JOURNAL OF MATERIALS SCIENCE **40** (2005) 1163– 1168

Synthesis of aniline—thiophene copolymer on β-PbO_2 electrode in acetonitrile

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Electrochemical copolymerization of aniline and thiophene was investigated on β-PbO_2 electrode in acetonitrile. Optimum experimental conditions were determined for copolymerization. Copolymer films synthesized on β-PbO_2 electrode were analyzed by cyclic voltammetry, dry conductivity measurements, FT-IR spectroscopy, elemental analysis and thermal methods. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Conducting polymers based on heterocycles such as polyaniline, polythiophene and polypyrrole have attracted considerable attention in recent years due to their high conductivity, interesting electrochemical properties and easy preparation. Several applications of these polymers are promising such as batteries [1], sensors [2], electrochromic devices [3], and electronic devices [4]. Electrochemically generated polythiophene and polyaniline films are advantageous for these applications as they show a good stability to oxygen and moisture in both undoped and doped forms. Conducting copolymers have high potential for modifying the physical properties of the homopolymers, providing materials with intermediate properties between two polymer systems and potentially soluble and processable conducting materials [5, 6].

Attempts have been made to copolymerize different kinds of heterocyclic compounds such as pyrrole-thiophene and pyrrole-terthienyl to improve the processability of the resulting conducting structure. However, only limited work was reported about aniline-thiophene copolymer due to the large difference between the oxidation potentials of two types of monomers. Bithiophene was used for copolymerization instead of thiophene [7], however thiophene is more conventional. Talu *et al.* [8] could synthesize aniline and thiophene copolymers and composites in acidic ($HClO_4$) medium on platinum electrode. Can *et al.* [9] also used acidified medium (HBF_4) and obtained aniline-thiophene copolymer on platinum electrode.

Metals and metal oxide electrodes can be used on electropreparation of conducting polymers. PbO_2 is a preferred metal oxide electrode because of its low electrical resistivity, good chemical stability, low cost and high oxygen overpotential [10]. PbO_2 anodes which may be readily electrodeposited are cheaper than platinum and able to withstand prolonged high positive potentials more effectively than graphite which undergoes degradation [11]. PbO_2 was used in the electrooxidation of organic and inorganic materials, ozone generation and in oxidative degradation of organic pollutants such as dimethylsulfoxide and phenols [12]. It is well known that PbO_2 exists in two different crystallographic forms (α and β]. However, it is also known that, the preferred form of PbO_2 in lead acid batteries, as well as for electrosynthesis applications is the β form [13]. In our previous studies, it was determined that PbO_2 surfaces can be used also for electropolymerization and β form of PbO_2 has stronger performance on electropolymerization with respect to α form. For example, aniline was polymerized on PbO_2 surfaces from acetonitrile and found that β-PbO_2 gave rise to the formation of polyaniline in higher yields (approximately 20 times) than α-PbO_2 [14]. Electropolymerization of thiophene in acetonitrile was also achieved on PbO_2 electrodes and again determined that the amount of the polythiophene was higher for β surfaces. β surfaces could also polymerize thiophene from aqueous solution [15].

The aim of the present work is to obtain the aniline-thiophene copolymer on β form of PbO_2 electrode in acetonitrile without any acid present and to investigate the properties of copolymer formed.

2. Experimental

2.1. Chemicals

Aniline and thiophene were vacuum distilled and were kept under a nitrogen atmosphere. The procedure used to purify acetonitrile (Merck) has been described elsewhere [16, 17]. It was kept under a nitrogen atmosphere after purification. Tetrabutylammoniumtetrafluoraborate ($TBAF_4B$) was prepared by reacting a 30% aqueous solution of tetrafluoroboric acid (Analar) with 40% aqueous solution of tetrabutylammoniumhydroxide (Aldrich). It was recrystallized from

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ethanol + water mixture and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120°C. Tetrabutylammonium perchlorate (TBAP) was prepared by reacting concentrated perchloric acid solution (Analar) with a 40% aqueus solution of tetrabutylammonium hydroxide (Aldirich). It was recrystallized from ethanol several times and kept under a nitrogen atmosphere after vacuum drying for 24 h at 120°C. Lead perchlorate ($Pb(ClO_4)_2$) was prepared by reacting concentrated perchloric acid with lead monoxide (Analar).

2.2. Electrochemical cell

Electrochemical measurements were carried out under nitrogen atmosphere in a three-electrode type cell with separate compartments for the reference electrode (Ag, AgCl (sat)) and the counter electrode (Pt spiral). The working electrodes were a platinum disc (0.0132 cm^2) and a macro platinum electrode (3 cm^2).

2.3. Instrumentation

The electrochemical instrumentation consisted of PAR model 173 potentiostat-galvanostat coupled to a PAR model 173 universal programmer and a PAR model 179 digital coulometer. The current-voltage curves were recorded using a BBC Metrawatt Goertz X-Y recorder.

FT-IR studies were carried out by Bruker type Vector model spectrophometer.

Elemental compositions of the polymers were determined by Carlo Erba EA1108 Elemental Analysis Instruments.

2.4. Preparation of β-PbO_2

Pure β-PbO_2 surface was electrodeposited on a platinum surface at a constant current density of 50.0 $mA \cdot cm^{-2}$ from a solution which had 6 M H_2O and 100 mM $Pb(ClO_4)_2$ in acetonitrile/0.1 M TBAP [18]. The adherence of PbO_2 layers were extraordinary and one could only remove these layers with chemical treatment. The surfaces were also smooth and homogeneous.

2.5. Differential scanning calorimetry (DSC)

DSC of the polymer samples were recorded using a DSC Seteram Scientific and Industrial Equipment. The samples were initially dried under vacuum. Specimens having typical weights of 10 ± 20 mg were used for DSC measurements. The heating runs were made at a constant heating rate of 10°C/min under nitrogen atmos.

2.6. Dry conductivity measurements

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.

3. Results and discussion

Cyclic voltammetric response of a solution containing 250 mM aniline in acetonitrile/100 mM $TBAF_4B$ and a solution containing 150 mM thiophene in acetonitrile/100 mM $TBAF_4B$ on β-PbO_2 surfaces are given in Fig. 1a and b. As can be seen, aniline has an oxidation peak potential of +0.8 V vs. Ag/AgCl and thiophene has an oxidation peak potential of +1.9 V vs. Ag/AgCI. As was mentioned earlier, the main difficulty with electrochemical copolymerization of aniline with thiophene is the large difference between the electrooxidation potentials of these two monomers. This problem can be solved by controlling the concentration of monomers and by finding a suitable potential value between oxidation potential values of aniline and thiophene. In order to find the optimum aniline/thiophene concentration ratio for copolymerization, electropolymerization solutions were prepared by holding aniline concentration constant at 250 mM and adding increasing amounts of thiophene (25, 50, 75, 100, 150, 200, 250, 300, 350, 400 mM) to acetonitrile containing 100 mM $TBAF_4B$. Electrolyses were carried out in these electropolymerization solutions at constant applied potentials between the oxidation potentials of aniline and thiophene using β-PbO_2 electrodes. Elemental analyses were made for deposited films and possible coexistence of sulfur and nitrogen in films as an indication of copolymer formation, was investigated. It was determined that, the films which were deposited at potentials below 1.7 V vs. Ag/AgCl for any combination of aniline and thiophene did not contain any sulfur. These potentials were not sufficient to oxidize thiophene monomers and resulting films were composed of only aniline homopolymer. Elemental analysis results for the films which were formed on β-PbO_2 electrodes as a result of electrolysis at a constant potential of +1.7 V vs. Ag/AgCl is given in Table I. It is clearly seen from Table I that, there is no sulfur in the structure of polymeric films which were deposited from electropolymerization solutions having thiophene concentration lower than 150 mM. These films gave same elemental analysis results with polyaniline film which was deposited at a constant potential of 1.7 V vs. Ag/AgCI on β-PbO_2 electrode from

TABLE I The elemental analyses results and conductivities of the polymer films which were synthesized on β-PbO_2 electrodes at a constant potential of 1.7 vs. Ag/AgCl from acetonitrile solutions containing 250 mM aniline, 100 mM $TBAF_4B$ and different concentrations of thiophene (S = sulphur, N = nitrogen)

Thiophene concentration (mM)	% N	% S	N/S ratio	Conductivity (S/cm)
25	10.3	–	–	0.8
50	10.4	–	–	1.2
75	10.4	–	–	3.4
100	10.5	–	–	3.9
150	9.1	2.6	3.5	2.8
200	8.7	3.5	2.5	2.3
250	7.0	5.3	1.3	1.5
300	5.1	12.7	0.4	1.0
350	–	29.9	–	0.05
400	–	30.0	–	0.05
Polyaniline	10.2	–	–	0.3
Polythiophene	–	30.3	–	0.04

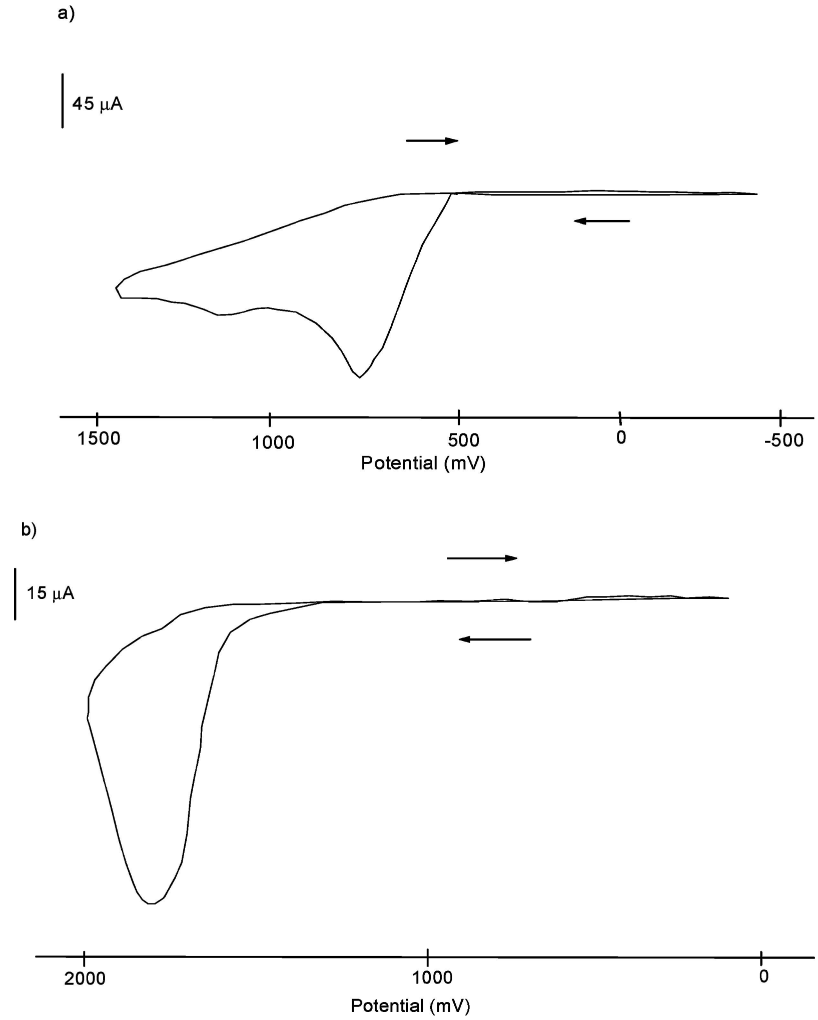

Figure 1 (a) Cyclic voltammetric response of a solution containing 250 mM aniline and 100 mM $TBAF_4B$ in acetonitrile (b) Cyclic voltammetric response of a solution containing 150 mM thiophene and 100 mM $TBAF_4B$ in acetonitrile (Working electrodes are β-PbO_2, Scan rate is 100 mV/s).

an acetonitrile solution containing 250 mM aniline and 100 mM $TBAF_4B$. However, it was found that the sulfur and nitrogen coexisted in the polymeric films which were electrodeposited from electropolymerization solutions having thiophene concentration between 150 and 300 mM. It was also found that the nitrogen to sulfur ratio in the polymeric structures decreased with the increase of thiophene concentration which might be an indication of incorporation of more thiophene rings into polymeric structure. After 300 mM thiophene concentration in electropolymerization solution, it was determined that the deposited films did not contain any nitrogen. These films gave same elemental analysis results with the polythiophene film which was deposited at a constant potential of 1.7 V vs. Ag/AgCI on β-PbO_2 electrode from an acetonitrile solution containing 150 mM thiophene and 100 mM $TBAF_4B$. These results indicated that, for possible copolymerization, concentration of aniline should be 250 mM and that of thiophene should be between 150 mm and 300 mM and 1.7 V vs. Ag/AgCI should be applied. This potential is on the highside for electropolymerization and partial overoxidation of deposited films is likely. Previous investigations using the in-situ UV-VIS spectroelectrochemical system and conductivity techniques showed, however, that, there was no degradation of the aniline-thiophene copolymer as a result of overoxidation at 1.7 V vs. Ag/AgCI on Pt electrode, although aniline homopolymer degrades considerably [19, 20]. Furthermore, the use of nonaqueous solvent is an advantage since it excludes any possibility of degradation due to OH attack to polymeric structure. Alternatively, the use of bithiophene which has lower oxidation potential than thiophene was proposed for copolymerization at lower applied potential [7]. In another study, Hu *et al.* lowered the onset oxidation potential of bithiophene by optimizing acetonitrile water ratio [21]. Alpatova *et al.* studied electrochemical synthesis of polylayer compositions from precursors of thiophene series (3,4-ethylenedioxythiophene (EDT), bi(3,4-ethylenedioxythiophene) (BEDT), bithiophene (BT)) [22]. It was determined that, when thin layers of PBEDT and PBT was deposited using potentiodynamic mode, electrochemical characteristics of the composition obtained are close to the copolymer including the same precursors.

Dry conductivity values of the polymer films were also measured. Table I lists the conductivity values of films which were deposited at constant potentials of 1.7 vs. Ag/AgCl on β-PbO_2 surfaces from electropolymerization solutions having 250 mM aniline, 100 mM $TBAF_4B$ and various amounts of thiophene in acetonitrile. As can be seen, the conductivity of deposited films increased with the addition of thiophene up to 100 mM due to electrocatalytic effect of thiophene radicals on polyaniline formation that was already proven by Can *et al.* [9]. In other words, the presence of increasing amounts of thiophene cation radicals in the medium caused higher conjugation of the polyaniline films and increased the conductivities. When the concentration of thiophene reached 150 mM, the conductivity of the deposited film decreased. This result showed that the deposited polymeric film is no longer polyaniline and instead it may consist of aniline and thiophene rings. This claim is also in good agreement with elemental analysis result which showed the presence of sulfur for the same film. For thiophene concentrations between 150 and 300 mM, the conductivity of deposited films showed changes possibly due to increasing amount of thiophene rings in polymer structures which was also supported by elemental analysis measurements indicating that nitrogen to sulfur ratio decreased from 150 mM thiophene concentration up to 300 mM thiophene concentration. It can also be seen from Table I that, the conductivity of deposited films after 300 mM thiophene concentration considerably decreased and had approximately the same conductivity as that of polythiophene film. The dry conductivity values, however, measured in this study are about two to three times lower than those measured for the copolymers prepared in acidic acetonitrile solution [9]. This may be explained by the overoxidation caused by the excessive catalytic action of the β-PbO_2 surface during the electropolymerization as was the case previously observed for the polyaniline and polythiophene films formed on the same catalytic surface [14, 15].

The films, which were deposited at constant potentials of 1.7 vs. Ag/AgCl on β-PbO_2 surfaces from electropolymerization solutions described above, were immersed into blank solutions (100 mM $TBAF_4B$ in acetonitrile) and their cyclic voltammetric responses were compared. It was determined that cyclic voltammetric responses of the films which were deposited from electropolymerization solutions containing thiophene concentration lower than 150 mM was the same except current values. The current values measured from the blank solution voltammograms of these films increased with the increase of thiophene concentration up to 100 mM thiophene concentration in electropolymerization solution. This is due to electrocatalytic effect of thiophene radicals on polyaniline formation. It must also be noted that, the blank solution responses of these films were also the same with the blank solution response of the polyaniline film which was prepared as described above. The cyclic voltammetric response of films which were deposited from electropolymerization solutions containing thiophene at a concentration range of 150 and 300 mM was very similar to each other but was different than the blank solution responses of films which were deposited from electropolymerization solutions containing thiophene concentrations lower than 150 mM. Cyclic voltammetric responses of the films, which were deposited from electropolymerization solutions containing thiophene concentration higher than 300 mM, was also different than the other blank solution responses mentioned above but was same with the behavior of polythiophene film which was prepared according to procedure described above. Cyclic voltammetric response of three films which were deposited from electropolymerization solutions containing 250 mM aniline, 0.1 M $TBAF_4B$ and 150 mM, 350 mM, and 100 mM thiophene respectively are shown in Fig. 2. The differences in blank solution responses can be clearly observed from Fig. 2. However, since the peaks were quite broad, It did not become possible to derive more clue about copolymer formation from these cyclic voltammograms.

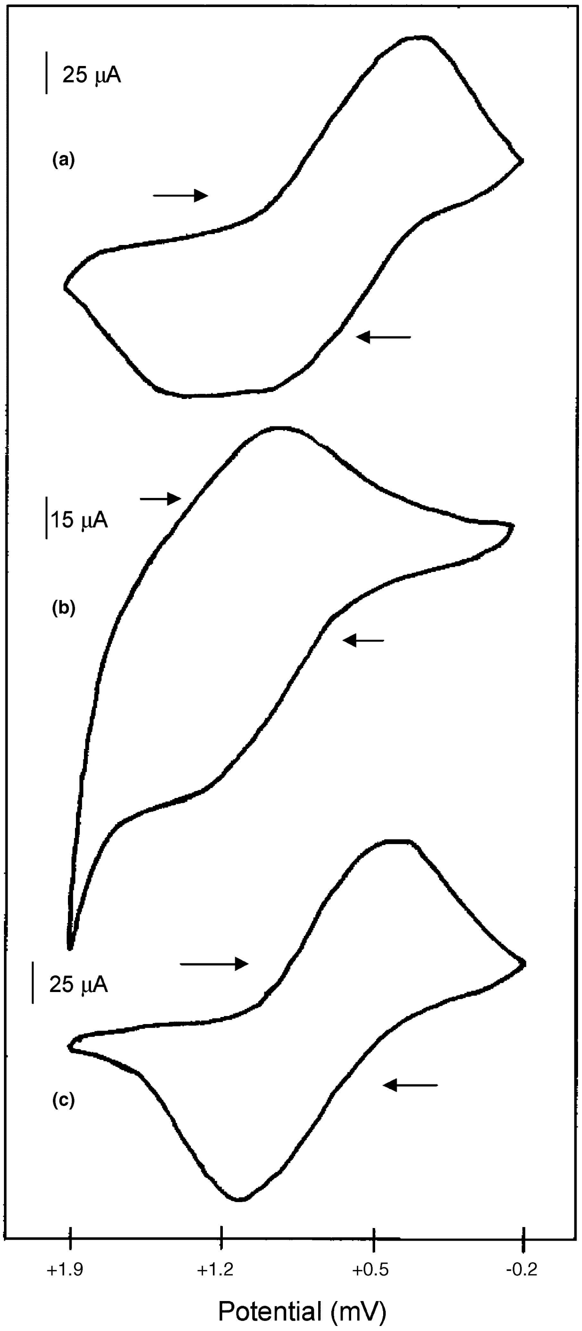

Figure 2 The blank solution cyclic voltammograms of polymeric films which were electrodeposited from acetonitrile solutions containing 250 mM aniline, 100 mM $TBAF_4B$ and thiophene (a) 150 mM, (b) 350 mM, and (c) 100 mM (Working electrodes are β-PbO_2, Scan rate is 100 mV/s).

Elemental analysis, cyclic voltammetric studies and dry conductivity measurements showed that possible copolymer formation starts with 150 mM thiophene concentration for an acetonitrile solution containing 250 mM aniline in 0.1 M $TBAF_4B$ and continues up to 300 mM thiophene concentration. After 300 mM thiophene concentration, polythiophene is formed on β-PbO_2 surface. However, in order to get more evidence about copolymer formation. FT-IR technique was also applied (Fig. 3). The films which were deposited on β-PbO_2 surfaces for electropolymerization solutions containing 250 mM aniline, 100 mM $TBAF_4B$ and thiophene that had a concentration lower than 150 mM gave the same bands with polyaniline which was prepared as described above. In the FT-IR spectrum of polyaniline, The 1576 and 1502 cm^{-1} bands are assigned to CC modes of the benzene ring. The 1241 and 1309 cm^{-1} bands correspond to the C—N stretching mode of polyaniline. The 828 cm^{-1} band corresponds to C—H bending vibrations [23]. The films which were deposited on β-PbO_2 surfaces for electropolymerization solutions containing 250 mM aniline, 100 mm $TBAF_4B$ and thiophene that had concentration higher than 300 mM gave the same bands with polythiophene which was prepared as described above. The major bands in the FT-IR spectrum of polythiophene can be interpreted as follows. The bands at 788 and 686 cm^{-1} are assigned to the CH out-of-plane bending vibrations. Absorption bands at 1491 and 1440 cm^{-1} are the C=C antisymmetric and symmetric stretching vibrations in the thiophene ring [24]. In FT-IR spectra of the films which were deposited on β-PbO_2 surfaces for thiophene concentrations between 150 and 300 mM the peaks which are characteristic for polythiophene (1491, 1440 and 788 cm^{-1}) and polyaniline (1576,1241,1309 and 828 cm^{-1}) also appeared and this observation clearly indicated that the films which were deposited at a thiophene concentration range of 150 and 300 mM had aniline and thiophene rings and supported our earlier results. In FT-IR spectra of copolymeric films, it can also be observed that, the intensities of the peaks which are characteristic for polythiophene increased when thiophene concentration in copolymerization solution was increased in the range of 150–300 mM. This result also supported our claim that, the increase of thiophene concentration in the range of 150–300 mM, leads to incorporation of more thiophene rings into polymeric structure.

As a final analysis, DSC curves of polythiophene, polyaniline, and the copolymeric film that was deposited on β-PbO_2 surface from an acetonitrile solution containing 150 mM thiophene and 250 mM aniline in 0.1 M $TBAF_4B$ were compared (Fig. 4). As can be seen, the glass transition temperature of the copolymeric film (230°C) is between the glass transition temperatures of the homopolymers, polyaniline (255°C) and polythiophene (210°C). It was also determined that, when thiophene concentration was increased in the range of 150 and 300 mM, the glass transition temperatures of the copolymeric films shifted to higher temperatures as another indication of incorporation of more thiophene rings [25]. However, glass transition temperatures of copolymeric films never exceeded 255°C. This is in good agreement with the expectation that the glass

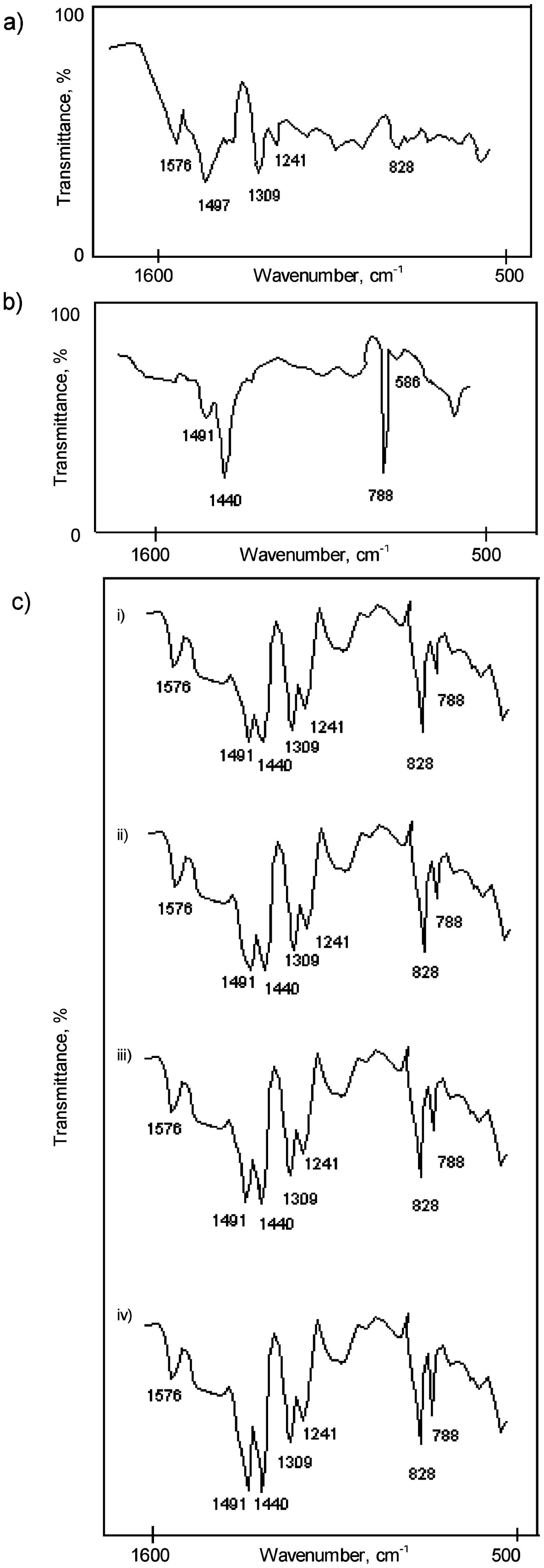

Figure 3 FT-IR spectra of (a) polyaniline which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 250 mM aniline and 100 mM $TBAF_4B$ (b) polythiophene which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 150 mM thiophene and 100 mM $TBAF_4B$ (c) the copolymeric films which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 250 mM aniline, 100 mM $TBAF_4B$ (i) 150 mM thiophene, (ii) 200 mM thiophene, (iii) 250 mM thiophene, and (iv) 300 mM thiophene. (Deposition potentials were 1.7 vs. Ag/AgCl.)

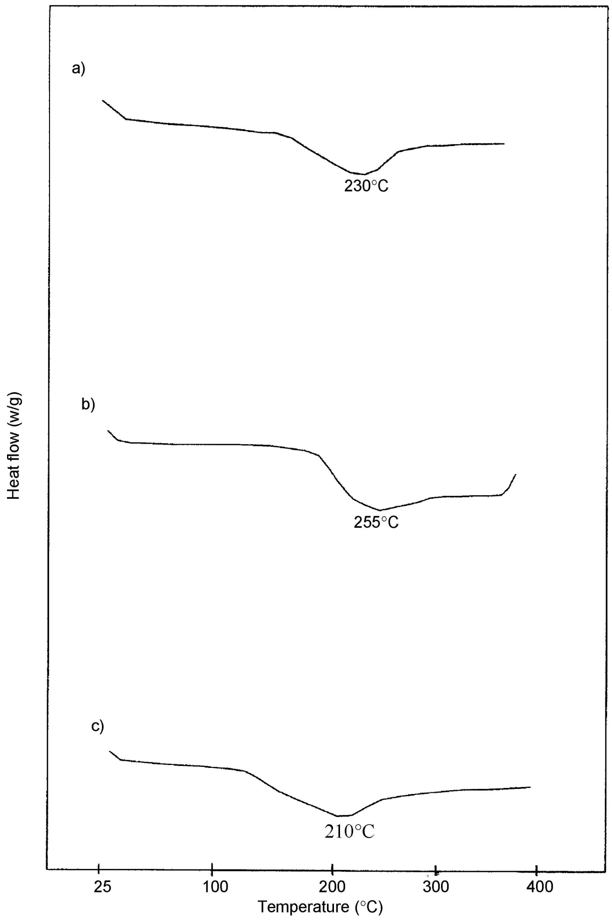

Figure 4 The DSC curves of (a) the copolymeric film which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 250 mM aniline, 150 mM thiophene and 100 mM $TBAF_4B$, (b) polyaniline which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 250 mM aniline and 100 mM $TBAF_4B$, and (c) polythiophene which was electrodeposited on β-PbO_2 surface from an acetonitrile solution containing 150 mM thiophene and 100 mM $TBAF_4B$ (Deposition potentials were 1.7 vs. Ag/AgCl).

transition temperature of the copolymer should be between the glass transition temperatures of the two homopolymers. These results exclude the possibility of the formation of the possible composite unequivocally.

It can be concluded from all these measurements aniline-thiophene copolymer can be formed on β type PbO_2 surfaces without any acid present. The necessary electrolysis potential for copolymerization is 1.7 V vs. Ag/AgCI. The suitable concentration range of thiophene for copolymerization is 150 mM $\leq C_{\text{thiophene}} \leq$ 300 mM for an acetonitrile solution containing 250 mM aniline and 0.1 M $TBAF_4B$. For thiophene concentration lower than 150 mM, polyaniline is formed and for thiophene concentration greater than 300 mM, polythiophene is formed on β-PbO_2 surface at the electrolysis potential of 1.7 V vs. Ag/AgCl

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Received 24 August
and accepted 22 November 2004