Electropolymerization of Thiophene with and without Aniline in Acetonitrile

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The electrooxidation behaviors of thiophene and 3-methylthiophene on a Pt surface in acetonitrile/tetrabutylammonium tetrafluoroborate solution were investigated using cyclic voltammetry. The electropolymerization of these monomers and electrochemical properties of polythiophene and poly(3-methylthiophene) were studied in neutral, acidic and basic media. Mechanisms related to the formation of polymers and electroactivity loss were proposed.

The effect of thiophene on the electropreparation and properties of polyaniline were also investigated. The presence of thiophene in solutions of aniline in acetonitrile accelerates the formation and causes an improvement in the conductivity of polyaniline films. Thiophene, which catalyzes the polyaniline formation, enters into the structure of the polymer in solutions containing higher thiophene to aniline concentration ratios and forms a copolymer.

Introduction

The electropreparation and electrochemical stability of conducting polymers are of major importance for their use in different electrochemical systems such as batteries, electrocatalysis materials, sensor devices and electronic components[1−6]. We have determined the optimum conditions for the electropreparation of polyaniline and polypyrrole films in acetonitrile solutions containing anhydrous acid[7,8]. The results related to the electroactivity loss of polyaniline and polypyrrole films were also reported and deactivation, reactivation and degradation mechanisms were proposed[8,9]. The added anhydrous acid was very effective in increasing the amount and quality of the polyaniline film formed in this medium. The use of optimum concentrations of the monomer and the added anhydrous strong acid constitute the ideal conditions for the preparation of polyaniline.

If the protons are abundantly available near the electrode surface where the polyaniline film is growing, various forms of polyaniline, including pernigraline become protonated. This way autocatalytic growth of

the film occurs since chemical generation as well as electrochemical generation of the anilinium cation radical takes place as a result of the oxidation of aniline by the protonated pernigraline[9].

It has been found that the formation of the polyaniline film is accelerated and conductivity improved by the presence of electrogenerated cupric ion[10]. A catalytic mechanism involing the chemical oxidation of the monomer and the polyaniline film by cupric ions has been proposed.

In this review we present results concerning the effects of monomer and acid concentrations in electropolymerization of thiophene and 3-methylthiophene in acetonitrile/tetrabutylammonium tetrafluoroborate solution and the stability of these electrochemically prepared films in the same medium[11,12]. Furthermore, the role of the thiophene cation radicals which are cogenerated with the anilinium cation radicals is also elucidated[13,14].

Experimental

The procedure used to purify acetonitrile (Merck) has been described elsewhere[15,16]. Aniline (Merck) and thiophene (Sigma) were vacuum-distilled. Acetonitrile and concentrated monomer solutions were kept in darkness under nitrogen atmosphere. A diethylether complex of tetrafluoroboric acid (Aldrich) was used as an anhydrous acid. Tetrabutylammonium tetrafluoroborate (TBAFB) was prepared by reacting a 30 % aqueous solution of tetrafluoroboric acid (Analar) with a 40 % aqueous solution of tetrabutylamonium hydroxide (Aldrich). It was recrystallized from ethanol-water mixture and kept under nitrogen atmosphere after vacuum drying for 14h at $120°C$. All electrochemical experiments were carried out under nitrogen (BOS) atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl(sat)) and the counter electrode (Pt spiral). The acetonitrile/0.1 M 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). The macrosamples of polyaniline films were prepared on a Pt macroelectrode (area, 1.0cm^2). The working microelectrode was cleaned by polishing with Al_2O_3 slurry. The working macroelectrode was cleaned by being held it in a flame for several 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 vacuum dried. The pellets from the films were obtained under a pressure of 5 ton/cm^2. The dry conductivity values were measured by 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 electrochemical instrumentation consisting 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

Cyclic voltammograms of thiophene and 3-methylthiophene in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate showed them to be oxidized with a peak potential of +1.96 V and +1.62 V, respectively, producing their cation radicals. Figure 1a shows the multisweep cyclic voltammograms of 3-methylthiophene. During the multisweep cyclic scans the Pt electrode surface is covered with a black film. When these films

are immersed in a blank solution, a broad oxidation and a broad reduction peaks are detectable in their cyclic voltammogram due to the following reactions (Figure 1b):
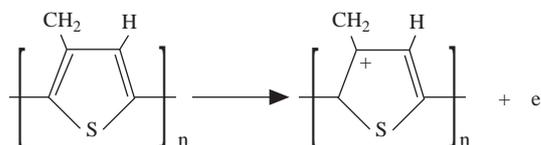
The charges measured from the cyclic voltammograms indicate the optimum thiophene concentration for polythiophene formation to be 400mM and the optimum 3-methylthiophene concentration for poly(3-methylthiophene) formation to be 200mM. The dry conductivity values were also found to be maximum at the optimum monomer concentrations of 22 S/cm and 67 S/cm, respectively.

The presence of a base such as pyridine in the electropolymerization solutions causes a significant decrease in the amount of the films produced because of the following deprotonation reactions of the cation radicals of monomers and polymers:
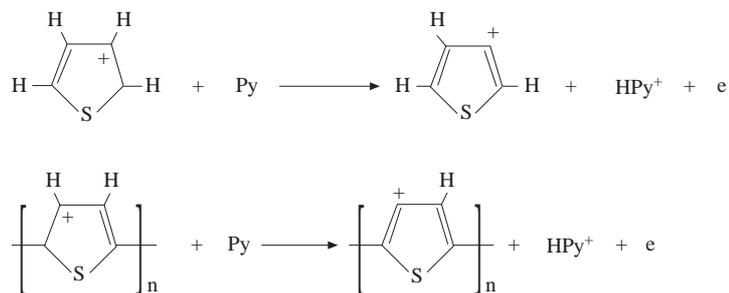
In contrast, the presence of anhydrous acid such as HBF_4 stabilizes the electrochemically produced cation radicals. In this way a substantial increase in the amount and the dry conductivity values is obtained. An approximately threefold increase in the amount of polythiophene was obtained when 400mM HBF_4 was present in the solution. The dry conductivity value increased as well, from 22 S/cm to 36 S/cm, when 100 mM HBF_4 was present in the solution. Similarly, an increase of about sixty percent in the amount of poly(3-methylthiophene) was obtained when 200mM HBF_4 was present in the solution. The dry conductivity value changed from 67 S/cm to 86 S/cm for poly(3-methylthiophene) when 25mM HBF_4 was present in the solution.

When polythiophene-type films are immersed in supporting electrolyte solution and multisweep cyclic voltammetric experiments are carried out at between 0.0 V and 1.8 V, the electroactivity of the films is lost gradually (Figure 2a). The electroactivity loss occurs much faster if the supporting electrolyte solution contains a free base such as pyridine (Figure 2b), whereas the presence of an added anhydrous acid causes almost no loss of electroactivity (Figure 2c). These results indicate the role of deprotonation reactions during the electropreparation. The overoxidation and the nucleophilic attack on overoxidized films causes degradation of the films.

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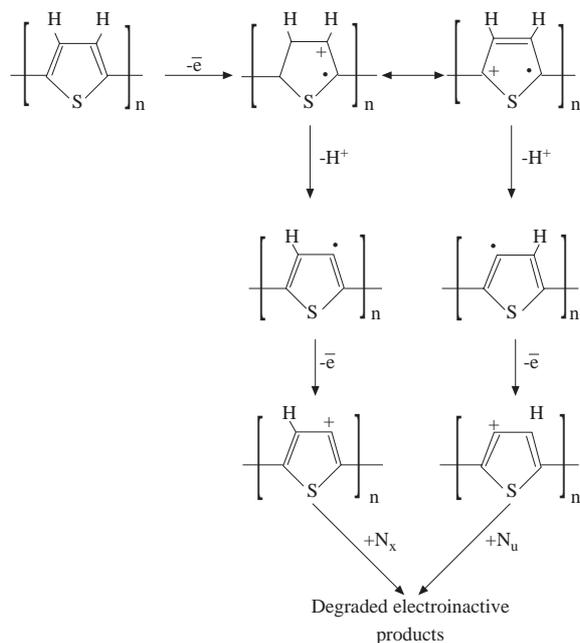
The degradation process is apparently irreversible since no recovery of the electroactivity was obtained when the degraded films were reduced in the presence of added acid at 0.1 V.
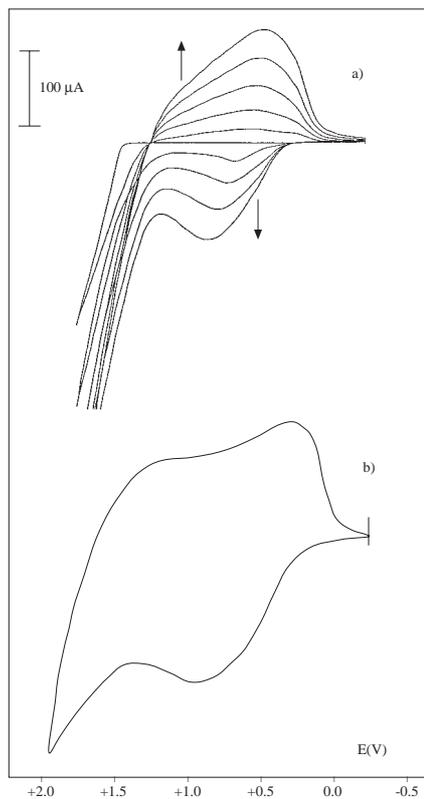
Figure 1. a) Multisweep cyclic voltammogram taken during the growth of poly(3-methylthiophene) in acetonitrile; $C_{thiophene} = 200$mM, b) The cyclic voltammogram of the poly(3-methylthiophene) in acetonitrile + 0.1 M TBAFB (blank solution) scan rate, 100 mV/s
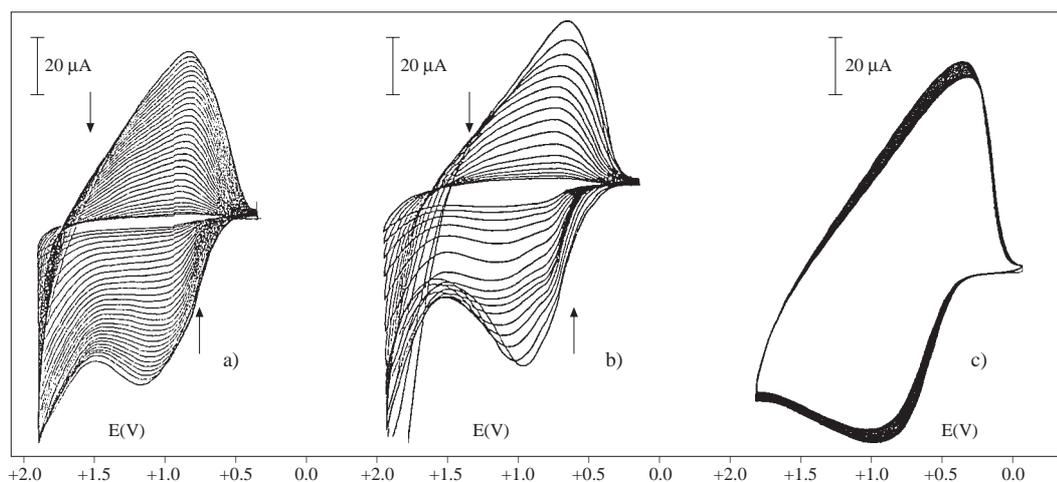
Figure 2. Multisweep cyclic voltammogram of poly(3-methylthiophene) a) in acetonitrile +0.1 M TBAFB (blank solution) b) in the same solution containing 100mM pyridine c) in the same solution containing 150mM HBF$_4$ scan rate, 100mV/s

Figure 3a shows the formation and growth the polyaniline film in acetonitrile solution containing 0.1M TBAFB, 250mM aniline and 75mM HBF$_4$. The increase of the peak intensities of polyaniline oxidation and reduction becomes much faster when 100mM thiophene is added to the same solution (Figure 3b). Only trace amounts of sulfur (0.5%) in the film structure were found in elemental analysis up to this concentration ratio of thiophene and aniline present in the electropolymerization solution. Furthermore, the dry conductivity values also improved when the polyaniline film was prepared in the presence of thiophene in solution. This value increased from 1.2 S/cm, when no thiophene was present initially, to 12 S/cm with the addition of 75mM thiophene to the electrolysis solution. After this concentration, the conductivity value started to decrease, reaching 2.0 S/cm at 400mM thiophene.

The above findings indicate the involvement of the following catalytic mechanism for polyaniline formation. Thiophene cation radicals which are coproduced with the cation radicals of aniline during the cyclic voltammetric scans, oxidize aniline monomer. Thus aniline cation radicals which initiate polyaniline formation are produced chemically as well as electrochemically:

$$
\begin{aligned}
ANI &\rightarrow ANI^{+\cdot} + e \\
T &\rightarrow T^{+\cdot} + e \\
T^{+\cdot} + ANI &\rightarrow T + ANI^{+\cdot}.
\end{aligned}
$$
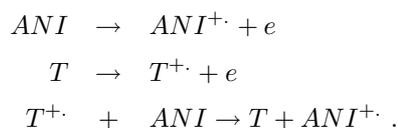
Thiophene radical cations are also capable of oxidizing the oligomers and eventually the polymers of shorter chain length which are responsible for the propagation of the polymerization. Fast-growing and better-conducting polyaniline films result.

At higher concentration ratios of thiophene to aniline, the elemental analysis results show that thiophene moieties are incorporated in the polymeric structure. The presence of about 20 % sulfur was measured in the polymer obtained from a solution initially containing thiophene and aniline at a concentration ratio of about 0.6. The cyclic voltammetry also demonstrated the presence of thiophene, through the existence of a polythiophene overoxidation peak at +1.8 V (Figure 3c). GCMS analysis of the solution remaining after electropolymerization was carried out under these latter conditions (at higher thiophene/aniline ratios) proved the existence of an aniline-thiophene dimer. More evidence for the formation of a new type

of conducting polymer was obtained by DSC analysis. The glass transition temperature, T_g, of the new polymer was found to be $285\,^\circ$C. This value was between the T_g of pure polyaniline ($315\,^\circ$C) and T_g of pure polythiophene ($224\,^\circ$C). These last results imply the formation of a possible new alternating-type copolymer of aniline and thiophene.
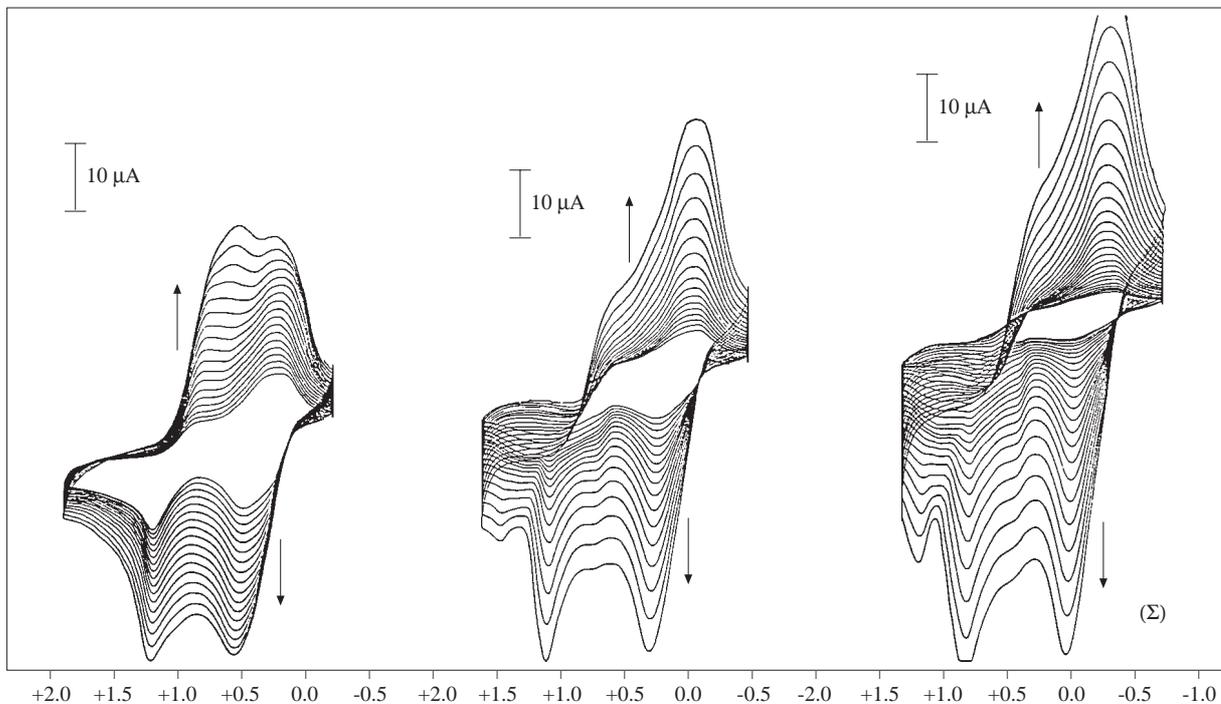
Figure 3. Multisweep cyclic voltammogram taken during the growth of polyaniline in acetonitrile, $C_{aniline} = 250$mM, $C_{HBF_4} = 75$mM a) in the absence thiophene b) in the presence 100mM thiophene c) in the presence 150mM thiophene scan rate, 100mV/s

Acknowledgements:

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