

Electrochemical Synthesis of Sulfonated Polypyrrole in FSO₃H/Acetonitrile Solution

Yücel Şahin,¹ Arzu Aydın,¹ Yasemin Arslan Udum,² Kadir Pekmez,² Attila Yıldız²

¹Anadolu University, Department of Chemistry, 26470 Eskişehir, Turkey

²Hacettepe University, Department of Chemistry, Beytepe, 06532 Ankara, Turkey

Received 22 July 2003; accepted 9 February 2004

DOI 10.1002/app.20473

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The incorporation of SO₃⁻ groups into a polypyrrole backbone was successfully carried out using FSO₃H/acetonitrile medium. The degree of sulfonation (sulfonation or sulfur-to-nitrogen ratio) of polymer was controlled by varying FSO₃H concentration while the film was being electrodeposited. The cyclic voltammograms of the electrodeposited films were taken between -1.00 and +2.00 V (versus Ag/AgCl) in blank solution. A substantial effect on the electrical conductivity was observed upon the incorporation of SO₃⁻ groups in the polypyrrole polymeric chain.

The elemental analysis results of the freshly prepared and reduced films give independent evidence that the SO₃⁻ groups are covalently bound to the structure. FTIR, UV-Vis, spectroscopy and SEM techniques were used to characterize the electrosynthesized polypyrrole films. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 526–533, 2004

Key words: polypyrroles; self-doped polypyrrole; electrochemistry; fluorosulfonic acid; conducting polymers

INTRODUCTION

In recent years, intrinsic conducting polymers with conjugated double bonds have attracted much attention as advanced materials. Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity. PPy can be used as biosensor,^{1,2} gas sensor,^{3,4} wire,⁵ microactuator,⁶ antielectrostatic coating,⁷ solid electrolytic capacitor,^{8,9} electrochromic window and display, polymeric battery, electronic device, and functional membrane.^{10–12} PPy coatings have excellent thermal stability and are good candidates for use in carbon composites.¹³ New application possibilities have also been explored during the past several years. For example, PPy-based polymers can be used to load and release drugs and biomolecules.¹⁴ PPy-based polymer blends were also found to protect some metals from corrosion.¹⁵

PPy can easily be prepared from aqueous and organic solvents by either chemical or electrochemical oxidative polymerization of pyrrole. The electrochemical polymerization is simple and rapid. PPy obtained electrochemically has high conductivity and a controllable film thickness.¹⁶

PPy is insoluble and infusible, which restricts its processibility and therefore applications in other fields. Several strategies have been developed to increase its solubility. Soluble PPys could be prepared via electrochemical polymerization of alkyl substituted pyrroles.^{17,18} The substituted polypyrroles were found to be soluble in chloroform or *o*-dichlorobenzene and the dry conductivity values measured were 10⁻² to 10 S/cm.¹⁷ Counter ion induced processibility of PPy was investigated by using dodecylbenzene sulfonic acid (DBSA), methyl benzene sulfonic acid (MBSA), and camphor sulfonic acid (CSA).¹⁹ Shen and Wan²⁰ studied the solubility in *m*-cresol, room-temperature conductivity, morphology, and thermal stability of PPy synthesized by polymerization and *in situ* doping in the presence of sulfonic acids. It was noted that good solvating ability of sulfonic acid, such as DBSA, renders PPy soluble, while sulfonic acids having large molecular size, such as CSA and MBSA, fail to make PPy soluble. The nature of sulfonic acid used also has an influence on the morphology of the resulting PPy films. The images of PPy films doped with CSA, DBSA, and MBSA have typical granular morphology while PPy doped with β -naphthalene sulfonic acid (NSA) is fibrillar.²¹

Pfluger and coworkers²² reported the existence of 33% of the pyrrole rings that are linked through 2,3 positions based upon the X-ray photoelectron spectroscopy study of electrochemically synthesized PPy-PF₆ samples, while most of the pyrrole units are linked at the 2,5 positions to form straight chains.

Correspondence to: Y. Sahin (ysahin@anadolu.edu.tr).

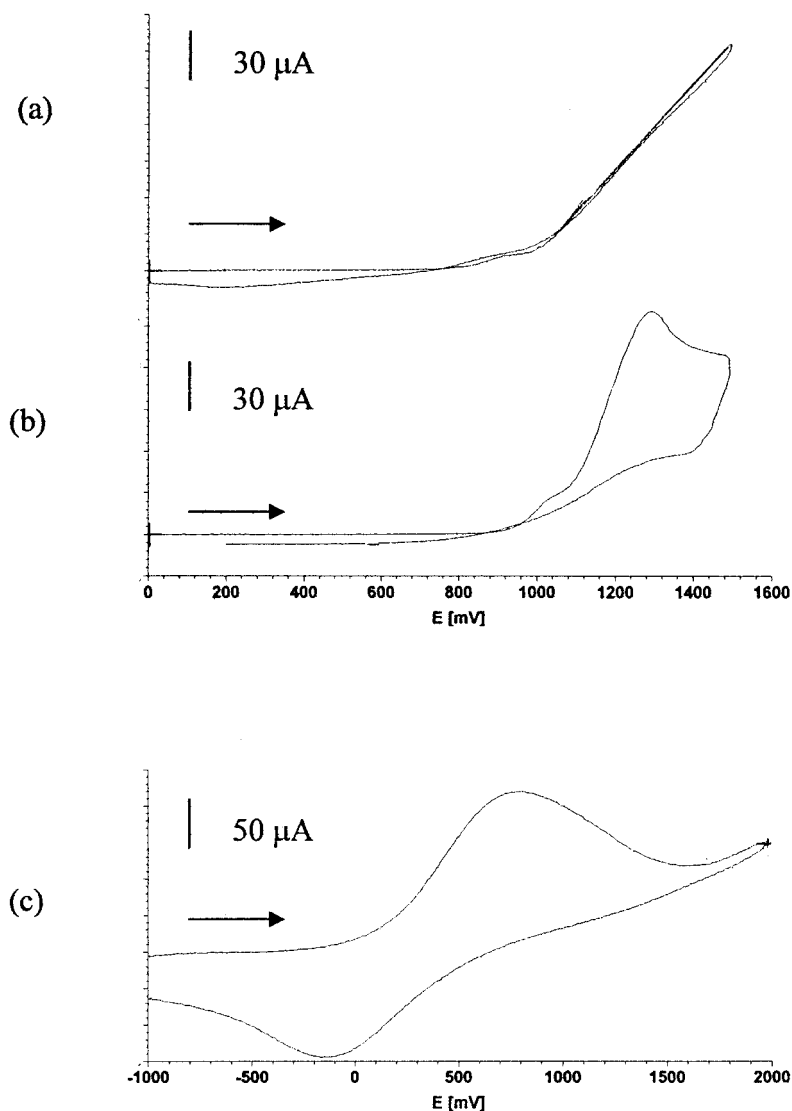


Figure 1 Cyclic voltammograms of the acetonitrile solution containing 0.1M pyrrole and (a) 0.1M FSO₃H; (b) 0.1M LiClO₄; (c) behavior of the polymer film, obtained from b, in blank solution (0.1M LiClO₄/acetonitrile); scan rate: 100 mV/s.

The interchains or side chains through the 2,3 coupling modes induce the decreased solubility of PPy in organic solvents and the variation in the conjugation length.²³

In situ controlled sulfonation of polyaniline (PANI) by use of fluorosulfonic acid (FSO₃H) was first reported by Şahin et al.^{24,25} Sulfonated PANI films were obtained in acetonitrile and water-acetonitrile mixture containing different ratios of aniline and FSO₃H. Sulfonation ratio was thus controlled by changing the aniline/FSO₃H ratio during electropolymerization.

In this study, a novel approach was attempted to synthesize sulfonated (self-doped) PPy. Sulfonated PPy films that have different sulfonation ratios were prepared by using FSO₃H as a sulfonated reagent as well as supporting electrolyte in acetonitrile. This way

it was possible to control the sulfonation ratio of the PPy films obtained. The effects of FSO₃H concentration and another electrolyte, LiClO₄, on the structure and the conductivity of the products were investigated. Structural properties of the films were characterized by elemental analysis and IR, UV-Vis, and SEM techniques.

EXPERIMENTAL

Pyrrole (99% Aldrich) was distilled and preserved under nitrogen atmosphere (99.99% BOS, Birleşik Oksijen Sanayii). All other chemicals were of special reagent grade and used without further purification. Anhydrous fluorosulfonic acid (FSO₃H, triple-distilled, Aldrich) was used as both sulfonation reagent and supporting electrolyte in the same solution. Pyr-

TABLE I
Results of Elemental Analysis and Dry Conductivity of PPy Films^a

FSO ₃ H concentration (M)	LiClO ₄ concentration (M)	S/N ratio (freshly prepared film)	S/N ratio (reduced film)	Conductivity σ (S/cm)
0.010	—	0.29	0.39	65
0.025	—	0.39	0.42	52
0.050	—	0.51	0.46	27
0.075	—	0.54	0.54	22
0.100	—	0.53	0.56	6.5
—	0.100	—	—	26

^a Prepared from acetonitrile solutions of 0.1M pyrrole with different concentrations of FSO₃H and 0.1M LiClO₄ at a constant potential of +1.00 V (versus Ag/AgCl).

role concentration was held constant in 0.1M and increasing amounts of FSO₃H were added to 0.1M in acetonitrile solution of pyrrole. In addition, 0.1M LiClO₄ was used as a supporting electrolyte. Electrodeposition was performed by constant potential electrolysis at the applied potential of +1.00 V (versus Ag/AgCl). While the film obtained from acetonitrile solutions of LiClO₄ was black, globular, and brittle, the film obtained from FSO₃H/acetonitrile solution was dark blue, fibrillar, and highly elastic. The films were reduced in LiClO₄ (0.1M)/acetonitrile solution for 2 h.

Electrochemical measurements were carried out under nitrogen (BOS) atmosphere in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl) and the counter electrode (Pt spiral). The working electrode was a Pt disc (area, 0.0132 cm²) and cleaned by polishing with Al₂O₃ slurry for the cyclic voltammetric studies. The macro-samples of the polymer films were prepared on a Pt macro electrode (area, 1.0 cm²), which was pre-cleaned by holding it in a flame for a few minutes. The micro-electrodes and macroelectrodes were rinsed with acetonitrile and dried before use. The films prepared electrochemically were immersed in acetonitrile to remove excess FSO₃H and pyrrole and then vacuum dried.

The electrochemical instrumentation consisted of a Bank Wenking POS 88 model Potentiostat and a Bank 175 model integrator. The current-voltage curves were recorded a universal software program.

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 ohmic contacts. At least 10 different current values were used in the measurement of the potential drop.

Infrared (IR) spectra of KBr discs were taken on a Jasco FT/IR 420 Fourier transform infrared spectrometer.

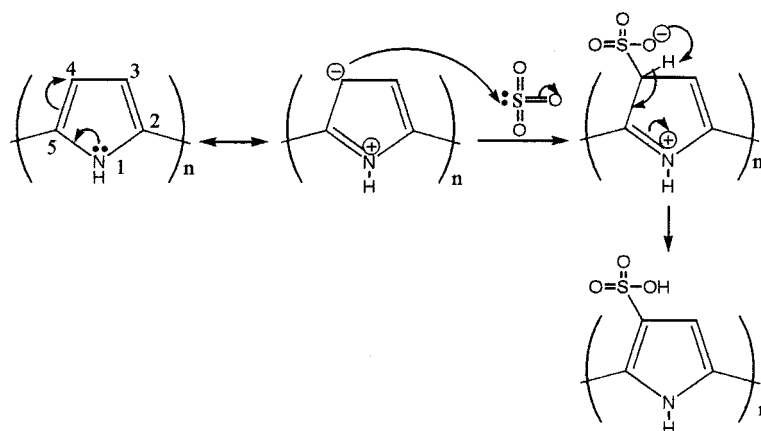
In situ spectroelectrochemical studies (*in situ* UV-Vis) were made using by combination of a Wenking POS 88 model potentiostat with a Shimadzu UV-2101 PC spectrophotometer.

Scanning electron microscopy (SEM) photographs of the films were taken by a Cam Scan Scanning Electron Microscope.

RESULTS AND DISCUSSION

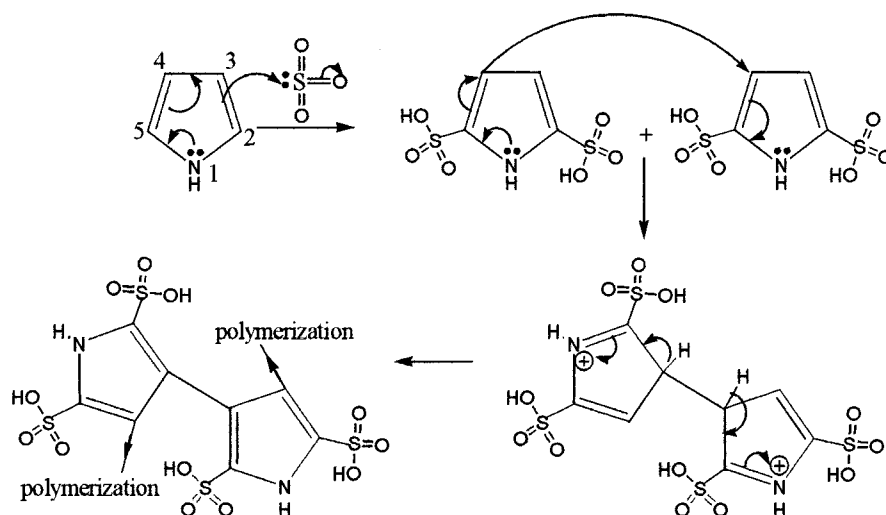
Cyclic voltammetric behavior of FSO₃H/acetonitrile solution was investigated in our previous study.^{24,26} The anodic limit of that solution was found to be +2.50 V versus Ag/AgCl. This limit is quite suitable for the electrooxidation of the pyrrole in this medium. A distinguishable oxidation peak of pyrrole was not seen in the acetonitrile/FSO₃H medium in the cyclic voltammogram because of the high resistance of the medium [Fig. 1(a)]. Figure 1(b) shows a cyclic voltammogram of pyrrole (0.1M) in 0.1M acetonitrile solution of LiClO₄. An anodic peak of pyrrole was observed at a peak potential of +1.30 V (versus Ag/AgCl). This oxidation corresponds to the formation of pyrrole radical cations. These radical cations couple, giving oligomers, which eventually precipitate on the electrode surface, forming nucleation sites for further polymer growth. Continued polymerization takes place at these nucleation sites, away from the electrode surface and eventually a black polymeric film is deposited on the electrode surface. There is no reduction peak of pyrrole on the cyclic voltammogram. The electroactivity of the electrodeposited film was studied by potential cycling between -1.00 V and +2.00 V (versus Ag/AgCl) in 0.1M acetonitrile solution of LiClO₄ (blank solution). A broad oxidation peak was observed at the peak potential of +0.75 V (versus Ag/AgCl) and a reverse cathodic peak was seen at a peak potential of -0.15 V (versus Ag/AgCl) [Fig. 1(c)].

In pyrrole, the nitrogen atom feeds electrons into the ring, increasing its reactivity toward electrophiles. Pyrrole undergoes electrophilic substitution readily, usually at the 2- and 5-positions. The electrophilic substitution reaction (sulfonation) can proceed by two different routes. Pyrrole can polymerize first at the 2- and 5- positions and then the sulfonation reaction can take place at the 3- or 4-position of pyrrole rings (Route 1).



As another possibility, pyrrole can undergo electrophilic substitution with SO_3^- groups at 2- and/or 5-positions before the polymerization process takes place. After the electrophilic substitution reaction, sulfonated pyrrole reacts with another substituted or unsubstituted pyrrole at the 3- or 4- position

to form a dimer. The sulfonated dimer may then react with a pyrrole or sulfonated pyrrole to form sulfonated polypyrrole (Route 2). Interchain links or side chains thus formed may be the reason of the observed insolubility of the films in organic solvents.^{22,23}



To investigate the sulfonation ratio (S/N) and the composition of the PPy films, elemental analysis of the PPy films obtained from 0.1M acetonitrile solutions of pyrrole containing different concentrations of FSO_3H (0.010–0.100M) and from 0.1M acetonitrile solutions of pyrrole containing 0.10M LiClO_4 M was carried out. The results of the elemental analysis are listed in Table I. As seen from the table, the sulfonation ratio (S/N) of the freshly prepared PPy film from 0.01M FSO_3H solution is 0.29. This value increases as the FSO_3H concentration reaches 0.075M and remains almost constant thereafter. To elucidate whether the $-\text{SO}_3$ group is covalently bound to the oxidized form of the polymer backbone (self-doped) or present as counter ion (doped) the elemental analysis of the reduced polymer

was also carried out. S/N ratios calculated from the elemental analysis results of the reduced film indicate clearly that the $-\text{SO}_3$ group is only covalently bound in the structure (Table I). The comparison of the S/N ratios of the oxidized and reduced films indicate that $-\text{SO}_3$ groups are mainly covalently bound to structure in both forms of the polymer. If $-\text{SO}_3$ groups were present only as counter ions, the measured S/N ratio should have been 0.0 for the reduced form of polypyrrole.

The dry conductivity values are also given in the same table. It can easily be seen that the conductivity of PPy films decreases substantially with increasing FSO_3H to pyrrole molar ratio. The conductivity of the film obtained from 0.1M acetonitrile solution of Li-

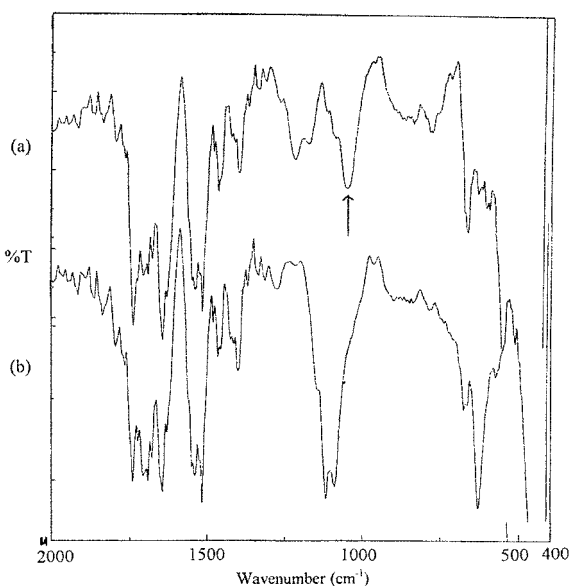


Figure 2 Baseline corrected IR spectra of the polymer obtained from the solution containing (a) 0.1M pyrrole + 0.05M FSO₃H and (b) 0.1M pyrrole + 0.1M LiClO₄ in acetonitrile showing the 2,000–400 cm⁻¹ region.

ClO₄ is about four times that of the film obtained from 0.1M acetonitrile solution of FSO₃H.

It is known from the previous results that sulfonation of the polyaniline backbone causes a decrease in dry conductivity values and an increase in the solubilities in organic solvents.^{24,25} It is interesting that the sulfonated PPy films obtained in this study are found to be insoluble in organic solvents such as dimethyl sulfoxide, ethyl alcohol, tetrahydrofuran, acetone, etc. despite the decrease in dry conductivity values.

FT-IR spectroscopy was used to determine the presence of -SO₃⁻ groups attached to the aromatic rings to prove whether the sulfonated polypyrrole was obtained during electropolymerization. The IR spectra in KBr discs of electrochemically prepared polypyrrole films with FSO₃H and LiClO₄ are shown in Figure 2(a) and (b). The peaks at 1,542 cm⁻¹ are attributed to C=C stretching vibration of pyrrole.²⁷ The peaks at 1,690 and 1,360 cm⁻¹ indicate the presence of C=N and C-N vibrations in PPy.²⁸ The peak at 1,040 cm⁻¹ can be assigned to the symmetric O=S=O stretching vibrations [Fig. 2(a)]. This peak confirms the presence of sulfonate groups in the polymer.²⁹ The S-O stretching band is seen at 700 cm⁻¹ and the peak at 630 cm⁻¹ is responsible for the C-S stretching vibrational mode [Fig. 2(a)].^{24,26} There is no peak at 1,040 cm⁻¹ in the IR spectrum of the film obtained from LiClO₄/acetonitrile solution [Fig. 2(b)]. However, the characteristic C-H out-of-plane bending vibration is seen at about 640 cm⁻¹ and this band may also overlap with that of the ClO₄⁻ ion.³⁰

Figure 3 illustrates *in situ* UV-Vis spectra of the sulfonated PPy film taken with an indium tin oxide

(ITO) glass electrode during the oxidation and reduction of the polymer at different applied potentials. The polymer film was first coated on the ITO electrode at an applied potential of +1.00 V (versus Ag/AgCl) from 0.1M pyrrole solution of acetonitrile containing 0.05M FSO₃H. About 1 min was found to be sufficient to obtain the film of desired thickness. Polymer films exhibit a bipolaron absorption at 475 nm,³¹ the broad near IR absorption band around 800 nm is assigned to the electronic transition from the valence band to the bipolaron band (a free-carrier tailing) of the conjugated chains of PPy.³² The latter is related to the doping state of the conducting PPy and to the conjugation length of the PPy chain. When the film loses its electrical conductivity the free-carrier absorption disappears³¹ at the cathodic potentials.

The films were immersed in 0.1M LiClO₄ solution in acetonitrile and different electrode potentials were applied under nitrogen atmosphere. First, the potentials were held at -1.00, -0.50, 0.00, +0.50, +1.00, +1.50, and +2.00 V (versus Ag/AgCl) and *in situ* UV-Vis spectra were taken at each potential [Fig. 3(a)]. The applied potential was then changed in a reverse order and the spectra were taken to show whether a degradation in the polymer occurred in a previous oxidation [Fig. 3(b)]. When the potentials were changed from -1.0 to +2.0 V, the color of the film changed from yellow to dark blue. A color change from dark blue of the doped state to yellow of the undoped state was reobtained upon the reverse reduction. The spectra also show that the PPy film did not change its structure during the previous oxidation since the same initial spectrum is obtained upon undoping. Complete reduction of the oxidized (doped) film occurs upon undoping, indicating that there was no degradation in the structure of the film during previous electrooxidation even at potentials as high as +2.0 V (versus Ag/AgCl) in acetonitrile medium.

SEM results show that structural properties of the PPy films are changed by the incorporation of SO₃⁻ groups into the polymeric chain [Fig. 4(a) and (b)]. The sulfonated films are fibrillar and highly elastic whereas the films obtained with LiClO₄ medium without the presence of sulfonation reagent are globular and brittle.

CONCLUSION

It can be concluded that controlled incorporation of SO₃⁻ groups into polypyrrole backbone has been successfully carried out, using FSO₃H as a supporting electrolyte and a sulfonation reagent in the electropolymerization solution. The elemental analysis results of the freshly prepared and reduced films give independent evidence that the SO₃⁻ groups are covalently bound to the structure. FTIR and UV-Vis results con-

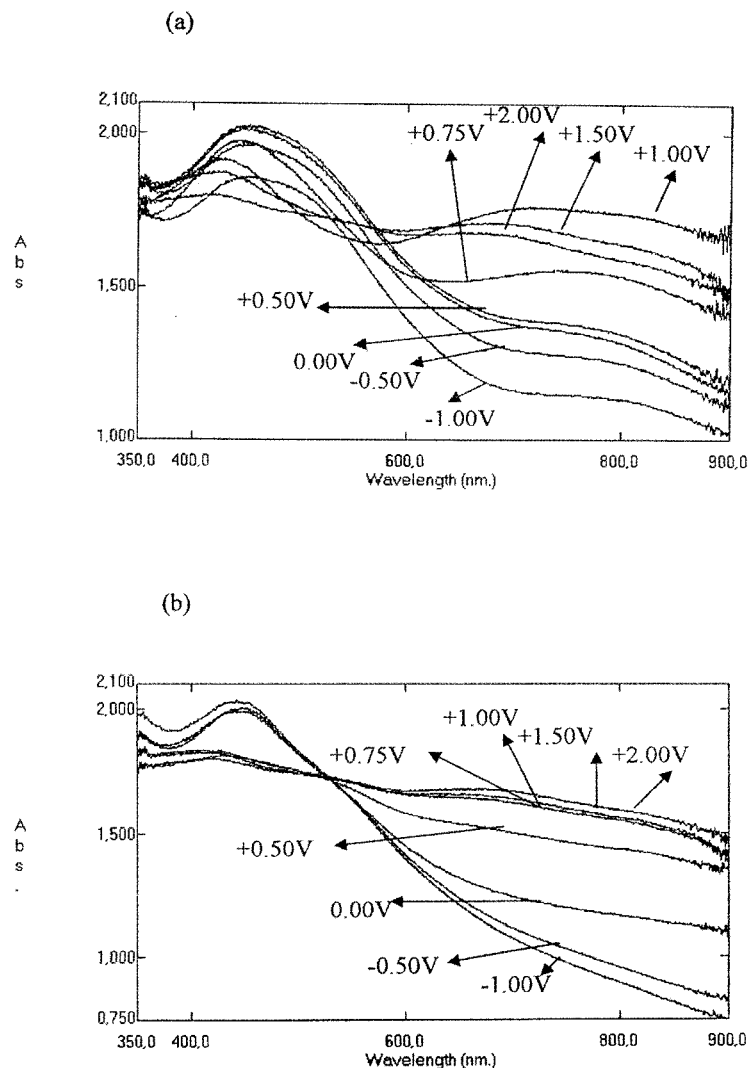


Figure 3 *In situ* UV-Vis spectra of the polymer coated from 0.1M pyrrole + 0.05M FSO₃H on ITO glass in 0.1M LiClO₄ acetonitrile solution at various applied potentials from (a) -1.00 to +2.00 V and (b) +2.00 to -1.00 V (versus Ag/AgCl).

firm the existence of SO₃⁻ groups in the synthesized polymer films.

The effect of the substitution of SO₃⁻ groups in the PPy polymeric chains is clearly seen in electrical conductivity values. When the FSO₃H concentration is increased, the degree of sulfonation increases, but the measured dry conductivity value decreases. The degree of sulfonation is known to be inversely related to the conductivity values.^{24,25} Furthermore it is clear that the electrolyte composition (FSO₃H/pyrrole ratio) allows control of the degree of sulfonation during electropolymerization. The lowered conductivity is caused by the decreased interchain diffusion of the charge carriers. This is induced by increased separation of the polymer chains due to the presence of SO₃⁻ groups, which force the chains out of planarity and lower the overlap of orbitals along the conjugated system by twisting the rings relative to one another.³³ Conductivity values of the PPy films were affected

negatively by the increase of FSO₃H concentration in the polymerization solutions. It should be noticed that the conductivity of the PPy film here is much higher than those in the literature for sulfonated PPy. The conductivity of the sulfonated PPy film produced by Shen and Wan²⁰ is only 2–18 S/cm.

Sulfonated polypyrrole is apparently resistant against electrooxidative degradation as evidenced from *in situ* UV-Vis data.

The drastic change in morphology of PPy films most probably arises from the existence of the SO₃⁻ groups in the polymeric backbone. The change from the globular structure to fibrillar structure upon sulfonation also causes an increase in the dry conductivity value substantially.

Yücel Şahin thanks Prof. Güleren O. Alsancak for recording of elemental analysis of the films. Y. Şahin, also thanks Mutlu Şahin for her valuable help and encouragement

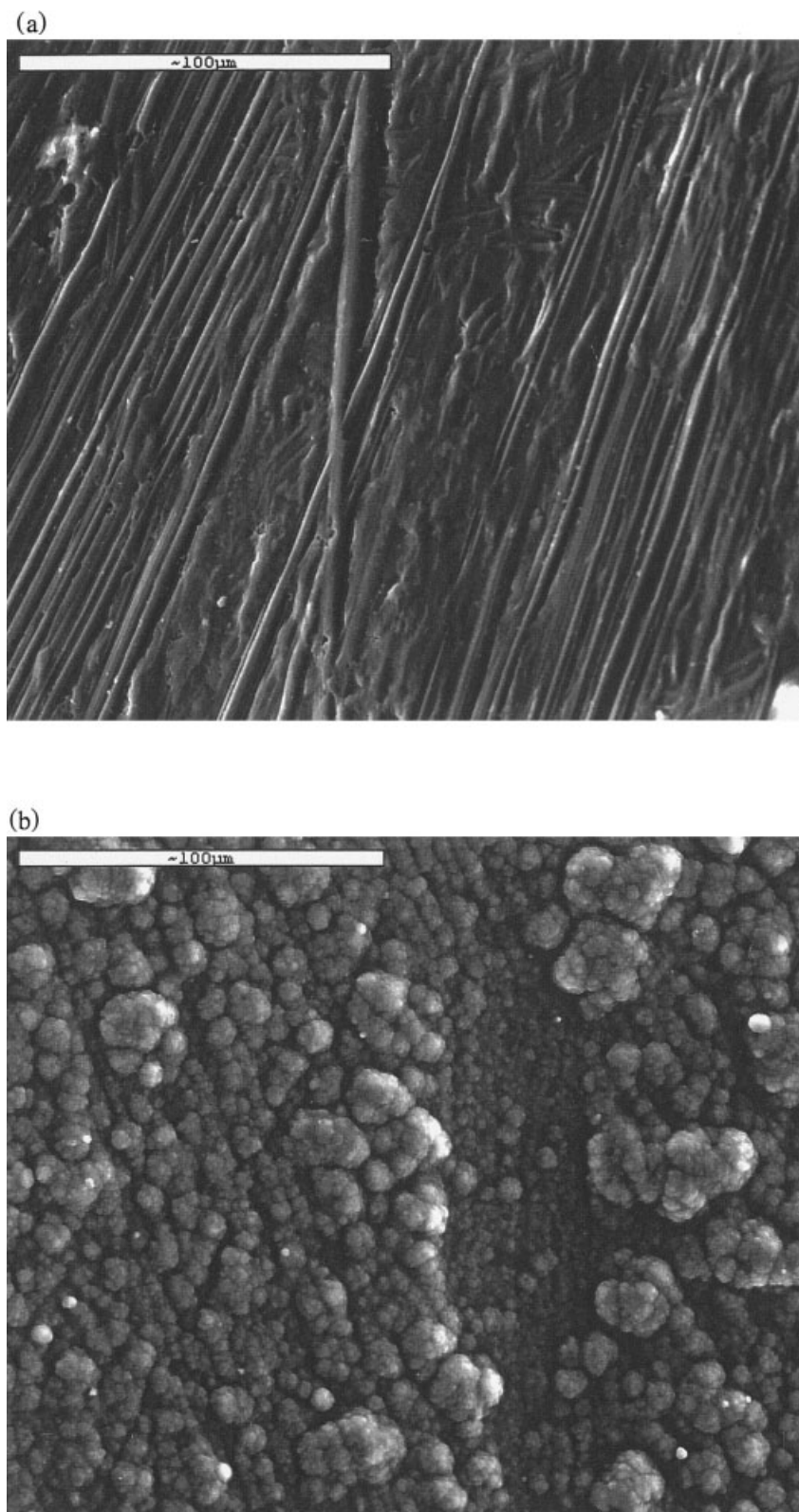


Figure 4 SEM pictures of the polymer obtained from the solution containing (a) 0.1M pyrrole + 0.05M FSO_3H and (b) 0.1M pyrrole + 0.1M LiClO_4 in acetonitrile.

throughout the work. This work was supported by Anadolu University Research Foundation under grant no. AUAF-011045.

References

1. Vidal, J. C.; Garcia, E.; Castillo, J. R. *Anal Chim Acta* 1999, 385, 213.
2. Campbell, T. E.; Hodgson, A. J.; Wallace, G. G. *Electroanalysis* 1999, 11, 215.
3. Kincal, D.; Kamer, A.; Child, A. D.; Reynold, J. R. *Synth Met* 1998, 92, 53.
4. Kemp, N. T.; Flanagan, G. U.; Kaiser, A. B.; Trodahl, H. J.; Chapman, B.; Partridge, A. C.; Buckley, R. G. *Synth Met* 1999, 101, 434.
5. Jerome, C.; Labaye, D.; Bodart, I.; Jerome, R. *Synth Met* 1999, 101, 3.
6. Smela, E. J. *Micromech Microeng* 1999, 9, 1.
7. Yang, S. C.; Liu, H.; Clark, R. L. *PCT Int Appl WO 99 22,380 (Cl. H01 B1/00)* (1999).
8. Takamatsu, T.; Taketani, Y. *Jpn Kokai Tokyo Koho JP11 121, 279 [99 121, 279]* (1999).
9. Kojima, Y.; Kamikawa, H.; Takamatsu, T. *Jpn Kokai Tokyo Koho JP11 121, 280 [99 121, 280]* (1999).
10. Skotheim, T. A., Ed.; *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. I and II.
11. Skotheim, T. A.; Elsenbaumer, R.; Reynolds, J., Eds.; *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998; Vols. I and II.
12. Wallace, G. G.; Spinks, G.; Teasdale, P. R. *Conductive Electroactive Polymers*; Technomic: New York, 1997.
13. Iroh, J. O.; Williams, C. *Synth Met* 1999, 99, 1.
14. Reynolds, J. R.; Hiep, L.; Selampinar, F.; Kinlen, P. J. *Polym Prepr* 1999, 40, 307.
15. Lu, W. K.; Elsenbaumer, R. A. *Annu Tech Conf Soc Plast Eng* 1998, 56, 1276.
16. Yang, C.; Dong, S. *Electroanalysis* 1998, 10, 173.
17. Ruhe, J.; Ezqurra, T. A.; Wegner, G. *Synth Met* 1989, 28, 177.
18. Audebert, A.; Aldebert, P.; Girault, N.; Kaneko, T. *Synth Met* 1993, 53, 251.
19. Lee, J. Y.; Song, K. T.; Kim, S. Y.; Kim, Y. C.; Kim, D. Y.; Kim, C. Y. *Synth Met* 1997, 84, 137.
20. Shen, Y. Q.; Wan, M. X. *Synth Met* 1998, 96, 127.
21. Shen, Y. Q.; Wan, M. X. *J Appl Polym Sci* 1998, 68, 1277.
22. Pfluger, P.; Street, G. B. *J Chem Phys* 1984, 80, 544.
23. Joo, J.; Lee, J. K.; Baek, J. S.; Kim, K. H.; Oh, E. J.; Epstein, J. *Synth Met* 2001, 17, 45.
24. Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 129, 107.
25. Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 131, 7.
26. Şahin, Y.; Pekmez, K.; Yıldız, A. *J Appl Polym Sci* 2002, 85, 1227.
27. Ustamehmetoğlu, B.; Kızılcın, N.; Saraç, A. S.; Akar, A. *J Appl Polym Sci* 2001, 82, 1098.
28. Chaubey, A.; Gerard, M.; Singhal, R.; Singh, V. S.; Malhotra, B. D. *Electrochim Acta* 2000, 46, 723.
29. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1991; 5th ed.
30. Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 129, 117.
31. Yin, W.; Ruckenstein, E. *J Appl Polym Sci* 2001, 79, 86.
32. Lei, J.; Martin, C. R. *Synth Met* 1992, 46, 53.
33. MacManus, P. M.; Cushman, R. J.; Yang, S. C. *J Phys Chem* 1987, 91, 744.