Electrodeposition of Polyaniline Films bearing Sulfonic and Hydroxyl Groups

Characterization and electrochemical stability

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New copolymers having 2-anilinoethanol and N-sulfopropylaniline acid, as units in the main chain were prepared by cyclic voltammetry from 1M H_2SO_4 aqueous solution, and deposited on Pt and ITO electrodes using solutions containing different monomers ratios of 1:1, 1:2 and 2:1. The electropolymerization processes were carried out by sweeping the working electrode potential between 0.0 V and 1.3 V at 50 mVs^{-1}, for 20 cycles. The copolymers were deposited as green layers on working electrode surface. All copolymers exhibit electrochemical activity in H_2SO_4 solution but they became unstable starting with the second cycle. Among all synthesised copolymers, only PAnEtOH-AnPS-12 shows electrochemical activity in acetate buffer solution, pH 6.5. Raman spectra recorded for PAnEtOH and PAnEtOH-AnPS-21 revealed the presence of the characteristic bands for polyanilines in both oxidized and reduced form. SEM and AFM micrographs revealed that the copolymers layers present a smooth and compact morphology with small roughnesses. It was evidenced that the change of the electrolysis medium pH induces changes in the morphology of the copolymers layers. Copolymers having both aniline monomers were obtained from acetate buffer solutions at pH 4.5 and characterized.

Keywords: self-dopable polyaniline; sulfonated polyaniline; 2-anilinoethanol; electrochemical deposition; cyclic voltammetry

Among all polyanilines, a special attention has been paid to sulfonated polyaniline, which possesses unique properties, different from other polyaniline derivatives, e.g. suppressed or not necessary in anion doping during oxidation or reduction processes, solubility in aqueous bases, extended redox activity for neutral and basic solution, etc. These unique properties make the sulfonated polyaniline very useful materials in fields like rechargeable batteries [1-3], sensing elements for sensors [4, 5] and biosensors [6-10], and for some polymer processing techniques. The presence of sulfonic groups induces changes in the geometry of polyaniline backbone, affecting their physico-chemical properties and enhancing their solubility in water [11-13]. Thus, sulfonated polyanilines present a better control of its electrical conductivity over a wide range of *p*H, improving thus some applications biocatalysts and biomedical sensors fields, where physiological *p*H values must be used [11, 14, 15]. A wide variety of sulfonated self-doped polyaniline can be prepared by polymerization of aniline derivatives substituted at nitrogen atom or at phenyl ring with sulfonic group, under chemical or electrochemical polymerization conditions. Recent researches revealed that the N-alkyl anilines do not have *p*H sensitivity [16] and this is due to the alkyl substituent, which is covalently bound to the nitrogen atom, preventing thus the formation of the EB form. The position of the sulfonic group substituent and the sulfonation degree influences the electric conductivity of the sulfonated polyaniline. The decrease of the electrical conductivity as compared with unsubstituted polyaniline can be explained by the higher twist of the phenyl rings relative to one another and increased interchain separation due to increasing density of sulfonated groups [17].

N-sulfopropyl aniline acid (AnPS) was studied already from the point of view of electrochemical and electrochromic activity. Homopolymers of this derivative have high solubility in water and basic aqueous solutions and thus hardly to be deposited on the electrode surface during the electropolymerization processes. There are some literature reports that describe the synthesis of copolymers obtained either by chemical, or by electro-chemical methods, which contain N-sulfopropyl aniline units in their backbone [18-21]. The electrochemistry of N-substituted derivatives of polyaniline is less complex than for PANI because the acid-base reaction (EB-ES transition) is hindered by the N-substituent.

2-anilinoethanol (2-AnEtOH) is an electroactive aniline derivative, which forms solid and adherent poly (2-anilinoethanol) films deposited on the working electrode surface during the anodic oxidation process [22]. Its copolymers with aniline exhibit good conductivity and thermal stability, high solubility in organic solvents, partial crystallinity and ability to produce freestanding films. Until now, the possibilities of using poly (2-anilinoethanol) in biosensors applications were not deeply studied. Only two papers reveal the electrochemical synthesis of homo- and copolymers based on this derivative [23, 24].

In this paper, we report the synthesis of new *co*polyanilines having hydroxy and sulfonic groups attached to the polymer chain as functional groups, by electrochemical polymerization. The electrochemical polymerizations of AnEtOH and AnPS were carried out, in 1M H_2SO_4 solutions, at room temperature, using different feed ratios of monomers. Because the properties and the morphology (porosity and thicknesses) of the deposited copolymers

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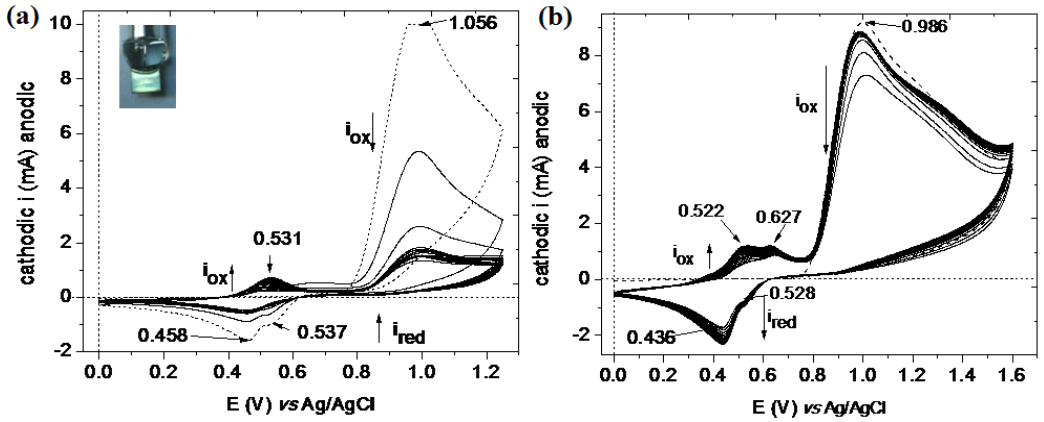

Fig. 1 CVs (20 cycles) recorded during the polymerization reaction of (a) 2-AnEtOH (10^{-2} M) (insert picture: the green layer deposited on Pt electrode surface) and (b) AnPS (10^{-2} M) at a Pt electrode (plate, 1.0 x 0.5 cm^2 area), in 1M H_2SO_4; scan rate: 50 mVs^{-1}; the first cycle is represented with dotted line

layers are susceptible to variations in working conditions, we studied the influence of the electrolysis medium *p*H. The electrochemical activity and stability of poly (2-AnEtOH) and poly[2-anilinoethanol-*co*-N-(3-sulfopropyl) aniline acid] were studied in 1M H_2SO_4 solutions and acetate buffer solution, *p*H 6.5.

Experimental part

Reagents

N-(3-sulfopropyl) aniline acid (AnPS) was synthesised as it is described in the literature [20, 25]. 2-AnEtOH (98%) was purchased from Sigma-Aldrich. 1M H_2SO_4 was prepared with freshly bidistilled water. Buffer acetate solution was prepared by mixing glacial acetic acid and sodium acetate and was adjusted at *p*H 4.5 and 6.5, by adding glacial acetic acid.

Instruments

All electrochemical experiments were performed, at room temperature, using a standard three-electrode electrochemical cell, Bioanalytical System, Potentiostat–Galvanostat (BAS 100B/W). The electrochemical cell contains three electrodes: a working electrode (a rectangular Pt plate with area of 1.0 x 0.5 cm^2, or ITO-glass, 8-12 Ω, with area of 2. 0 x 2.5 cm^2 purchased from Sigma Aldrich), a Pt wire as auxiliary electrode, and Ag/AgCl as reference electrode. Prior to electrochemical experiments a continuous flux of argon gas was purged in electrolytic solutions for 15 min. The copolymer films morphology was investigated by Atomic Force Microscopy (AFM) with a MultiView 4000 Nanonics System, working in non-contact mode using probes with the resonance frequency of 38–40 kHz, and by Scanning Electron Microscopy (SEM) performed with a Zeiss EVO 50XVP microscope on samples coated with Au to prevent electrical charging [$V_{acceleration}$ = 20 kV; 30 kV].

Results and discussions

Electropolymerization of N-substituted aniline

2-AnEtOH (10^{-2} M) was dissolved in 1M H_2SO_4 and cycled in the range of 0.0 - 1.3 V, at 50 mV s^{-1} scan rate. The recorded CVs are presented in figure 1(a). As it can be seen from the first scan, an oxidation wave assigned to the oxidation of the monomer appears at 1.056 V. During this process radical cations are formed which are highly reactive and can react with another cation radical or with parent molecule generating dimers. The intensity of this oxidation peak gradually decreases during subsequent cycle due to the consumption of the monomer at the electrode surface, while the polymer poly (2-AnEtOH) is deposited on the electrode. On the reverse scan, two cathodic peaks appear at 0.537 V and 0.458 V corresponding to the reduction processes of the oxidized species at the electrode-solution interface. Starting with the second cycle, two anodic peaks (0.506 V and 0.672 V) and two reduction peaks (0.527 V and 0.458 V) appear and these can be attributed to the oxidation and reduction processes of poly (2-AnEtOH). These redox peaks increase in intensity as the polymer film grows with successive scans. After 20 cycles, the electrode surface was covered with a green thin film of polymer PAnEtOH (fig. 1).

Figure 1 (b) shows the successive scans recorded during the polymerization of AnPS in 1M H_2SO_4, by potential cycling between 0.0 V and 1.6 V versus Ag/AgCl, at a scan rate of 50 $mV.s^{-1}$. On the first scan, AnPS undergo an oxidation process with an oxidation potential value of 0.986 V generating cation- radicals, which are highly reactive intermediate species. Electrochemically generated species react in the next step with solute monomers, yielding either oligomers or polymers, depending on reaction variables. The oligomers or polymers thus formed are diffused into the surrounding solution because of their high water solubility.

Electrocopolymerization of AnEtOH with AnPS

An attempt to obtain sulfonated polyaniline deposited on the electrode surface, by anodic oxidation of AnPS monomer failed, and the copolymerization seems to be an easy and efficient method to obtain stable and solid films. Furthermore, both aniline derivatives, AnEtOH and AnPS, have oxidation potential values appropriate and thus, the copolymerization reaction will be favourable.

Copolymerization of 2-AnEtOH and AnPS in three feed molar ratios 1:1, 1:2, and 2:1, was performed at Pt electrode and ITO electrode. The electrolysis of monomers mixtures were carried out in 1M H_2SO_4, at room temperature by sweeping the electrode potential between 0.0 V to 1.3 V, at a scan rate of 50 mVs^{-1} for 20 cycles (fig. 2). In figure 2 (a) are presented the cyclic voltammograms recorded during the copolymerization of AnEtOH and AnPS in 1:1 molar feed ratio, at Pt electrode. On the first scan one anodic peak appear at 0.998 V, attributed to the oxidation of the amine groups of both monomers. The anodic potential necessary to oxidise the 1:1 monomers mixture is slightly higher than the oxidation potential of monomers. The intensity of the first anodic peak gradually decreased during subsequent scans, and this is because of the consumption of monomers at the electrode-solution interface, while the number of the potential cycles is increased.

On the second cycle, two new anodic peaks (0.491 V and 0.630 V) and two reduction peaks (0.578 V and 0.470 V) appear. This step can be considered as a chain growth stage in which a copolymer having both monomers units in the backbone is formed. The subsequent cycles indicate that the polymerization reaction occurred and this is

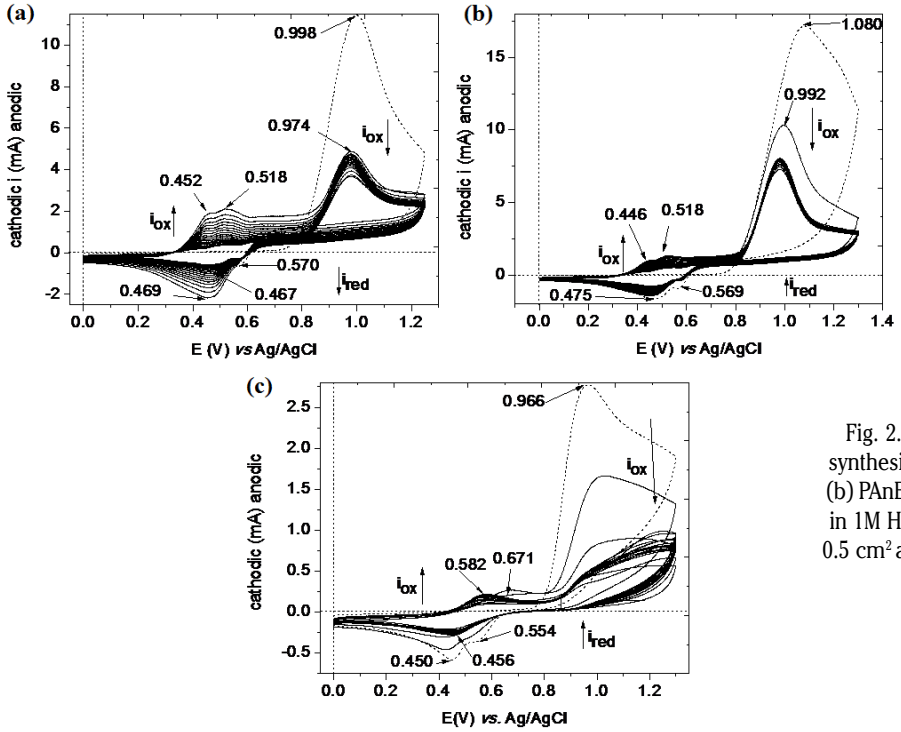

Fig. 2. CVs (20 cycles) recorded during the synthesis of *co*polymers: (a) PAnEtOH-AnPS-11, (b) PAnEtOH-AnPS-12, and (c) PAnEtOH-AnPS-21, in 1M H_2SO_4 as electrolyte and at Pt plate (1.0 x 0.5 cm^2 area); scan rate: 50 mV/s; the dotted line represents the first scan

evidenced by the gradual increase of the new anodic and cathodic peaks intensities as the number of the cycles is increased. Thus, at the end of the 20th cycles the cyclic voltammogram presents three anodic peaks located at 0.452 V, 0.518 V and 0.973 V, and one broad cathodic peak at 0.469 V. These peaks can be assigned to oxidation and reduction processes of the PAnEtOH-AnPS-11 copolymer, deposited on the Pt electrode as a solid green layer.

By increasing the amount of the AnPS in the monomers mixture, and by sweeping the working electrode potential between 0.0 V and 1.3 V, at a scan rate of 50 mVs^{-1}, the CVs presented in figure 2 (b) were obtained. On the first cycle one broad anodic peak at 1.080 V can be evidenced. The width of this peak can be interpreted as two overlapped anodic peaks assigned to the oxidation processes of the two aniline derivatives. The oxidation peak is shifted to higher potential values and this was induced by the increase of the amount of AnPS derivative related to AnEtOH, in the monomers mixture. On the reverse scan two cathodic peaks appear at 0.569 V and 0.475 V. As the scanning continues, the second cycle revealed the presence of two new anodic peaks located at 0.524 V and 0.642 V, and two cathodic peaks at 0.570 V and 0.475 V. These peaks increase in intensity while the anodic peak from the first cycle is shifted to lower values of potential and diminished in intensity, as the number of the scan increased. This fact suggests that new adherent copolymer is formed on Pt electrode surface. Indeed, at the end of the experiment a green layer of PAnEtOH-AnPS-12 was observed. Thus, the 20th cyclic voltammogram shows three anodic peaks located at 0.446 V, 0.518 V and 0.974 V and one cathodic peak at 0.456 V, which correspond to oxidation and reduction processes of the new copolymer film.

A mixture containing 2:1 molar feed ratio of AnEtOH and AnPS was submitted to electrolysis process and the recorded CVs are presented in figure 2 (c). The first cycle reveals an oxidation peak located at 0.966 V, and two cathodic peaks at 0.554 V and 0.450 V, on the reverse scan. The anodic potential necessary to oxidise the 2:1 AnEtOH-AnPS mixture is lower than in the previous two cases. As it can be seen, starting with the second scan the oxidation peak diminished in intensity and new oxidation peaks starts to grow (0.537 V and 0.671 V). Like in previous two cases, the subsequent cycles seems to be the chain growth stages in which the copolymer is formed and deposited on the electrode surface. This is proved by the fact that starting with the fourth cycle, the new anodic peaks and cathodic peaks increase in intensities as the number of scanning increase. After 20 cycles, the electrolysis was stopped and a green layer covered the working electrode. The 20th cyclic voltammogram revealed only one anodic peak at 0.582 V and one cathodic peak at 0.456 V because of oxidation and reduction processes of the deposited PAnEtOH-AnPS-21 copolymer.

Structural characterization of the copolymers

Because of the insolubility of all (co)polymers in any organic solvent, their structural characterization was not possible by usual solution techniques e.g ^1H NMR. Thus, the polymer PAnEtOH and PAnEtOH-AnPS-21 were characterized by RAMAN spectroscopy. For this, thin layers of (co)polymers were deposited on ITO-glasses by electrochemical polymerization, using the same conditions used for electropolymerization on Pt electrode. After 20 cycles, the electrolysis was stopped and the (co)polymers were washed with electrolyte solution and bidistilled water.

The Raman spectra of two copolymers, PAnEtOH and PAnEtOH-AnPS-21 were recorded at an excitation wavelength of 1064.0 nm (fig. 3). Spectra present all wavelength regions characteristic to polyaniline.

Within the wavenumber region ranging from 1500 to 1650 cm^{-1}, C–C and C=C stretching vibrations of benzene and quinone rings are most prominent. PAnEtOH and PAnEtOH-AnPS-21 layers present a wide band with maximum located at 1618 cm^{-1} and 1617 cm^{-1} respectively, which correspond to benzenoid ν(C-C) vibration from the emeraldine salts. By digital decomposition, three components was detected, 1618, 1594, 1574 cm^{-1} for PAnEtOH, and 1617, 1600, 1584 cm^{-1} for PAnEtOH-AnPS-21. These components were assigned to C=C stretching vibration from quinonoid ring and to C~C stretching vibration from semiquinone ring.

The band at 1480 cm^{-1} characteristic to oxidized polyaniline, is missing in PAnEtOH spectrum and this is because the resulting polymer is in the reduced form after

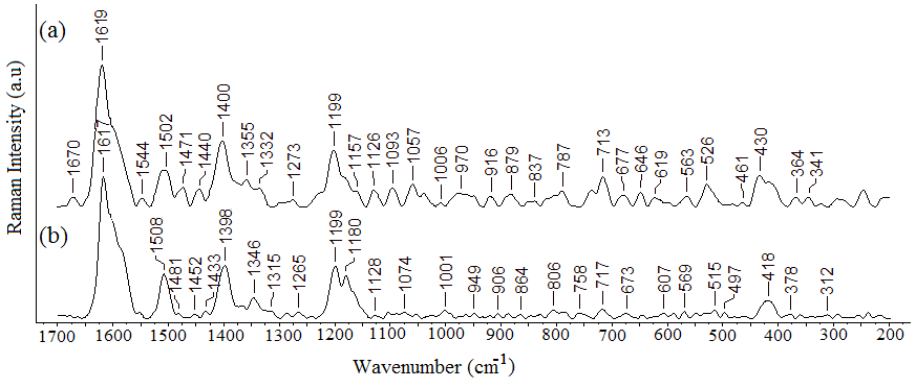

Fig. 3 FT-Raman spectra of thin layers of copolymers PAnEtOH (a), PAnEtOH-AnPS-21 (b), deposited on ITO-glass electrode by cyclic voltammetry. The excitation wavelength is 1064 nm

the reduction processes suffered during the deposition. Only in case of PAnEtOH-AnPS-21 appears a small band at 1481 cm^{-1} assigned to the C=N stretching mode.

The wavenumber range 1400-1300 cm^{-1} contains the stretching vibration of charged nitrogen segments ν(C~N^+) and can provide information on the charge delocalization in the polymer chains. In this case, the vibration bands located at 1359 cm^{-1} (PAnEtOH) and 1347 cm^{-1} (PAnEtOH-AnPS-21), indicate that the distribution of semiquinone radical structure in the chain is not uniformly, two types of differently organized polarons are present.

In case of PAnEtOH it can be seen a vibration band at 1271 cm^{-1} corresponding to stretching C-N vibration band from benzenoid ring of phenazine segments. This band does not appear in the PAnEtOH-AnPS-21 spectra.

The wavenumber range of 1200 -600 cm^{-1} contains C-H bending in-plane vibrations corresponding to quinonoid and benzenoid rings, 1177 cm^{-1} (PAnEtOH) and 1179 cm^{-1} (PAnEtOH-AnPS-21).

The morphology of the deposited layers was studied by SEM and AFM microscopy techniques. The SEM images recorded for all (co)polymers reveal smoother and uniform morphology. The observed smoother morphology is attributed to well-defined grain-to-grain attachment causing a compact deposition. In figure 4, we present only the scanning electron micrographs for PAnEtOH (a) and PAnEtOH-AnPS-21 (b). The cracks that appear in the PAnEtOH-AnPS-21 (b) copolymer layer may be the result of the rapid evaporation of the solvent but we can not exclude their formation during the electrochemical deposition.

In the case of copolymers PAnEtOH-AnPS-11, PAnEtOH-AnPS-12 and PAnEtOH-AnPS-21, the scanning electron micrographs do not revealed any significant morphology, they show a thin, uniform and compact structure (fig. 4).

As it is presented in figure 5, in AFM images, it can be seen a substantial difference between all three copolymer layers. As the ratio of AnPS units increase in the copolymer structure, its morphology became more dense and compact.

The presence of AnEtOH units in copolymer structure increases the bundle size and thus the surface became more dense and compact. The copolymer layers have small roughness factor Root Mean Square (Sq) and Average Roughness (Sa) of 14.30 nm and 10.74 nm for PAnEtOH-AnPS-11, 11.38 nm and 16.57 nm for PAnEtOH-AnPS-12 and 27.18 nm and 16.57 nm for PAnEtOH-AnPS-21 respectively.

Knowing that the *p*H of the synthesis medium represents a key factor in controlling the structure of polyaniline, we carried out the electrolysis of the solutions having different ratios between monomers, in acetate buffer solution with *p*H 4.5. In figure 6 are displayed SEM images of copolymers layers obtained during the cyclic voltammetry deposition (20 cycles at 50 mVs^{-1} scan rate, between 0.0 V and 1.3 V) on ITO electrode.

From the SEM images it can be seen that the morphology of copolymers layers changed with the increase of the pH of the electrolysis medium. In figure 6 (a) it can be seen the presence of a populated area of small spheres having dimensions between 700-800 nm, with a tendency to agglomeration. Increasing the amount of the AnPS units in the copolymer structure, its morphology is denser and more porous, with 200-400 nm pores size.

In the case of PAnEtOH-AnPS-11, this copolymer layer can be use as substrate to immobilize different biological molecules, such as enzymes, because this layer shows a high surface from entrapment.

Electrochemical activity of (co)polymers

The stability of the copolymers layers was investigated by sweeping the Pt-polymer electrode for several cycles in acidic (1M H_2SO_4) and in slightly acidic solutions (acetate buffer solution, *p*H 6.5). In figure 7 (a) are presented the cyclic voltammograms of PAnEtOH recorded in 1M H_2SO_4. It can be observed that the first voltammogram is similar to that obtained during the polymerization process of 2-anilinoethanol, except the fact that the peaks are shifted to more negative values. Two anodic peaks appear at 0.487 V and 0.946 V and two cathodic peaks appear at 0.443 V and 0.303 V being associated with oxidation and reduction

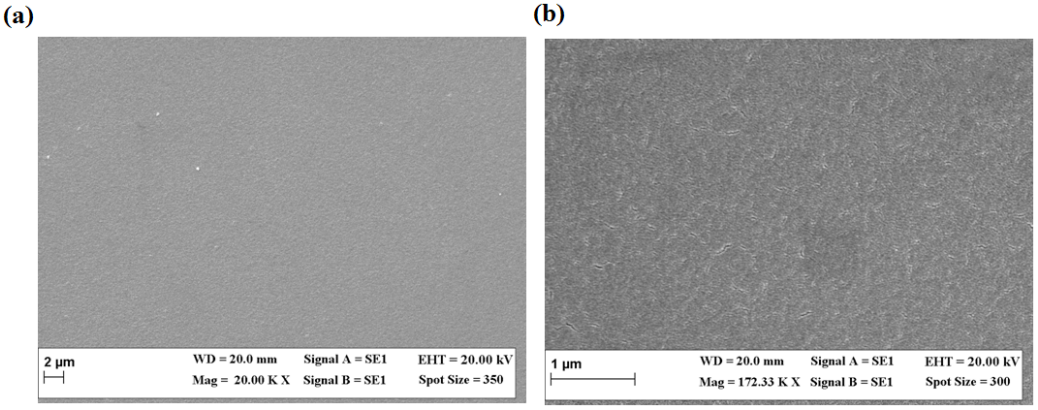

Fig.4 Scanning electron micrographs of polymeric layers deposited on ITO electrodes from 1M H_2SO_4 solution (20 cycles at 50 mVs^{-1} scan rate between 0.0 V and 1.3 V) for (a) PAnEtOH and (b) PAnEtOH-AnPS-21; scale bar is 2 µm for (a) and 1 µm for (b)

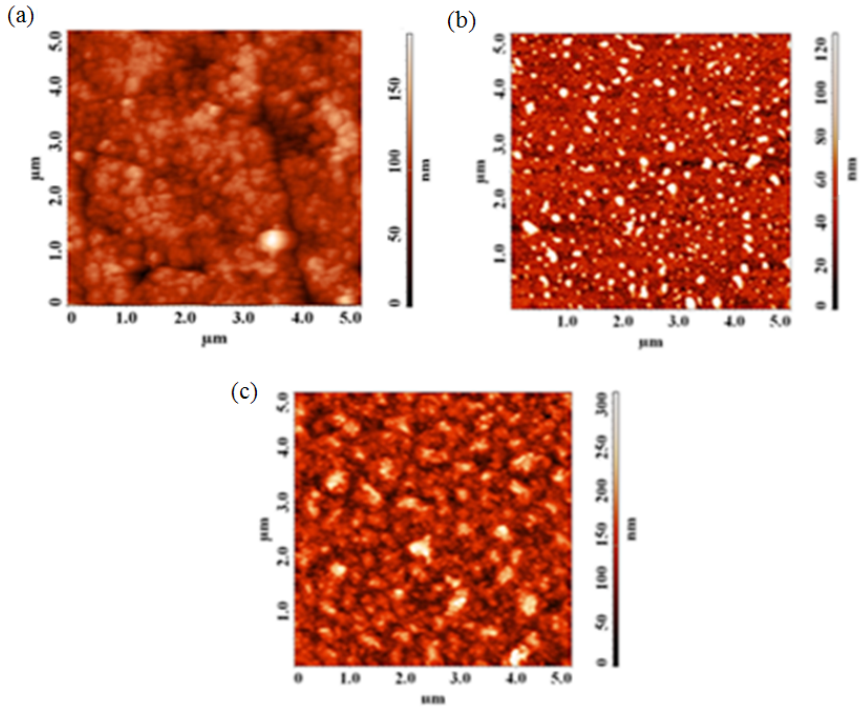

Fig.5 AFM images of (a) PAnEtOH-AnPS-11, (b) PAnEtOH-AnPS-12 and (c) PAnEtOH-AnPS-21 copolymers depsited on ITO electrodes from 1M H_2SO_4 solution (20 cycles at 50 mVs^{-1} scan rate between 0.0 V and 1.3 V)

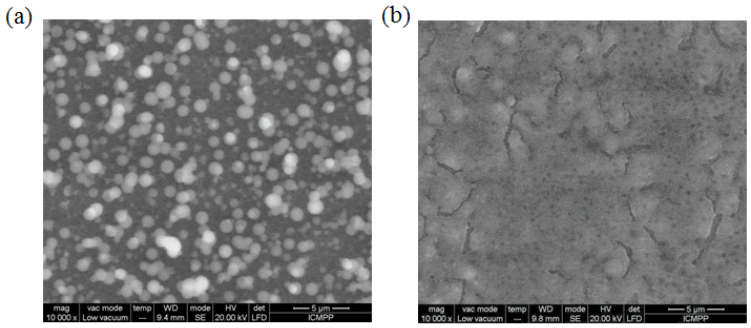

Fig. 6 Scanning electron micrographs of copolymer layer deposited on ITO electrodes from acetate buffer solution, pH 4.5 (20 cycles at 50 mVs^{-1} scan rate between 0.0V and 1.3 V) for (a) PAnEtOH-AnPS-11 and (b) PAnEtOH-AnPS-12

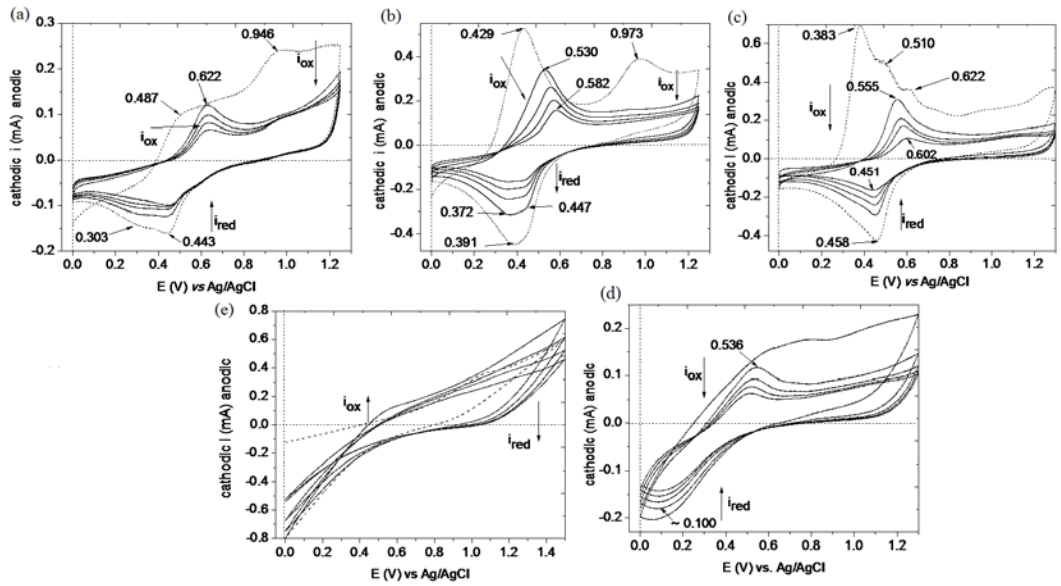

Fig. 7 CVs recorded during the cycling of (a) PAnEtOH (b) PAnEtOH-AnPS-11 (c) PAnEtOH-AnPS-12 layers in aqueous solution of H_2SO_4 (1M) as electrolyte and (d) PAnEtOH-AnPS-12 and (e) PAnEtOH-AnPS-11 layers in acetate buffer solution at *p*H 6.5, as electrolyte; scan rate is 50 mVs^{-1}; the first cycle is represented with dotted line;

processes of poly (2-anilinoethanol) backbone. Continuing the scan, it was observed that the layer is not stable. The first peak is shifted to 0.622 V while the second anodic peak disappeared. On the reverse scan, two cathodic peaks appear at 0.456 V and 0.303 V. The intensities of both redox peaks decrease as the number of the scans are increased, indicating that the copolymer is unstable.

In case of copolymer PAnEtOH-AnPS-11, on the first scan the voltammograms presents two anodic peaks at 0.429 V and 0.973 V and one cathodic peak at 0.391 V (fig. 7 (b)). During continued cycling, the copolymer exhibit only one anodic peak at 0.530 V while two cathodic peaks appear at 0.447 V and 0.372 V. These peaks are further shifted to more positive values and their currents intensities decreased as the scan number increased which indicate that the layer is unstable.

Increasing the amount of the monomer AnPS in the copolymer backbone, the PAnEtOH-AnPS-12 copolymer layer exhibits three anodic peaks at 0.383 V, 0.510 V and 0.622 V and one cathodic peak at 0.458 V (fig .7 (c)). These redox peaks correspond to the oxidation or reduction processes suffered by the polymer backbone during the positive sweeping in the monomer free H_2SO_4 aq. solution. On the second cycle, the copolymer exhibits only one anodic peak at 0.555 V and one cathodic peak at 0.455 V.

According to the data reported in the literature [27], during the oxidation process the anions move from the electrolyte solution into the copolymer layer and adversely, they are expelled from the layer during the reduction process. As well, during the oxidation-reduction processes, cation (e.g proton) can be transported into or from the copolymer layer [28].

Only the copolymer PAnEtOH-AnPS-12 exhibit an electrochemical activity in acetic buffer solution, *p*H 6.5 (fig. 7 (d)), showing on the second scan one oxidation peak at 0.536 V and one reduction peak at 0.100 V. This redox activity can be explained by the presence of a high amount of AnPS units in the copolymer backbone which ensure so -called "self-doping" properties. In case of PAnEtOH-AnPS-11 it can be seen a very small electrochemical activity, the voltammograms do not exhibit any redox peaks (fig. 7(e)).

Conclusions

New copolymers having two functional groups (hydroxyl and sulfonic groups) were synthesised by cyclic voltammetry from 1M H_2SO_4 and acetic buffer solution, *p*H 4.5. The copolymerization reactions were carried out at room temperature at Pt and ITO electrodes, using mixed monomer solutions with AnEtOH: AnPS monomer feed ratios of 1:1, 1:2 and 2:1, by sweeping the working electrode potential between 0.0 V and 1.3 V at 50 mVs^{-1}, for 20 cycles. At the end of the electropolymerization process, green layers of copolymers were deposited on the electrode surface. In order to investigate the electrochemical activity and the stability of the copolymers, they were swept in H_2SO_4 and acetic buffer solution (*p*H 6.5), between 0.0 V and 1.2 V, at 50 mVs^{-1} scan rate. The copolymers exhibit electrochemical activity in H_2SO_4 solution but they became unstable starting with the second cycle. Only PAnEtOH-AnPS-12 copolymer shows electrochemical activity in acetate buffer solution, *p*H 6.5. The Raman spectroscopy recorded for PAnEtOH and PAnEtOH-AnPS-21 revealed spectra that contain the characteristic bands for polyaniline in both oxidized and reduced form. SEM and AFM micrographs revealed that the copolymer layers present a compact and dense morphology with small roughnesses. There were evidenced some changes in the morphology of the copolymers as the *p*H of the electrolysis medium was increased at 4.5. Green layers of copolymers having both aniline monomers included in their chain were obtained by cyclic voltammetry from acetate buffer solution at *p*H 4.5.

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