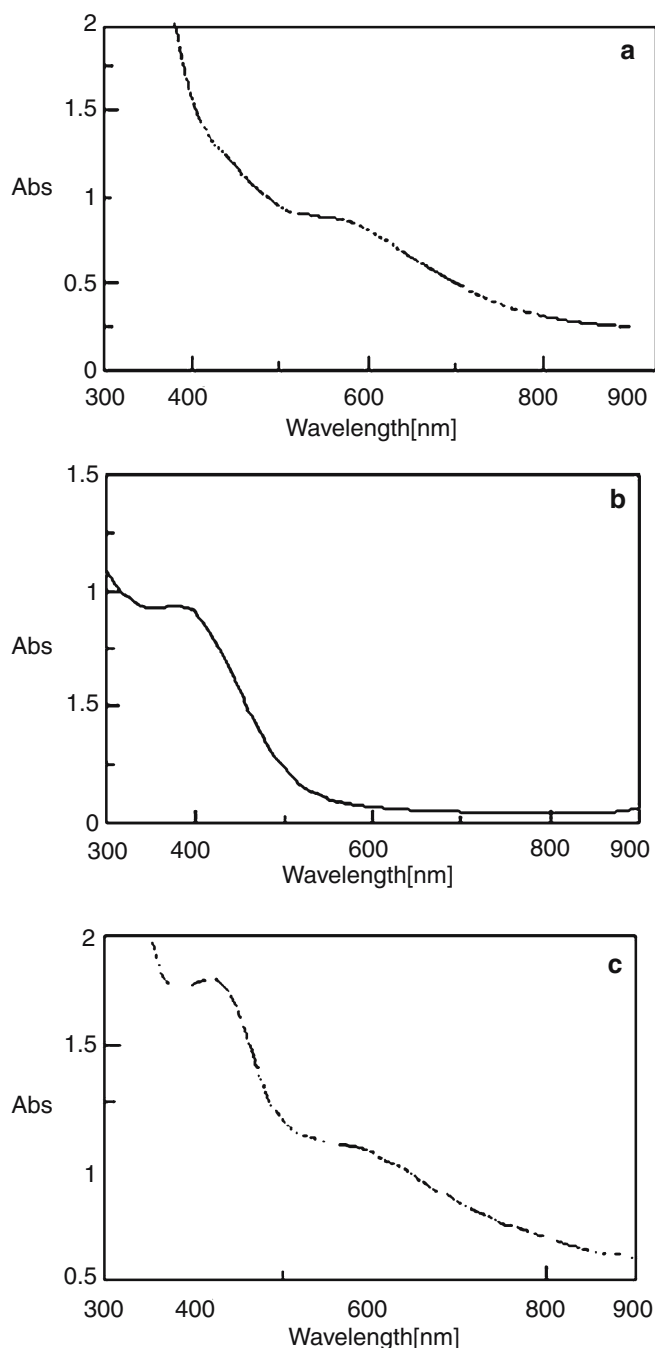


Fig. 3 UV-Vis absorption spectra of the polymers dissolved in DMSO **a** sulfonated polyaniline, **b** sulfonated poly(3-methyl thiophene), **c** sulfonated (3-methyl thiophene/aniline) copolymer

centration in electrolysis solution. The conductivities of the sulfonated copolymer, vary between 2.3 S cm^{-1} and 12 S cm^{-1} depending on the S/N ratio.. The solubility values of the sulfonated copolymers in DMSO and KOH solutions are about two to three times more than those of the sulfonated homopolymers [7, 9].

Since the contribution to the conductivity from poly(3-methyl thiophene) is far more than that of polyaniline, the conductivity values increase with the incorporation of nonsulfonated 3-methyl thiophene ring units

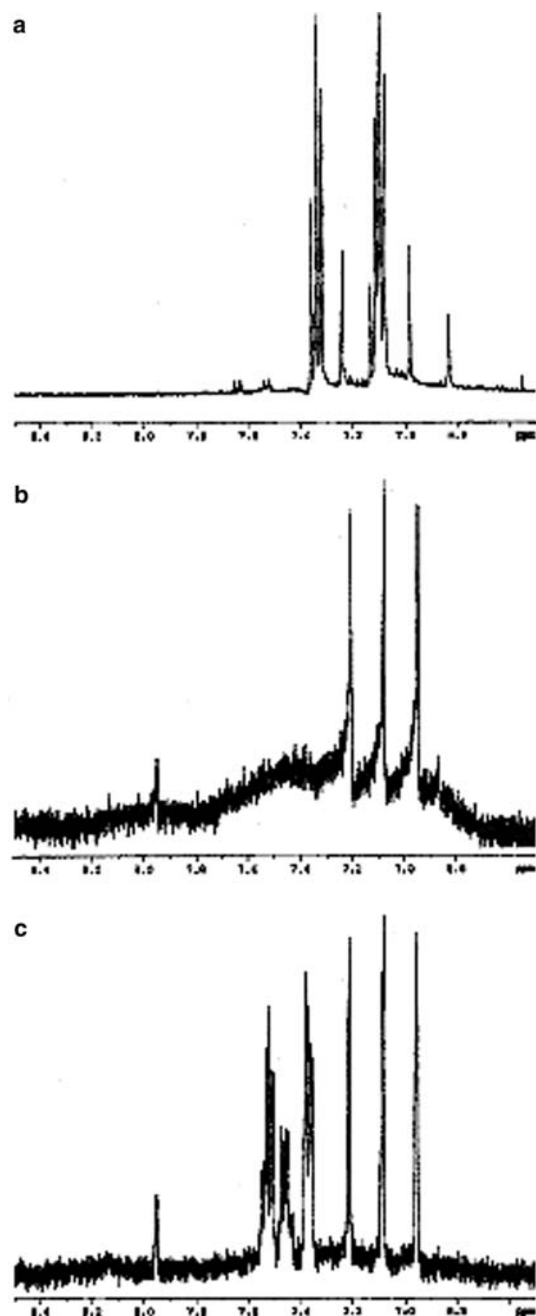


Fig. 4 $^1\text{H-NMR}$ spectra of **a** sulfonated polyaniline, **b** sulfonated poly(3-methyl thiophene), **c** sulfonated copolymer of 3-methyl thiophene-aniline in DMSO-d_6

into the polymeric structure, providing further evidence for the formation of the copolymer films.

FT-IR spectroscopy was used to determine the presence of $-\text{SO}_3^-$ groups in the copolymer films and to obtain evidence about copolymer films [20, 21]. FT-IR spectral characteristics of copolymer film were found to be slightly different from those of homopolymer films, but the differences were not distinct. In the FT-IR spectrum of the sulfonated homopolymer films there are absorption bands at 700 cm^{-1} (S-O stretching) and at 630 cm^{-1} (C-S stretching) belonging to the presence of –

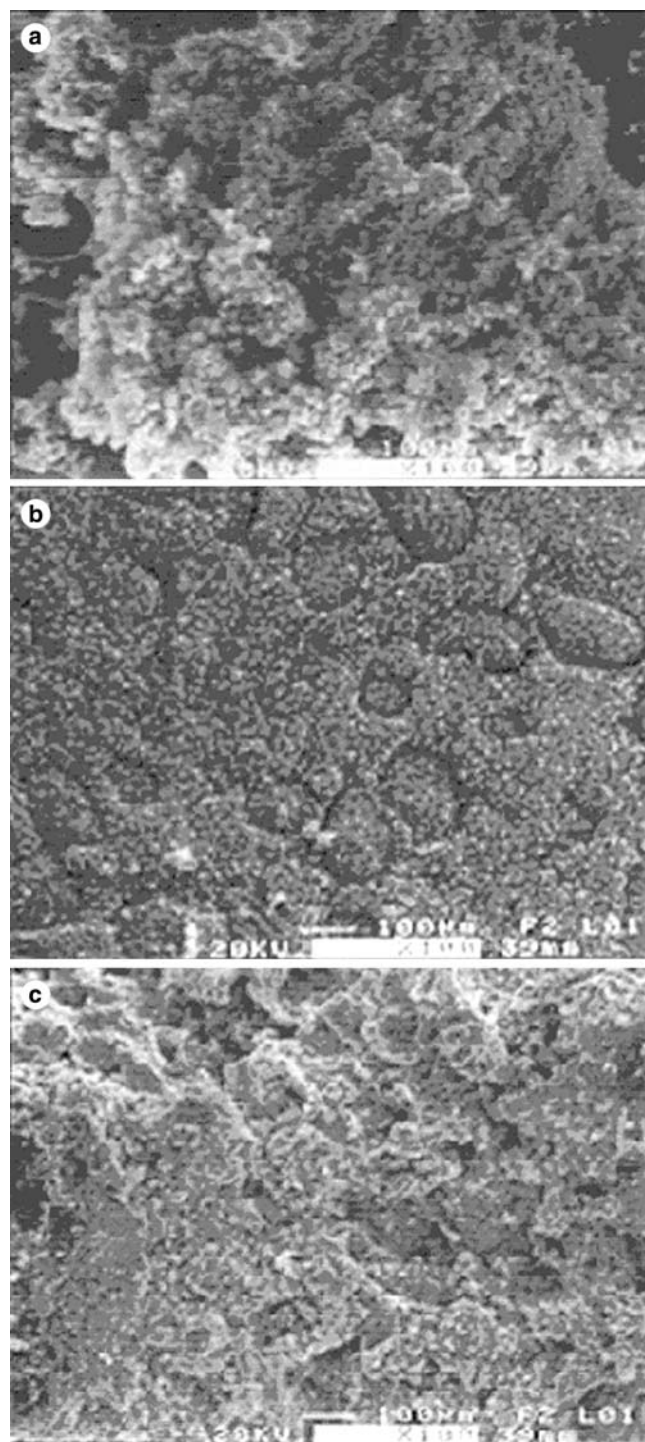


Fig. 5 Scanning electron micrographs of **a** sulfonated poly(3-methylthiophene), **b** sulfonated polyaniline, **c** sulfonated copolymer of 3-methyl thiophene/aniline

SO_3^- groups. But the peaks at $1,080$ and 630 cm^{-1} (ClO_4^- anion) overlap with the $-\text{SO}_3^-$ peaks at $1,080\text{ cm}^{-1}$ (S=O stretching) and 630 cm^{-1} (C-S stretching).

The UV-Vis absorption spectra of polyaniline, poly 3-methyl thiophene and copolymer film were obtained. There is a clear difference in the UV-Vis spectra of these polymeric films. Figure 3a and b shows UV-Vis

Table 2 The solubility values of the polymers obtained from the acetonitrile solutions containing 100 mM aniline, 25 mM FSO₃H/0.1 M TBAP and different concentrations of 3-methyl thiophene in DMSO and basic aqueous solution. Table 1

Composition of the polymerization solution	Solubility of the film in DMSO (mg/ml)	Solubility of the film in 0.1 M KOH (mg/ml)
100 mM aniline	–	–
100 mM aniline + 25 mM HSO ₃ F	8	6
100 mM aniline + 25 mM HSO ₃ F + 100 mM 3-MTy	18	15
100 mM aniline + 25 mM HSO ₃ F + 150 mM 3-MTy	21	17
100 mM aniline + 25 mM HSO ₃ F + 200 mM 3-MTy	19	14
100 mM aniline + 25 mM HSO ₃ F + 250 mM 3-MTy	17	11
100 mM aniline + 25 mM HSO ₃ F + 300 mM 3-MTy	16	10
200 mM 3-MTy + 25 mM HSO ₃ F	6	2
200 mM 3-MTy	–	–

spectra of the sulfonated polyaniline and sulfonated poly(3-methyl thiophene) dissolved in DMSO. The sulfonated polyaniline and sulfonated polythiophene show absorption bands at approximately 600 and 400 nm, respectively. These absorption bands are associated with the π - π^* interband transition, as is the case in other polyaniline and polythiophene homopolymers [20, 22]. The UV-Vis spectrum of the sulfonated poly(3-methyl thiophene/aniline) copolymer film dissolved in DMSO obtained from acetonitrile solution containing (100 mM aniline, 200 mM 3-methyl thiophene and 25 mM FSO₃H) was also taken. As can be seen from Fig. 3c, there are two absorption bands belonging to sulfonated polyaniline and sulfonated poly(3-methyl thiophene) in UV-Vis spectrum of the copolymer film.

¹H-NMR spectra of the poly(3-methyl thiophene) based sulfonated copolymer was taken in order to obtain a much better proof for the formation of copolymer since these are all soluble in DMSO to some extent. Figure 4 compares the details of ¹H-NMR signals of the aromatic protons of three samples. It is known that the interpretation of the fine structures are quite complicated due to the fact that the polymer structures are often regiorandom and rarely regioregular. It is reported that soluble regioregular polyalkylthiophene gives a single aromatic proton peak at 6.97 ppm whereas soluble regiorandom polyalkylthiophene gives a complicated aromatic proton signal between 6.90 ppm and 7.10 ppm arising from different linkages leading to a number of conformations [23]. In spite of this difficulty in interpretation the three spectra are convincingly different from each other. As seen from the spectra the aromatic proton signal of the aniline moieties in the copolymer sample is shifted considerably to lower fields, providing an independent and unequivocal evidence for the fact that copolymers that are not composite formed during the electrolysis of the solution containing two monomers.

However, the morphology of the poly(3-methyl thiophene) film obtained from acetonitrile solution containing HSO₃F was affected by the addition of aniline to the electrolysis solution. Sulfonated poly(3-methyl thiophene) film surface has a cauliflower-like structure; on the other hand, sulfonated polyaniline

morphology is granular (Fig. 5). Morphology of copolymer film shows similarity with sulfonated poly(3-methyl thiophene).

Sulfonated copolymer films dissolve in DMSO and aqueous KOH as sulfonated homopolymers. Table 2 lists the solubility characteristics. It is seen that the solubility values increase with an increase in the sulfonation ratio in polymeric backbone as expected. Since the FSO₃H concentration was held constant for each of the films, the solubility values start to decrease after certain 3-MTy concentration. This is due to the increased amounts of nonsulfonated units incorporated into the copolymer chain with increasing monomer concentrations in electrolysis solutions. Intrinsic viscosity of the polymer obtained from acetonitrile/0.1 M TBAP solution containing 100 mM aniline, 200 mM 3-methyl thiophene and 25 mM FSO₃H and dissolved in DMSO was measured and found to be 0.17 dl/g. When this value is compared with the other self-doped conducting polymers such as polyaniline [24] and polythiophene [8], it corresponds to a molecular weight range of approximately 9,000–12,000.

Conclusion

The electrochemical behavior of the films, elemental analysis results, conductivity measurements, UV-Vis spectrum and solubility results indicate that the electrocopolymerization reaction takes place between aniline and 3-methyl thiophene. Better conductivity and solubility of this copolymer were demonstrated compared to the other soluble copolymers in literature. The copolymerization reaction is strongly affected by the monomer concentration. The electrochemical method is more convenient to synthesize the copolymer films. Cyclic voltammetric results demonstrated that the significantly increased electroactivity and reversibility for the copolymer can be achieved under optimum electrolysis conditions.

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