Electropreparation and Electrochemical Stability of Polythiophenes in Acetonitrile Containing Anhydrous HBF$_4$

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ABSTRACT: The electrooxidation behavior of thiophene and 3-methylthiophene on a Pt surface in an acetonitrile + tetrabutylammonium tetrafluoroborate solution were investigated. The electropolymerization of these monomers was studied in neutral, acidic, and basic media. The effects of thiophene concentration and the added acid were elucidated. The polythiophene and poly(3-methylthiophene) films formed were characterized by their cyclic voltammograms in a blank solution and dry conductivities were measured. Electrochemical properties of these polymers in the same medium were investigated in the absence and in the presence of added anhydrous acid and base. The behavior of the freshly prepared films was compared with that which lost its electroactivity as a result of electrooxidation using cyclic voltammetry, controlled potential coulometry, and FTIR spectroscopy. The mechanisms related to the formation of the polymers and their electroactivity loss were proposed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 312–322, 2000

Key words: polythiophene; poly(3-methylthiophene); electropolymerization; degradation; conducting polymers

INTRODUCTION

The electrochemical synthesis of polythiophene was accomplished successfully and the preparation of this interesting conducting polymer was carried out generally in nonaqueous media under controlled potential, potential sweep, and constant current conditions.[1–4] The effects of various supporting electrolytes, temperature, and added bases and the dependence of the morphology and conductivity of the film on the film thickness were investigated[5–12] and the mechanisms of polymerization were proposed. In one of the mechanisms proposed, the key step was the electrophilic addition of the neutral thiophene monomer to the electrolytically produced cation radical.[7,8] The other proposed mechanism was based on the dimerization of the cation radicals and the subsequent deprotonation.[7] The electrooxidation of thiophene can be carried out at rather high potentials, such as beyond +1.8 V. By adding bithiophene to the thiophene solutions or converting thiophene to its oligomers in the presence of acid prior to electrolysis, the electropolymerization potential can be lowered substantially.[3,4,13]

The electrochemical stability of conducting polymers is of major importance for their use in different electrochemical systems such as batteries, electrocatalysis materials, sensor devices, and electronic components. A recent review article summarized the work published related to the electrooxidative degradation of various conduct-

ing polymers.[14] It is well established that even traces of water and/or oxygen promote degradation during electrooxidation and the physical properties these materials are modified irreversibly. In the case of polyaniline, for example, hydrogen-bonded water, which may exist between the polymer chains, is sufficient to induce degradation when polyaniline is used in rechargeable battery applications.

We showed in a recent study[15] that some oxidative decomposition processes in polyaniline in nonaqueous media are not irreversible in nature and are the result of a decrease in the proton content of the film. Electroactivity can be restored when the protons are reintroduced into the film electrolytically. Depending upon the proton content of the polyaniline film and the availability of protons in the medium, completely resistive films or electroinactive but conducting films or electroactive and conductive films can be obtained.[15] Although the stability of polythiophene is known to be better than that of polyaniline, the degradation can be induced at high anodic polarizations as a result of overoxidation. The product of overoxidation is the dication which is quite reactive toward nucleophiles.[14]

Takenaka et al. studied the degradation of polythiophene by XPS using undoped, doped, and degraded films.[9] Doping and undoping and the subsequent degradation were achieved upon pulsing the potential applied to the film between -2 and $+4$ V, with a pulse frequency of 0.5 Hz. According to this study, the hydrolysis of BF_4^- with water, present as an impurity, produces hydrogen fluoride which reacts with the film. Based on IR and UV spectroscopical results, Wang and co-workers reported that polythiophene film loses its electroactivity when the applied potential is scanned between 0.0 and $+2.2$ V in the monomer-free electrolyte solution.[16] The degraded films were found to contain $C{=}O$ groups which are formed by direct oxidation and/or hydrogen migration followed by oxidation by molecular oxygen. The degraded films have a shorter π-conjugation length and are no longer dopable as a result. The deactivation of the polythiophene films was also investigated in the presence of various nucleophiles.[17,18] The oxidatively deactivated films can be reactivated by polarizing at very positive potentials under certain conditions and the irreversibly degraded films are entirely different in nature than are the deactivated films.[17] The synthesis of these films at as low a positive applied potential as possible in a solution containing no nucleophiles and the use of some additives in the electropolymerization solution are suggested for preventing degradation and deactivation.[17] Introduction of different substituents into the thiophene ring was also found to affect the stability of polythiophene.[19] Poly(3-methylthiophene), for example, is much better in this respect than is polythiophene.

Previously, we investigated the effect of monomer concentration on the electrochemical behavior of polypyrrole[20] and the effects of monomer and acid concentrations on the formation and properties of polyaniline.[21] In this article, we present the results related to the electropolymerization of thiophene and 3-methylthiophene in an acetonitrile + tetrabutylammonium tetrafluoroborate solution using anhydrous HBF_4. The effects of the monomer and acid concentrations were elucidated. Furthermore, the electrochemical behavior and the electroactivity loss of these electrochemically prepared films were investigated in the absence and in the presence of anhydrous HBF_4 and base in the same medium.

EXPERIMENTAL

The procedure used to purify acetonitrile (Merck) was described elsewhere.[22,23] Thiophene (Sigma) and 3-methylthiophene (BDH) were vacuum-distilled. Acetonitrile and the concentrated monomer solutions were kept in the dark under a nitrogen atmosphere. The diethylether complex of tetrafluoroboric acid (Aldrich) was used as the anhydrous acid. Pyridine of 99.5% purity (Analar) was used without further purification. Tetrabutylammonium tetrafluoroborate (TBAFB) was prepared by reacting a 30% aqueous solution of tetrafluoroboric acid (Analar) with a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich). It was recrystallized from an ethanol + water mixture and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120°C. All electrochemical experiments were carried out under a nitrogen (BOS) atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode [Ag,Ag-Cl(sat) in acetonitrile] and the counterelectrode (Pt spiral). The acetonitrile + 0.1M TBAFB solution in the reference electrode compartment was saturated with AgCl. The working electrode for the cyclic voltammetric studies was a Pt disc (area, 0.0132 cm^2). Macrosamples of the polythio-
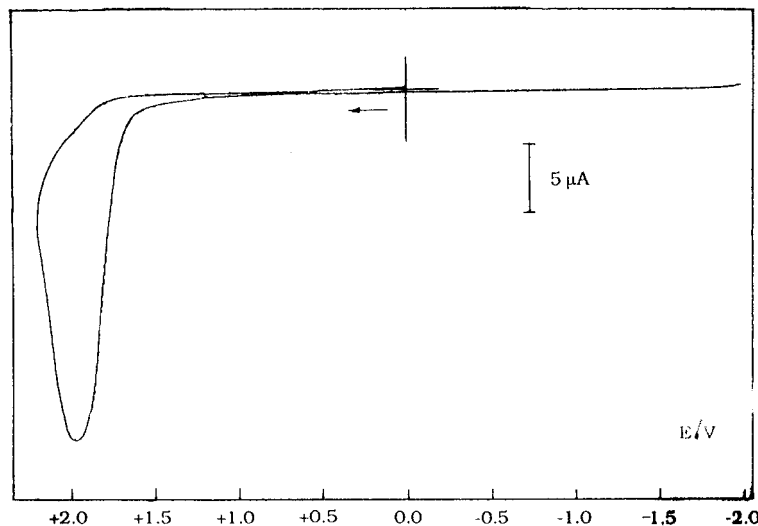
Figure 1   Cyclic voltammogram of the oxidation of thiophene in acetonitrile + 0.1M TBAFB; $C_{thiophene}$ = 5 mM; scan rate, 100 mV s^{-1}.

phene and poly(3-methylthiophene) films were prepared on a Pt macroelectrode (area, 1.0 cm^2). The working microelectrode was cleaned by polishing with an Al$_2$O$_3$ slurry. The working macroelectrode was cleaned by holding it in a flame for a few minutes. The electrodes were rinsed with acetonitrile and dried before use. The films prepared electrochemically were immersed in acetonitrile to remove TBAFB and the soluble oligomers and then vacuum-dried. The pellets from the films were obtained under a pressure of 5 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 10 different current values were used in the measurement of the potential drop.

Macrosamples were obtained with a PAR Model 273 potentiostat–galvanostat. Cyclic voltammograms were taken with the electrochemical instrumentation that consisted of a PAR Model 173 potentiostat–galvanostat 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 Goertz x–y recorder.

RESULTS AND DISCUSSION

Electrochemical Formation of Polythiophenes

Effect of Monomer Concentration

Figure 1 shows the cyclic voltammogram of thiophene in acetonitrile. Thiophene is oxidized with

a peak potential of +1.96 V. 3-Methylthiophene behaves similarly with an oxidation peak potential of +1.62 V. The product of the monomer electrooxidation is its unstable cation radical as evidenced from the absence of the reverse peak in the cyclic voltammogram of thiophene (Fig. 1). A black film is formed on the Pt surface if one carries out a multisweep experiment. The formation and growth of the polythiophene film is seen in Figure 2(a). Figure 2(b) shows the cyclic voltammetric behavior of the film in a supporting electrolyte solution (blank solution). The film exhibits broad oxidation and broad reduction peaks. Poly(3-methylthiophene) film behaves similarly. To determine the effect of the monomer concentration on the growth of the films, the films were grown in solutions of varying monomer concentrations for the same period of time (5 min). The charge passed during the electrooxidation of these films in a blank solution was then measured. The charge was measured during the second oxidative cycle of the cyclic voltammograms of the films in a blank solution. As long as there is no loss of electroactivity during the second cyclic voltammetric run in a blank solution, the amount of the film deposited can be assumed to be proportional to the charge passed during the oxidative cycle.

As seen in Figure 3, the optimum thiophene concentration for polythiophene formation is about 400 mM and the optimum 3-methylthiophene concentration for poly(3-methylthiophene) formation is about 200 mM. Beyond these concen-
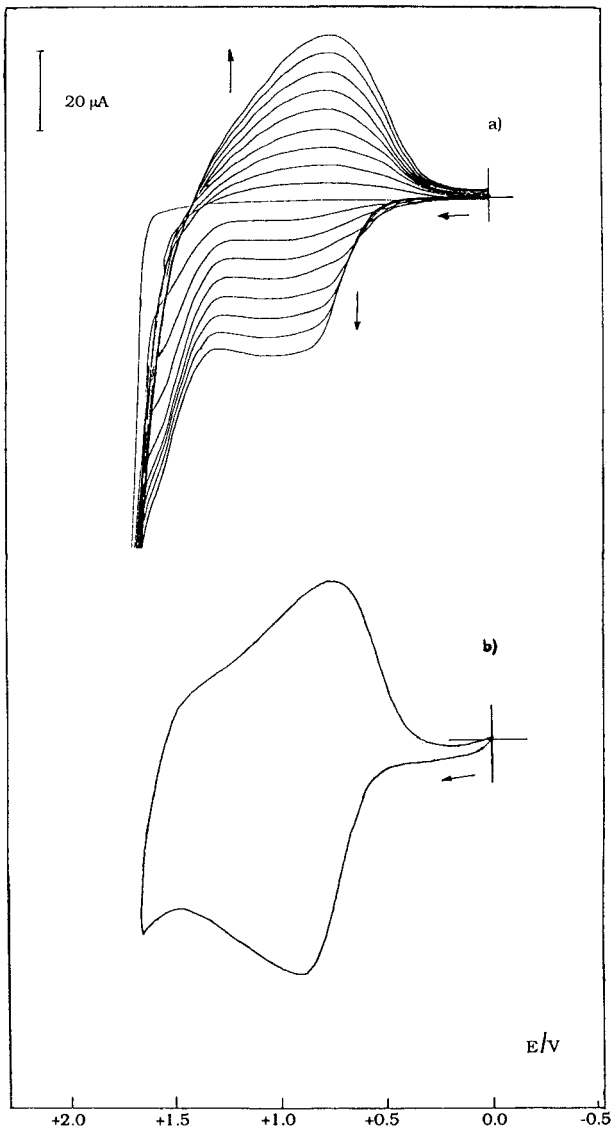
The maximum value in dry conductivity was also obtained with the same optimum monomer concentrations (Fig. 4). The dry conductivity values drop after reaching a maximum around the optimum monomer concentration, especially for poly(3-methylthiophene) films.

If one adds varying amounts of a base such as pyridine to the electropolymerization solution, containing the optimum amount of monomers, the amounts of the films produced decrease significantly, as seen in Figure 5. The fact that the deprotonation is the major factor in the decrease of the film formation in these experiments was verified by the detection of the cyclic voltammetric response of the protonated pyridine. Figure 6 shows the cyclic voltammograms of the electropolymerization solution before and after the polythiophene film is produced electrolytically in the
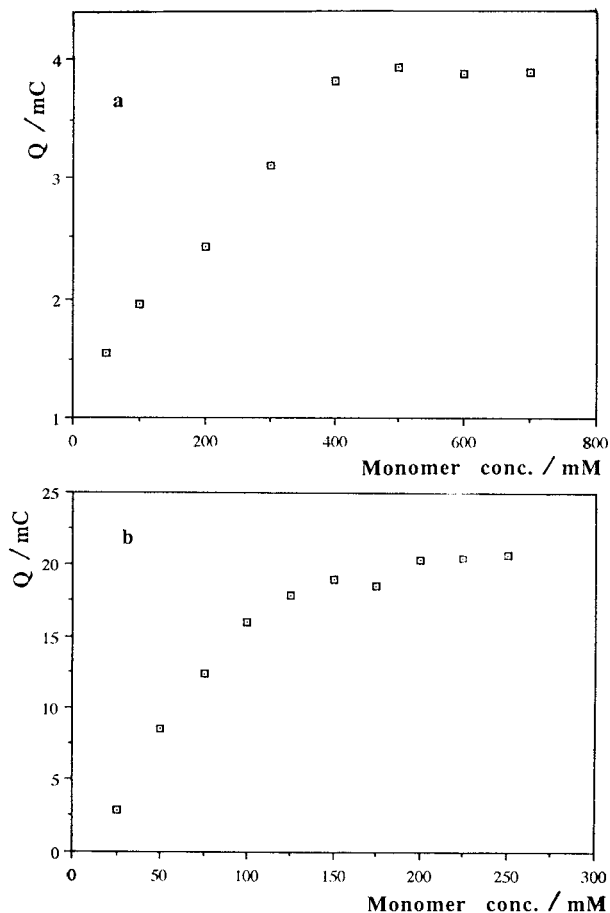
Figure 2 (a) Multisweep cyclic voltammogram taken during the growth of polythiophene in acetonitrile; $C_{thiophene}$ = 400 mM: (b) cyclic voltammogram of polythiophene in acetonitrile + 0.1M TBAFB (blank solution); scan rate, 100 mV s^{-1}.

trations, there appears to be no further improvement in the film formation. A methyl substituent in the 3-position in the latter monomer stabilizes the cation radical formed during electrooxidation. This ensures the participation of most of the cation radicals in the electropolymerization. A relative instability of the cation radicals of unsubstituted thiophene causes an increase in the amount of the monomer required in the polymer formation.

Figure 3 Variation of the charge measured from cyclic voltammetric curves in blank solution with monomer concentration: (a) for polythiophene; (b) for poly(3-methylthiophene); scan rate, 100 mV s^{-1}.
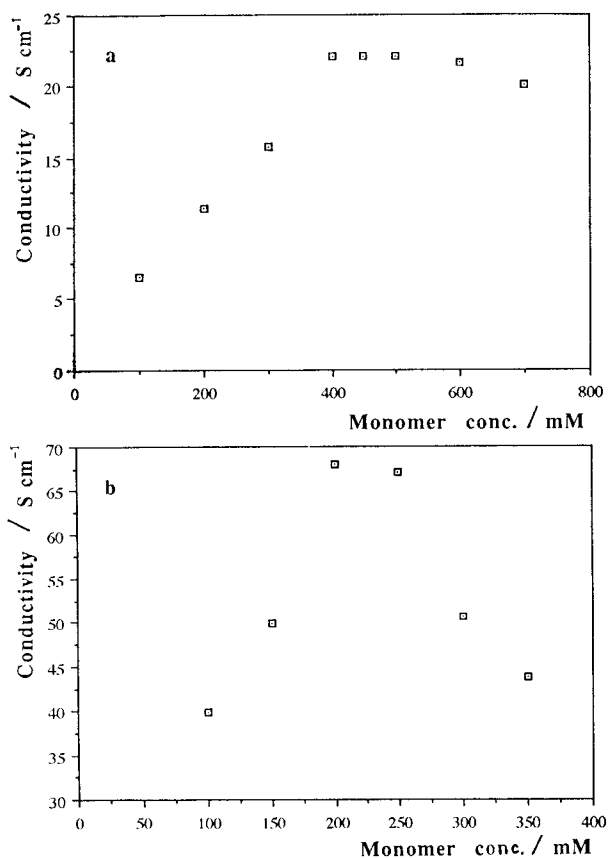
Figure 4 Variation of dry conductivities with monomer concentration: (a) for polythiophene: (b) for poly(3-methylthiophene).

presence of added 100 mM pyridine. Exactly the same curve was obtained when the electropolymerization was carried out with 3-methylthiophene. These cyclic voltammograms matched exactly that of protonated pyridine prepared in the same solution.

It appears that the unreacted monomer causes deprotonation of the doped polymer, forming a nonconducting degraded form of the polymer. The presence of a methyl substituent in the 3-position is even more effective in deprotonation. That is why the decrease in the conductivity value is more pronounced in poly(3-methylthiophene) beyond the optimum monomer concentrations.

Effect of Anhydrous Acid Concentration

The above results emphasize the importance of the stability of the cation radicals that initiate the electropolymerization. To ensure the stability of the cation radicals, increasing amounts of anhy-

drous HBF$_4$ were added to the electropolymerization medium, keeping the optimum monomer concentrations constant. As seen in Figure 7, the amount of the film increases with added acid. After the stoichiometric concentrations of the added acid, the amount of the film produced remains constant. The effect of the added acid is more pronounced in the case of polythiophene formation. The cation radical of thiophene is much less stable than that of 3-methylthiophene. The presence of the acid in the medium stabilizes the cation radical of 3-methylthiophene less effectively since it is already relatively stabilized by the existence of a methyl group in its structure.

The presence of anhydrous acid in the electropolymerization solutions containing the optimum amounts of monomers causes also an increase in the dry conductivities of the polymers formed. Figure 8 shows that the maximum dry
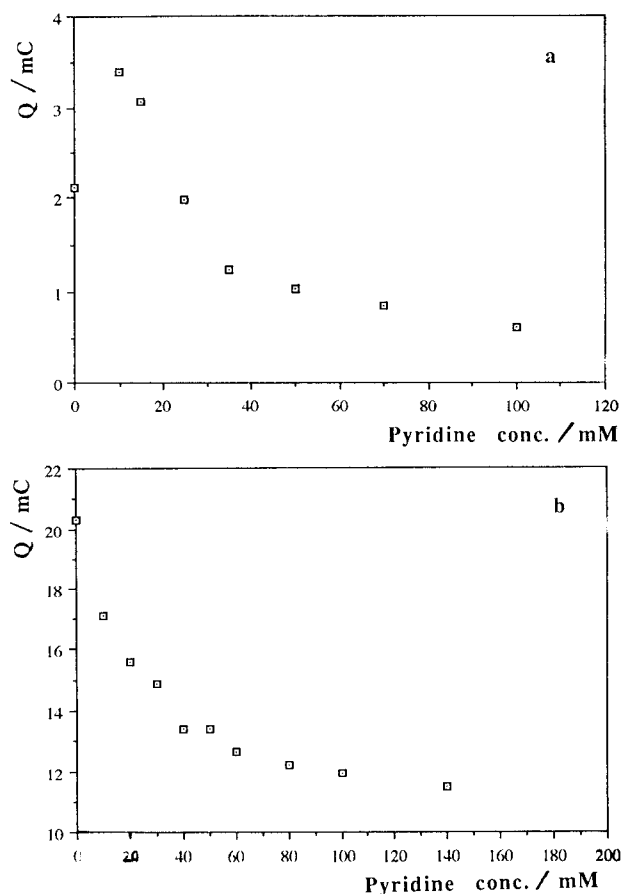

Figure 5 Variation of the charge measured from cyclic voltammetric curves in blank solution with pyridine concentration: (a) for polythiophene; (b) for poly(3-methylthiophene); scan rate, 100 mV s^{-1}.
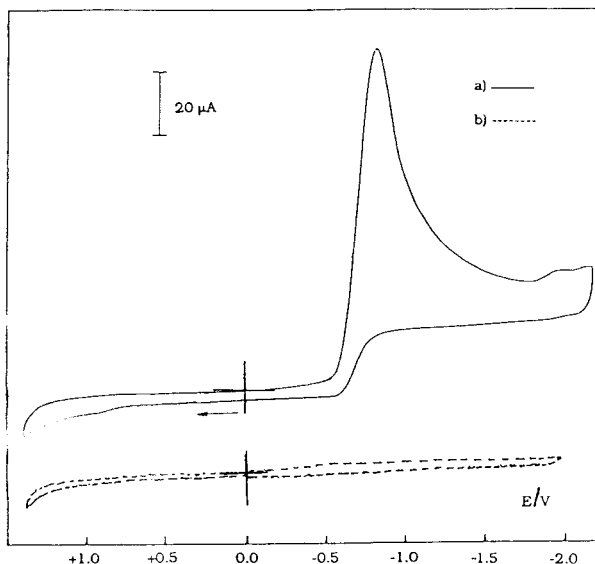
Figure 6 Cyclic voltammogram of electrolysis solution obtained (a) before and (b) after polythiophene formation, on a Pt electrode, in the presence of added 100 mM pyridine; scan rate, 100 mV s^{-1}.

conductivity was obtained when the solution contained 400 mM of thiophene and 150 mM HBF$_4$ in the case of polythiophene and 200 mM of 3-methylthiophene and 25 mM of HBF$_4$ in the case of poly(3-methylthiophene). It is interesting to note that the higher conductivity values obtained at low temperatures for polythiophene[6,10] can be achieved at room temperatures when anhydrous acid is used in the solution.

Another feature in the conductivity versus the acid concentration curves is the fact that the conductivities decreased after reaching a maximum value as the amount of the acid is increased. The radical–radical coupling is apparently an important step in the formation of the polymer:
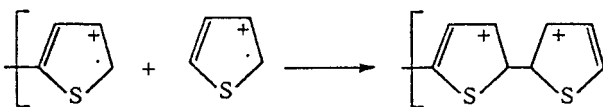
This dication must lose a proton forming a neutral species in order for a polymeric chain with a higher degree of conjugation to grow:
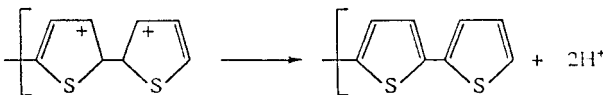
At higher acid concentrations, this deprotonation step is hindered and polymer chains with a lower degree of conjugation and lower conductivities are formed. But at lower acid concentrations, the increased stability of the monomeric cation radical is achieved, which causes an initial increase in the conductivity values.

Electrochemical Stability of Polythiophenes

The cyclic voltammogram of poly(3-methylthiophene) which was freshly prepared in acetonitrile containing 0.1M TBAFB is shown in Figure 9(a). The first oxidation peak corresponds to the formation of the radical cation. The second oxidation which is also called overoxidation produces the dication.[14] In the same supporting electrolyte solution containing 100 mM pyridine, the overoxidation peak in the cyclic volta-
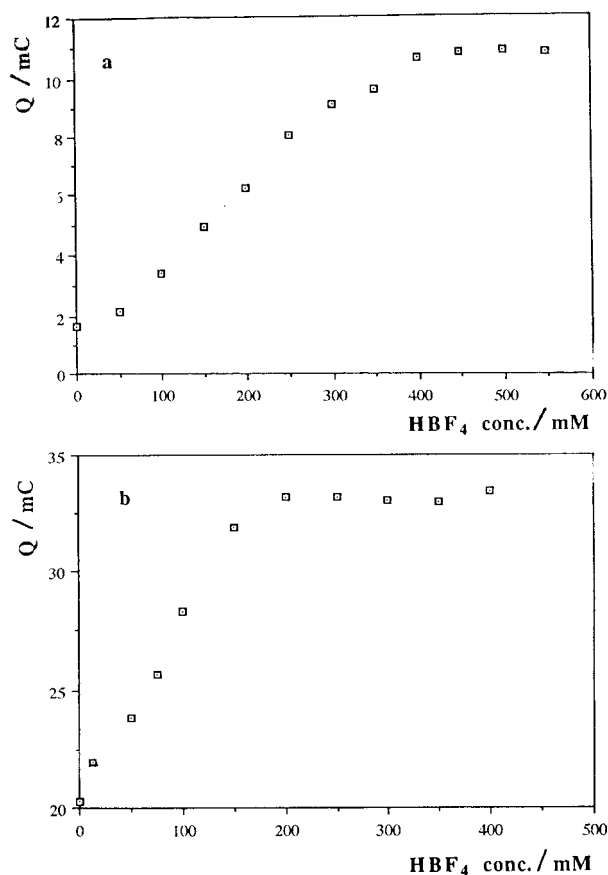

Figure 7 Variation of the charge measured from cyclic voltammetric curves in blank solution with HBF$_4$ concentration: (a) for polythiophene; (b) for poly(3-methylthiophene); scan rate, 100 mV s^{-1}.
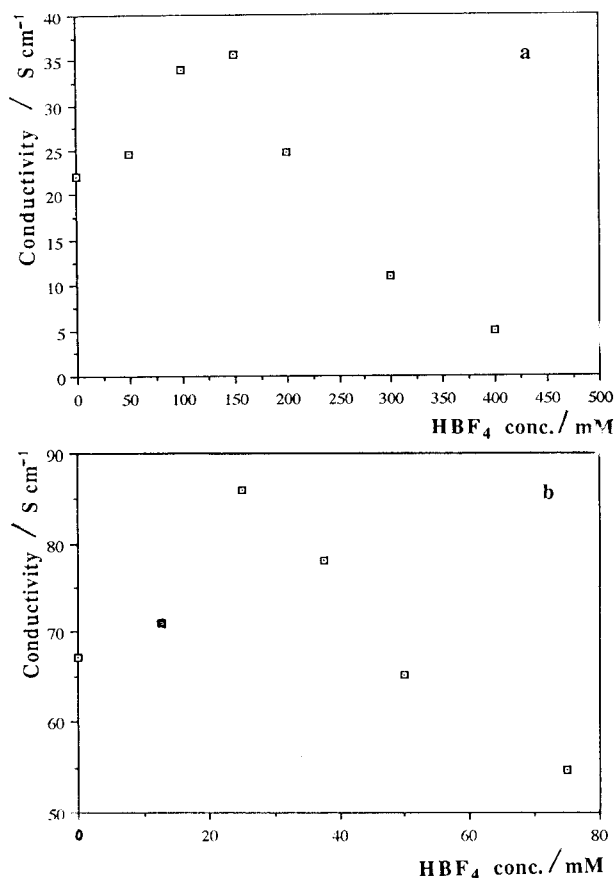
Figure 8 Variation of dry conductivities with HBF$_4$ concentration: (a) for polythiophene; (b) for poly(3-methylthiophene).

mmogram is shifted from +2.3 to +1.3 V [Fig. 9(b)]. When the same film is exposed to the supporting electrolyte solution and multisweep cyclic voltammetric scans between 0.0 and +1.8 V are applied, a gradual electroactivity loss was observed [Fig. 10(a)]. After about 50 scans with a scan rate of 100 mV/s, the electroactivity was almost completely lost. The same degree of electroactivity loss occurred much faster (after five scans) under the same experimental conditions in a supporting electrolyte solution containing 100 mM pyridine [Fig. 10(b)]. If the supporting electrolyte solution contains 150 mM added anhydrous acid, there was almost no loss of electroactivity after the multiscan experiments [Fig. 10(c)]. Similar results were obtained with the polythiophene films.

Figure 11(a) shows a cyclic voltammogram of the polythiophene film taken in acetonitrile

containing 0.1M TBAFB. Figure 11(b) is a cyclic voltammogram of the same film in the same solution after the film was electrolyzed at a constant applied potential of +1.5 V in the same supporting electrolyte solution until almost no charge was measurable. As seen, the electroactivity of the film was almost completely lost. As expected, much more rapid electroactivity loss was observed when the supporting electrolyte solution contained added base, under the same constant potential electrolysis conditions [Fig. 11(c)]. In contrast, very little loss of electroactivity was observable if the supporting electrolyte solution contained added anhydrous acid [Fig. 11(d)].

Figure 12(a) shows a part of the FTIR spectrum of the polythiophene film prepared under constant current electrolysis in acetonitrile. Under these conditions, polythiophene is electrolytically formed and doped simultaneously. The band at 790 cm^{-1} is assigned to be due to the out-of-plane aromatic C—H bending vibration.[24–27] If the same doped film is immersed in a supporting electrolyte solution containing pyridine, an increase in the intensity of this band was observed [Fig. 12(b)]. The same experiment which was repeated with the poly(3-methylthiophene) film gave no such increase in any band intensity in the same region of the IR spectrum [Fig. 13(a,b)].

Rapid electroactivity loss of the freshly prepared polythiophene-type films in solutions containing pyridine and the prevention of this deactivation in solutions containing anhydrous acid under potential scan or constant potential electrolysis conditions indicate the importance of the deprotonation reactions taking place during prolonged electrolytic doping of these films. The overoxidation and the attack of the nucleophiles on the deprotonated moieties follow. In another experiment, the deactivated film was reduced in a solution containing anhydrous acid at a potential about −0.10 V. Electroactivity of the film was not recovered. This result indicates that the oxidative degradation in polythiophene films was not reversible as opposed to the case in polyaniline. The overoxidation and the subsequent electroactivity loss occurred at less positive potentials if the doping was carried out in the presence of a strong nucleophile such as pyridine. A decrease in the out-of-plane aromatic C—H bending band intensity for the electroinactive films was easily detectable. Increase in the band intensity of the aro-
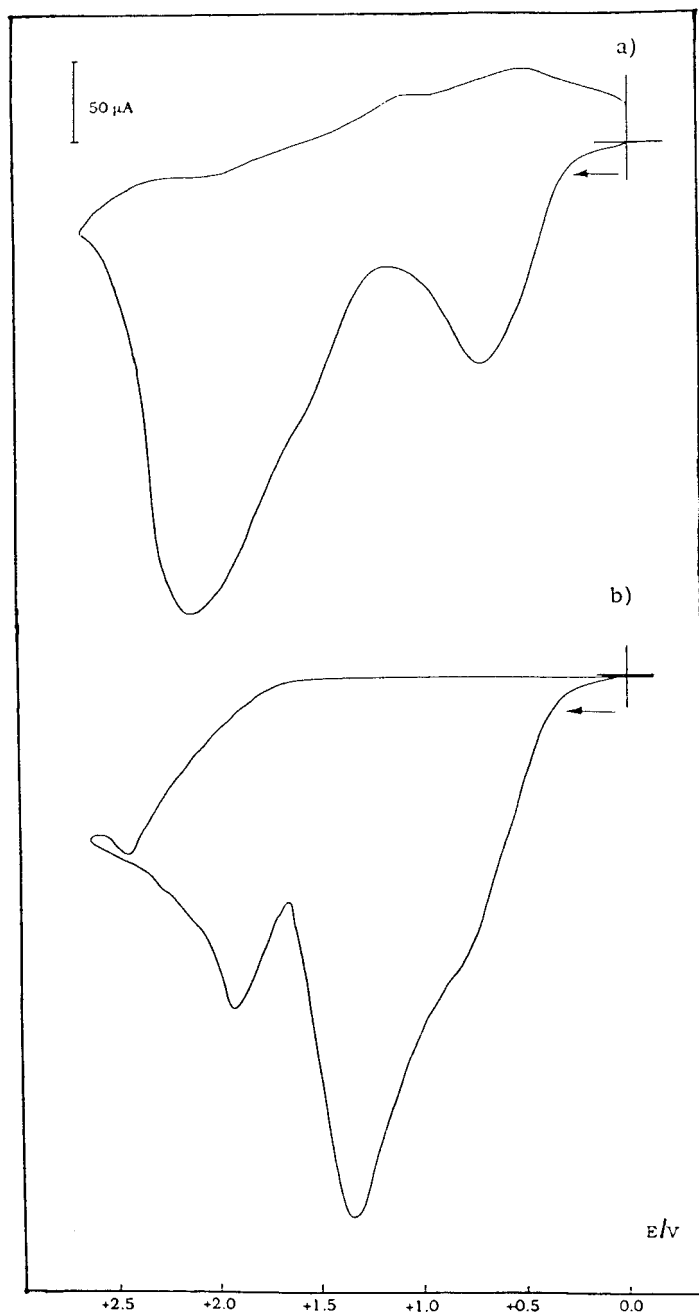
Figure 9   Cyclic voltammogram of poly(3-methylthiophene): (a) in acetonitrile + 0.1M TBAFB (blank solution); (b) in same solution containing 100 mM pyridine; scan rate, 100 mV s^{-1}.

matic C—H bending vibration upon immersing the freshly prepared doped polythiophene film in the pyridine solution also gives evidence for the important initial role of deprotonation (Fig. 12). No such increase should have been observed in the band intensity of the aromatic C—H out-of-plane bending vibration had the following direct initial nucleophilic attack occurred. Furthermore, no IR peaks (the aromatic C—H out-of-plane bending vibration at 748 and 703 cm^{-1}) due to pyridine were observed in the doped films immersed in pyridine:
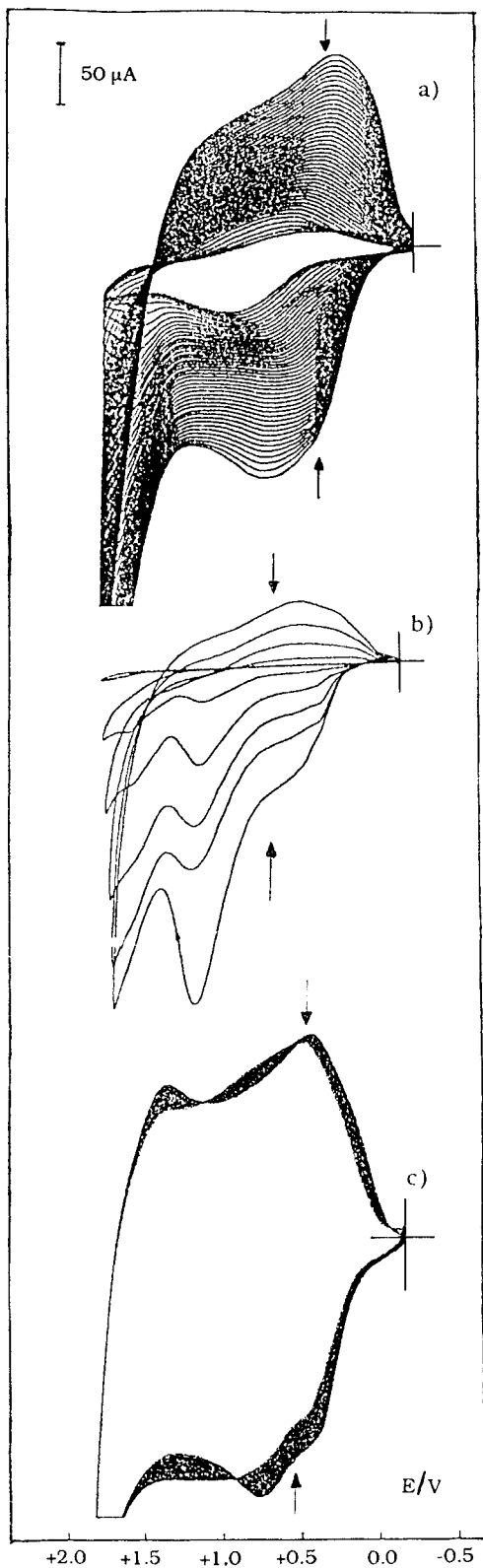
Figure 10 Multisweep cyclic voltammogram of poly(3-methylthiophene): (a) in acetonitrile + 0.1M TBAFB (blank solution); (b) in same solution containing 100 mM pyridine; (c) in same solution containing 150 mM HBF$_4$; scan rate, 100 mV s^{-1}.
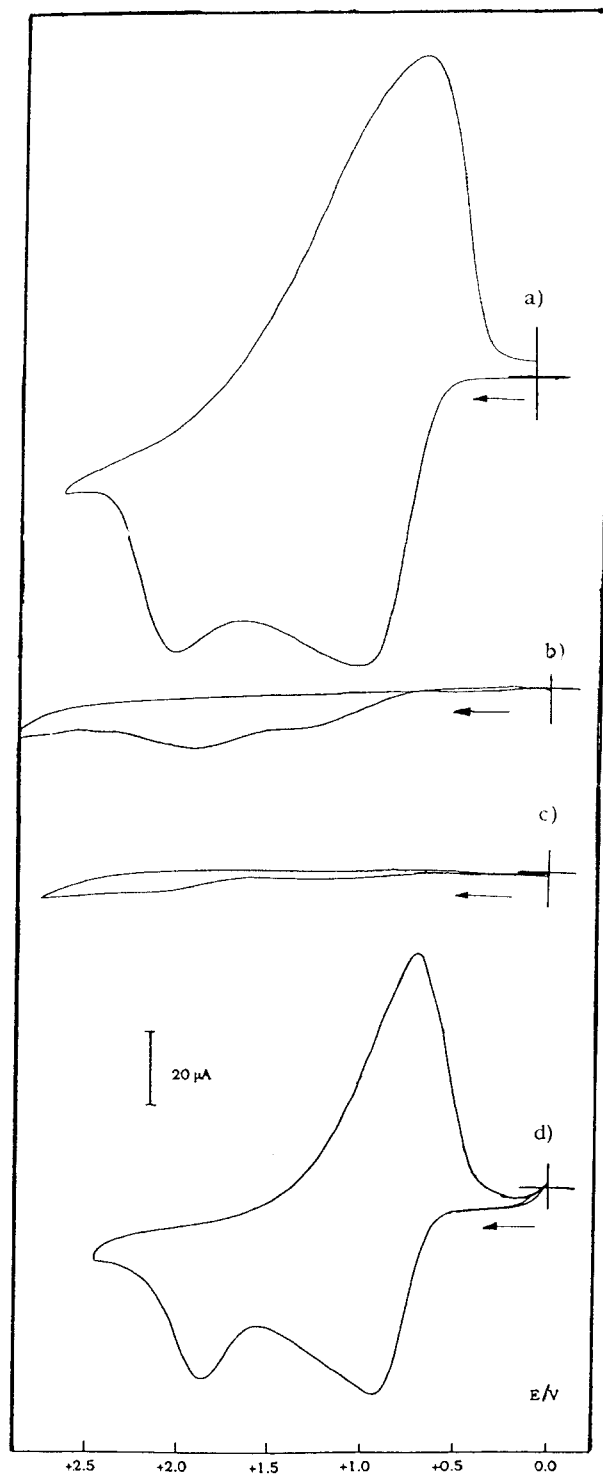

Figure 11 Cyclic voltammogram of polythiophene film: (a) in acetonitrile + 0.1M TBAFB (blank solution): (b) after the film was electrolyzed at +1.5 V in blank solution; (c) after the film was electrolyzed at +1.5 V in a solution containing 100 mM pyridine: (d) after the film was electrolyzed at +1.5 V in a solution containing 150 mM HBF$_4$; scan rate, 100 mV s^{-1}.
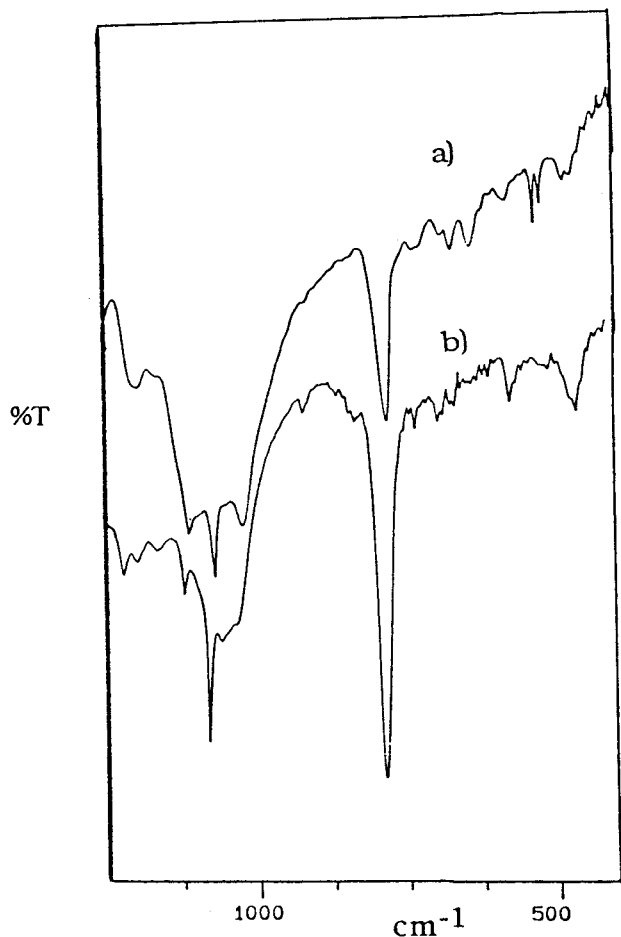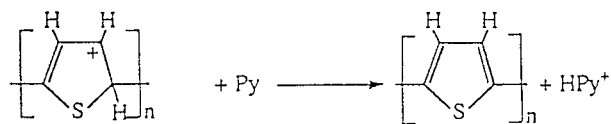
Figure 12 FTIR spectra of polythiophene film: (a) prepared under constant current electrolysis in aceto-nitrile +0.1M TBAFB; (b) after the film was immersed in a blank solution containing 100 mM pyridine.

The number of aromatic C—H bonds remained unchanged when the doped poly(3-methylthio-phene) was treated with pyridine, and no increase in the corresponding bond intensity occurred as a result:
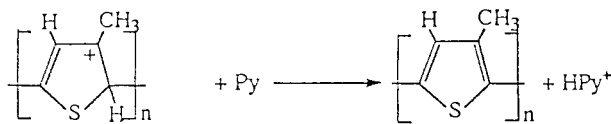
The formation of the HPy^+ was evidenced independently during the electrooxidation of polythio-

phene and poly(3-methylthiophene) in the supporting electrolyte solution containing pyridine through observation of its characteristic cyclic voltammogram, the same as that which is shown in Figure 6.

The above findings indicate the importance of the presence of anhydrous acid in the medium during electropolymerization. The added anhydrous acid improves the amount and the quality of the polythiophene-type films, as was also the case in polyaniline formation.[15] The substantial increase in the conductivity value was achieved at ambient temperatures working under acidic conditions. Similar improvements in the conductivity value were obtainable only at much lower temperatures working under nonacidic media in previous studies.[28] The use of optimum concentrations
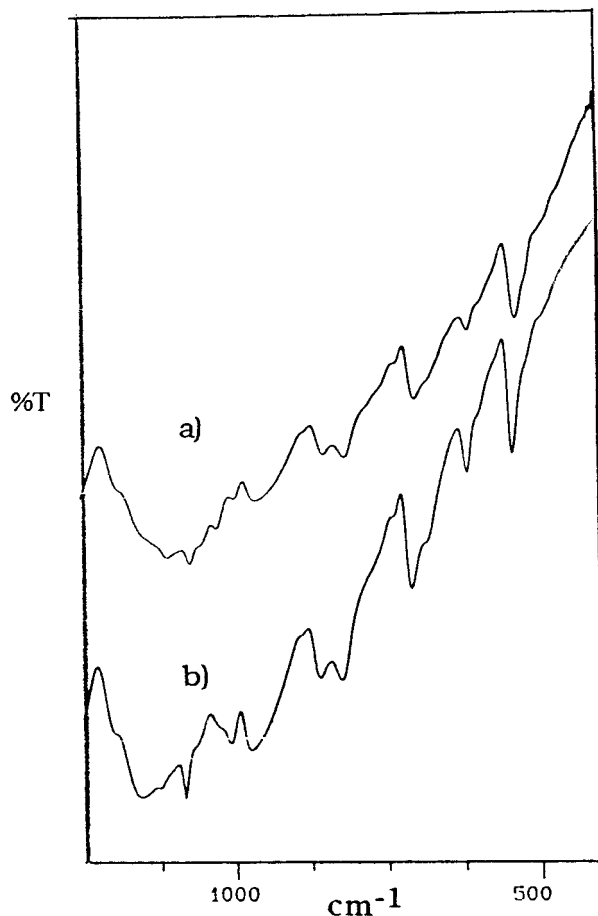

Figure 13 FTIR spectra of poly(3-methylthiophene) film: (a) prepared under constant current electrolysis in acetonitrile +0.1M TBAFB; (b) after the film in (a) was immersed in a blank solution containing 100 mM pyridine.

of the monomer and the added anhydrous acid provides ideal conditions for the electrosynthesis of the polythiophene-type samples in acetonitrile.

It can also be concluded that the deprotonation reaction is of utmost importance in the degradation of polythiophene-type films. The overoxidation and the nucleophilic attack which eventually causes degradation of the films follow the deprotonation reaction. Deprotonation can be minimized if anhydrous acid is added to the nonaqueous medium. Apparently, the nucleophilic attack to the positively charged centers of the polymer followed by deprotonation, as suggested in the literature,[1] is of less importance during the degradation of polythiophene-type films.

Improvements in the amount and the quality during electropreparation as well as the increased stability in the presence of anhydrous acid may have important beneficial effects for polythiophenes during their practical use.

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