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Electrochemical synthesis and structural studies of polypyrroles, poly(3,4-ethylenedioxythiophene)s and copolymers of pyrrole and 3,4-ethylenedioxythiophene on carbon fibre microelectrodes

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Abstract

Polypyrrole, poly(3,4-ethylenedioxythiophene) and the copolymer of pyrrole and 3,4-ethylenedioxythiophene films were synthesized electrochemically on carbon fibre microelectrodes (CFME). Deposition conditions on the carbon fibre and the influence of monomer concentrations on the copolymerization, as well as the electrochemistry of the resulting polymers and copolymers, were studied. Structural studies of the polymers were conducted using different techniques such as cyclic voltammetry, *in situ* spectroelectrochemistry, FTIR and scanning electron microscopy. The effect of the monomer ratio on the formation of copolymer is reported. A high level of stability to overoxidation was also observed for poly(3,4-ethylenedioxythiophene) as the polymer on this CFME substrate shows limited degradation of its electroactivity at potentials 1.2 V above its half-wave potential.

1. Introduction

Conducting polymers have been the subject of intensive research since the late 1970s [1–3]. Polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been the materials in many investigations. Functional conjugated PPy and polythiophenes, in which the electronic properties inherent to the p-conjugated systems are associated with new specific properties afforded by covalently attached functional groups, have been the focus of considerable attention during the past decade [4]. 3,4-ethylenedioxythiophene (EDOT) has recently emerged as a new thiophene derivative combining high conductivity, low bandgap, good electrochemical properties and exceptional thermal stability in the oxidized state of its polymer [5–7]. On the basis of these properties, PPy and PEDOT have been used in antistatic coatings or electrolytic capacitors [8], for the metallization of insulators [9], as active elements in thin-film transistors [10], as anode materials for light-emitting diodes [11] and in electrochromic devices [12,13].

In view of the wide spectrum of these potential applications, it is obvious that further control and development of the electropolymerization conditions, use of different substrates and the stability of the resulting polymer can contribute to extend the scope for the technological applications of conducting polymers. For instance, polymer coated CFME might have many potential applications due to their good physical, chemical and electrochemical properties, and they even could be used for bio-electrochemical purpose, such as biosensors and micron–sized reversible conductive polymer electrodes and actuators. Several research groups, to improve the surface properties of carbon fibres, use such carbon fibres as electrode materials. Thus, electrochemical polymerization of electroactive monomers, such as pyrrole [14–17], 3-methylthiophene [18] and aniline [19,20], and carbazole copolymers [21–25] onto carbon fibres have been studied.

In this work, the electrochemistry of PPy, PEDOT and copolymers of pyrrole and EDOT on the CFME was studied. Since PEDOT is one of the most stable polymers under ambient conditions and retains its conductivity even after storage at 120 °C for 1000 h [26] and the C-fibres used as electrodes, on the other hand, are very flexible and biocompatible, the study of these polymers and their copolymers on these flexible substrates will pioneer the applications of both PPy and PEDOT, their copolymers and the C-fibres for several purposes, particularly in the biological systems.

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2. Experimental details

2.1. *Materials*

All chemicals were used as received from Aldrich Chemical without further purification. High strength (HS) carbon fibres [C 320.000A (CA)-Sigri Carbon, Meitingen, Germany) were used as working electrode. Indium tin oxide (ITO) coated glass slides (0.7 cm × 5 cm, $R \leqslant 10$ ohm cm^{-2}) were used for some of the *in situ* spectroelectrochemical studies.

2.2. *Preparation of the CFMEs*

A single filament of the CFME was used as working electrode. All the electrodes were prepared by using 3 cm of the CFME (dia. 7 μm) attached to a copper wire with a Teflon tape. Only 0.5 cm of the carbon fibre was dipped into the solution to keep the electrode area constant ($\sim 1.0 \times 10^{-3}$ cm^2). The rest of the fibre was covered with the Teflon tape.

2.3. *Electropolymerization and characterization*

Polymerization reactions were performed electrochemically at a constant potential or current in propylene carbonate (PC) solution containing 0.1 M $LiClO_4$ and the monomers. A Fluke-715 calibrator was used as a current source for galvanostatic depositions. Electrochemistry and cyclic voltammetry (CV) of the polymers were performed with a Potentioscan Wenking POS 73 potentiostat in a three-electrode setup employing the CFMEs (area 1.0×10^{-3} cm^2) as working electrode, a platinum flag as a counter electrode and a silver wire pseudoreference in a solution of 0.1 M $LiClO_4$/PC. The pseudoreference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc^+) in the electrolyte ($E_{1/2}(Fc/Fc^+) = +0.13$ V vs silver wire in of 0.1 M $LiClO_4$/PC). Note that 1.0 V vs Fc/Fc^+ = 1.07 V vs Ag/Ag^+ = 0.7 V vs SCE [27]. All potentials are reported against SCE. Electrodepositions were carried out from a 10^{-2} M solution of monomer in 0.1 M electrolyte at a scan rate of 100 mV s^{-1} for 10 cycles.

In situ spectroelectrochemical studies were performed using the same electrolyte system and potentiostat. ITO coated glass electrodes were used as working electrode for spectroelectrochemistry. A UV–visible spectrophotometer (Shimadzu UV-160A) was used.

The IR spectra of products were recorded with a FTIR-reflectance spectrometer (Perkin Elmer, Spectrum One, Überlingen (Germany), with an ATR attachment Universal ATR with a diamond and ZnSe crystal).

The morphologies of the polymers were analyzed using a Hithachi S-2700 scanning electron microscope (SEM) (Nissei Sangyo, Rathingen, Germany), connected to an energy dispersive X-ray microanalyser (EDX) (Kevex type delta V, Foster City, CA, USA). The excitation energy was 10 keV at a beam current of 0.5 nA.

3. Results and discussions

3.1. *Synthesis and characterization of the polymers*

Electropolymerization was performed for the monomers and their mixtures using multiple scan cyclic voltammetry in 0.1 M $LiClO_4$/PC. The electrodeposition of PPy and PEDOT on the CFMEs (area 1×10^{-3} cm^2) by cyclic voltammetry at a scan rate of 100 mV s^{-1} between −1.4 V and +1.55 V vs SCE are shown in Figure 1. The monomer concentration was 10^{-2} M. The oxidation potentials of the monomers were determined from the first cycles as 1.20 V and 1.45 V vs SCE for pyrrole and EDOT, respectively. These monomer oxidations are very close to the oxidation potentials of both monomers on the Pt electrode reported elsewhere [7,28]. The irreversible oxidation of the monomer appears clearly

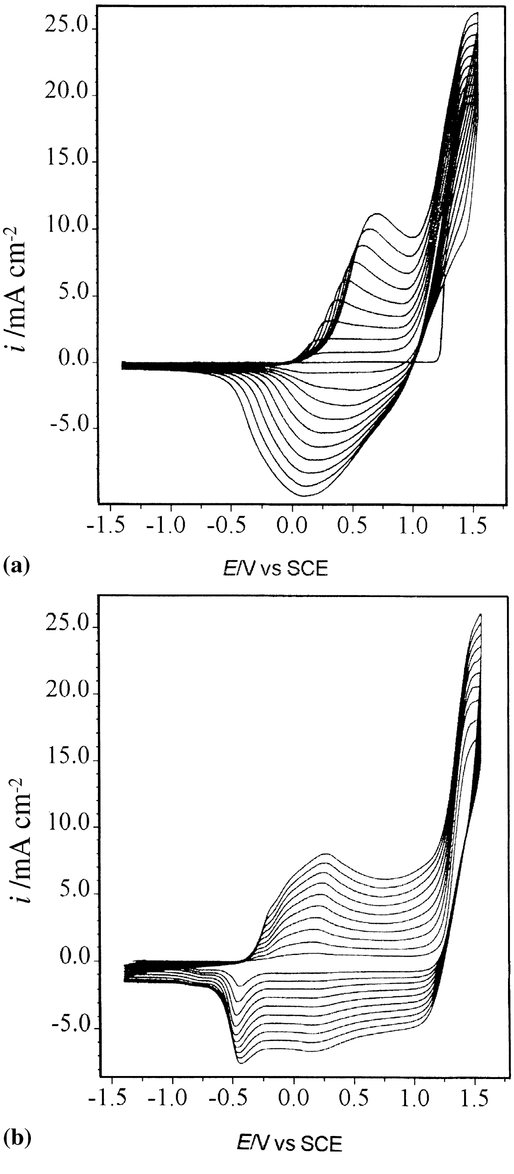

Fig. 1. Electrodeposition of PPy (a) and PEDOT (b) by potential scanning from a 10^{-2} M solution of monomer in 0.1 M $LiClO_4$/PC at 100 mv s^{-1} on the carbon fibre micro-electrodes (electrode area 1.0×10^{-3} cm^2).

on the first cycle followed by a nucleation loop for both monomers. On subsequent cycles monomer oxidation occurs at slightly lower potentials as a result of the modification of the electrode surface after the first cycle. A regular growth was observed for both polymers with a deposition rate that appeared to be faster in the case of PPy. For instance, anodic redox process for PPy reaches to the current density of 11 mA cm^{-2} after 10 cycles, which is 8 mA cm^{-2} for PEDOT (Figure 1). This is not surprising because pyrrole monomer has a lower oxidation potential than EDOT ($E_{m/ox}$ (EDOT) − $E_{m/ox}$(pyrrole) = 250 mV), and the same potential window was used to compare deposition of both monomers under the same conditions, resulting in a faster deposition for PPy. PPy has one redox process at about +0.3 V vs SCE (Figure 1(a)) and PEDOT has two redox processes at about −0.4 and +0.25 V vs SCE (Figure 1(b)).

Figure 2 presents the cyclic voltammogram of thin films of PPy (Figure 2(a)) and PEDOT (Figure 2(b)) on the CFME at scan rates of 50, 100, 150 and 200 mV s^{-1} in 0.1 M $LiClO_4$/PC. The films were grown by cyclic voltammetry at 100 mV s^{-1}, and the electrodepositions were performed over three cycles for both monomers in 0.1 M $LiClO_4$/PC. Both polymers present well defined and reversible redox processes. The half wave oxidation potentials of the polymers ($E_{1/2}$) are observed at about +0.3 V vs SCE and PEDOT has two redox processes at about −0.4 and +0.25 V vs SCE. The electroactivity and very well defined electrochemistry of both polymers on the CFME as much as the Pt electrodes suggest the possibility of using these electrodes as actuators for bio-applications instead of gold–myler substrate.

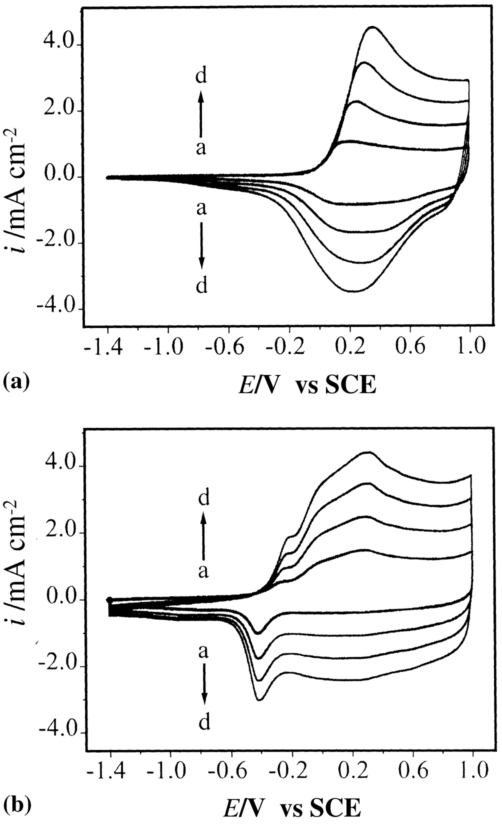

Fig. 2. Cyclic voltammogram of PPy (a) and PEDOT (b) in monomer free solution of 0.1 M $LiClO_4$/PC at a scan rate of (a) 50, (b) 100, (c) 150 and (d) 200 mV s^{-1}.

The scan rate dependence of the anodic and cathodic peak currents shows a linear dependence on scan rate as illustrated in Figure 3 for PEDOT. This demonstrates that the electrochemical process is not diffusion limited and is extremely reversible even at high scan rates. The ability to be switched reversibly in a non diffusion limited process at scan rates as high as 500 mV s^{-1} is unusual for conducting polymers and may stem from the thickness of the polymer films (about 30 nm).

3.2. *Stability of the polymers*

Although PPy is known to be highly sensitive to overoxidation [29], PEDOT is one of the most stable polymers reported to date [30]. At high potentials, oxidation can occur in position 3- or 4- of the pyrrole and thiophene rings, thus degrading the conducting polymer by breaking the conjugation in the polymer backbone. The presence of a substituent such as the alkylenedioxy group avoids this type of degradation [31]. Consequently, the polymer is stable up to higher potentials. Thus, it is important to investigate the stability of the polymer on these new substrates (i.e., CFME) for the practical applications as much as the switching properties. Several films of PEDOT have been exposed to a series of potentials above the $E_{1/2,p}$ (from +0.25 to 2.0 V) for 3 min. After each high potential exposure, a cyclic voltammogram was then carried out by scanning at 100 mV s^{-1} between −1.50 V and +0.60 V vs SCE. The relative electroactivity of each polymer film, measured as the ratio of the total charge involved in the redox process after high potential exposure, to the charge integrated from the cyclic voltammogram of the freshly prepared film, was then

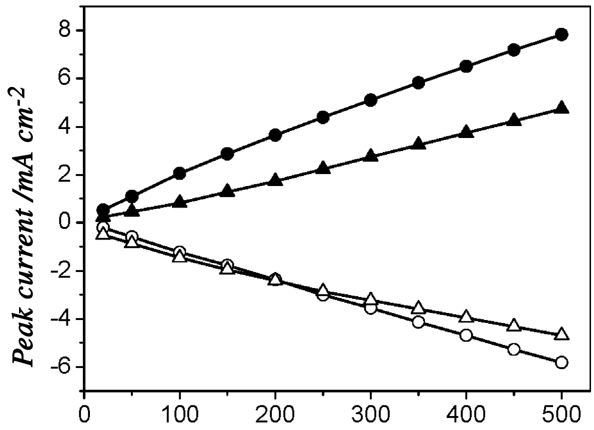

Fig. 3. Scan rate dependence of PEDOT film in monomer free solution of 0.1 M $LiClO_4$/PC: change in anodic and cathodic peak currents with scan rate (**1**) redox process at −0.4 V vs SCE, (**2**) redox process at +0.25 V vs SCE. Key: (▲) i_{pa} (**1**); (△) i_{pc} (**1**); (●) i_{pa} (**2**); (○) i_{pc} (**2**).

determined. The results, presented in Figure 4, show the outstanding stability of PEDOT on the CFME to overoxidation as only a slight decrease of the electroactivity was observed when the holding potential was raised to about 1.2 V over $E_{1/2,p}$. It should be noted that this outstanding stability of PEDOT on the CFME to overoxidation is important for the practical use of this combination of PEDOT on the CFMEs.

3.3. *Preparation and characterization of copolymer films*

Thin films of PEDOT, PPy and copolymers of EDOT and pyrrole with different mole fractions were deposited on the CFMEs galvanostatically using a total charge of 50 mC cm^{-2}. Copolymer films were obtained from the mixture of both monomers with different mole fractions. Total monomer concentration was 10^{-2} M, and 0.1 M $LiClO_4$/PC was used as electrolyte. The mole fraction x is calculated as $n_{EDOT}/(n_{EDOT}+n_{pyrrole})$ in the solution. The cyclic voltammograms of these films are compared for different mole fractions and given in Figure 5. In each case, polymer films were rinsed in monomer free electrolyte solution for 5 min and then three voltammograms were recorded to ensure reproducibility. The first cycles are reported in each case. All the polymers are electroactive with different characters depending on the mole fractions.

In the previous sections, it was explained that EDOT and pyrrole monomers have different oxidation potentials (1.45 V and 1.20 V vs SCE, respectively) and $E_{1/2}$ of their polymer films. This characteristic of monomers and polymers suggest the use of different mole fractions of monomer solutions for the copolymerizations. Since EDOT monomer is more difficult to oxidize, the concentration of this monomer was kept high compared to pyrrole. The reason for use of high concentrations of EDOT can easily be seen from Figure 5. The PEDOT film shows a main oxidation wave at +0.30 V with a shoulder at −0.35 V vs SCE, followed a broad flat plateau with a peak at +0.20 V and the main reduction

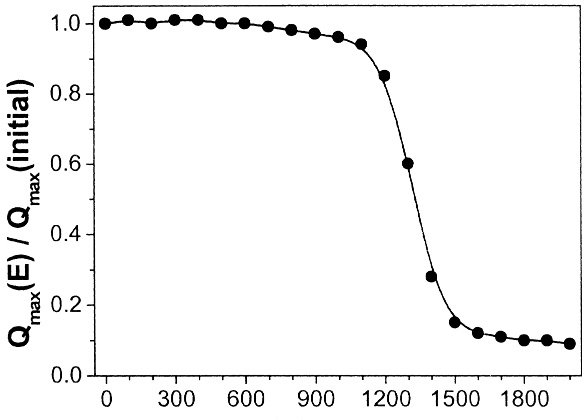

Fig. 4. Comparison of the stability to over-oxidation for galvanostatically deposited films (100 mC cm^{-2}) of PEDOT on the carbon fibre microelectrodes, as the ratio of the maximum charge stored in the polymer film after holding 2 min at a potential over $E_{1/2}(Q_{max}(E))$ to the charge initially stored in the as grown film (Q_{max}(initial)).

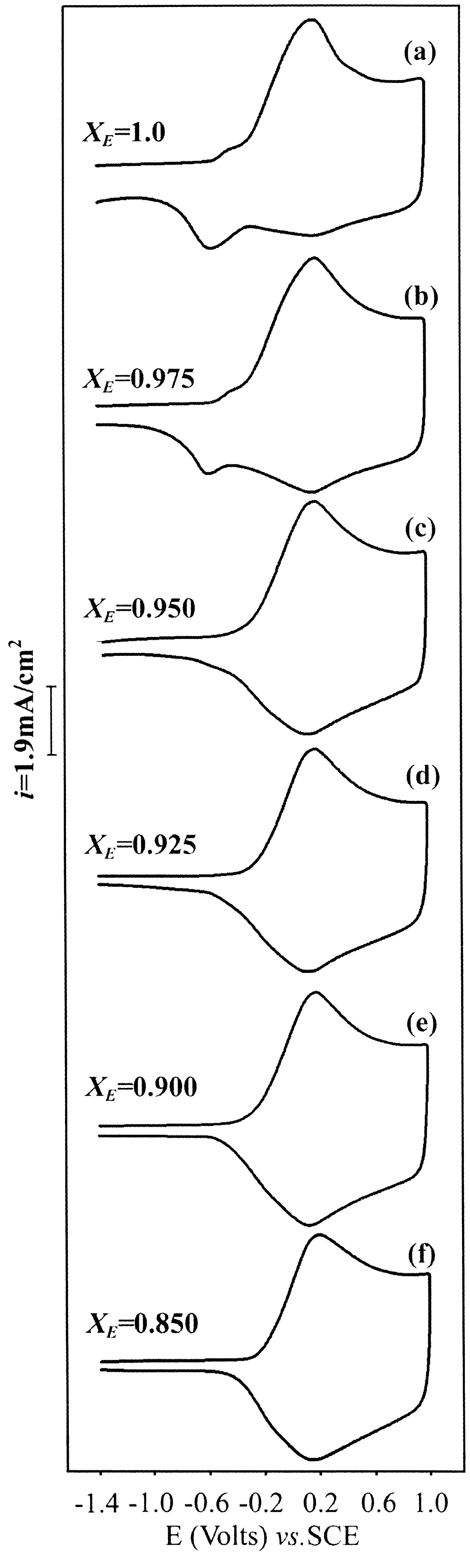

Fig. 5. Cyclic voltammogram of the P(Py-EDOT) on the carbon fibre microelectrodes in 0.1 M $LiClO_4$/PC. ($Q_{polym.}$ = 50 mC cm^{-2}, Scan rate = 100 mV s^{-1}, $X_E = n_{EDOT}/n_{EDOT} + n_{pyrrole}$).

peak at −0.45 V vs SCE (see Figure 5(a)). The potentials at −0.35 and −0.45 V vs SCE shifts to more positive potentials (i.e., −0.25 and −0.40 V vs SCE, respectively) after several cycles. These findings are not very different from the first electrochemical report about PEDOT [7]. Disappearance of the redox process at negative potentials (−0.35 and −0.45 V vs SCE) with increasing pyrrole concentration in the monomer mixture solution can be seen in Figure 5. For example, when the pyrrole concentration increases to over 10% of the total monomer concentration in the mixture, the redox process at negative potentials completely vanishes. In addition, the reduction peak at about 0.20 V vs SCE appears clearly, and a considerable decrease in the current difference at lower potentials than −1.0 V vs SCE during anodic and cathodic scans is observed with increase of the pyrrole content in the mixture. Finally, when the mole fraction of EDOT, x, is less than 0.90, the CV of the polymer looks like the CV of PPy. It can be concluded from the Figure 5 that at very high concentrations of EDOT in the total monomer concentration (i.e., $x > 0.90$), there are EDOT sequences in the copolymer structure.

To determine the relative polymerization efficiencies and film formation capabilities, the rates of potentiostatic electropolymerization with concurrent film growth were monitored for each monomer at an applied potential equal to half of the summation of the monomer peak potentials of pyrrole and EDOT (1.325 V vs SCE) on an ITO-coated glass substrate (Figure 6). The absorbance in the near-infrared (NIR) at 1100 nm due to the charge carrier absorption was recorded as a function of time up to a charge of 50 mC cm^{-2}. The value of 1100 nm does not correspond to the maximum absorbance in the NIR region but is a useful value which can be used without saturating the detector. PPy exhibits a faster deposition rate than PEDOT, suggesting that the reactive intermediate radical cations couple quickly to form a macromolecular chain that deposits and continues to polymerize on the electrode surface without involving soluble oligomers. For PEDOT, an induction period before deposition as fast as PPy was observed. The deposition rate of the PEDOT reached that PPy after 6 min. This diversity may stem from the different oxidation potentials of the monomers. When the mole fraction of the EDOT in the monomers, X_E, was selected as 0.925 where the copolymer exhibited the best results from cyclic voltammograms, the rate of electrodeposition was observed to lie between that of PPy and PEDOT which is very fast and regular. These results are also indicative of the appropriate selection of the mole fraction of 0.925 for the copolymerization of pyrrole and EDOT.

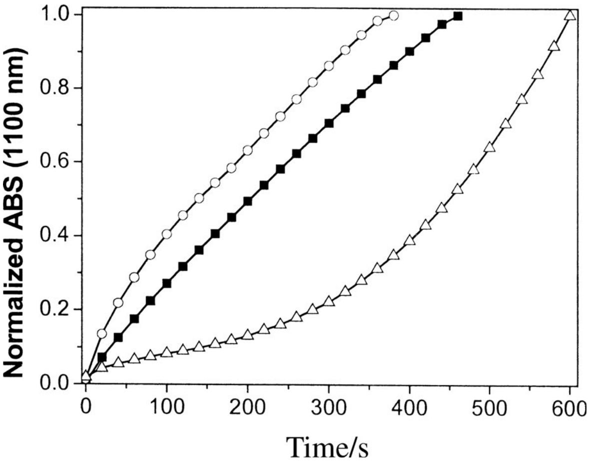

Fig. 6. Comparison of the growth of polymer followed by NIR spectroscopy. Electrodepositions of a 50 mC cm^{-2} film were performed from a 10^{-2} M solution of monomer in 0.1 M LiClO$_4$/PC at a potential of 1.325 V vs SCE. Normalized absorbances at 1100 nm [ABS(t)/ABS(final)] are presented as a function of time for PPy (○), PEDOT (△) and copolymer of EDOT and pyrrole (■). X_E: (○) 0.000; (■) 0.925; (△) 1.000.

3.4. *FTIR spectroscopy*

Free-standing films of PEDOT, PPy and copolymers of EDOT and pyrrole prepared by galvanostatic deposition on stainless steel electrodes at 0.1 mA cm^{-2} were analysed by FTIR-ATR spectroscopy to confirm the presence of both monomers inside the polymer. Figure 7 shows the corresponding spectra between 550 and 4000 cm^{-1}. Comparison of the FTIR-ATR spectra of PPy, PEDOT and P(Py-EDOT) free-standing films show the incorporation of both pyrrole and EDOT monomers to the resulting desired copolymer at the high concentrations of EDOT monomer ($X_E = 0.925$). There are several indications of this suggestion. For example, FTIR-ATR spectra of PPy and PEDOT homopolymers have such characteristic peaks at 827, 936, 1140, 1182, 1372, 1552, 2677, 2829 cm^{-1} and 813, 1016, 1126, 1192, 1225, 1424, 1571, 1846, 2008, 2663, 2824 cm^{-1}, respectively. In the case of the copolymer, in addition to these peaks, there are some shifts or new peaks corresponding to the interaction of the monomers. For instance, the peaks around 1200 cm^{-1} corresponding to the ring vibrations for the pyrrole and

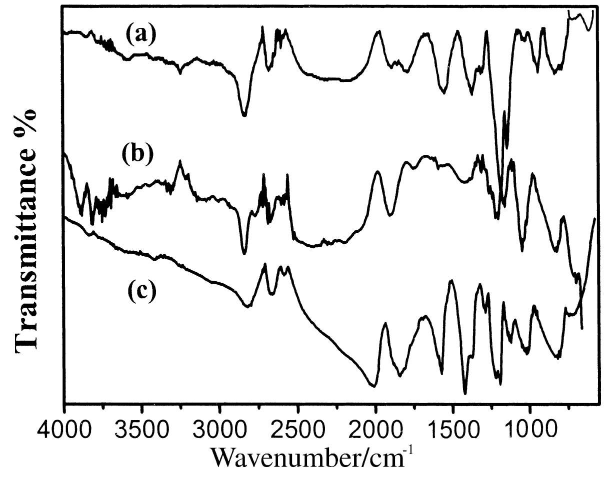

Fig. 7. FTIR-ATR of PPy (**a**), P(Py-EDOT) (**b**) and PEDOT (**c**) free-standing films.

EDOT in the copolymer, looks like the combination of the peaks at 1140 and 1182 cm^{-1} in the PPy and 1192 and 1225 cm^{-1} in the PEDOT. Intensive peaks at 1552 cm^{-1} in PPy and 1571 cm^{-1} in PEDOT disappear in the case of the copolymer. Moreover, the ratio of the bands at 1900 to 1780 cm^{-1} in PPy increases in the copolymer because of the strong absorption at 1860 cm^{-1} in PEDOT, and a strong absorption appears at 1900 cm^{-1} in the copolymer.

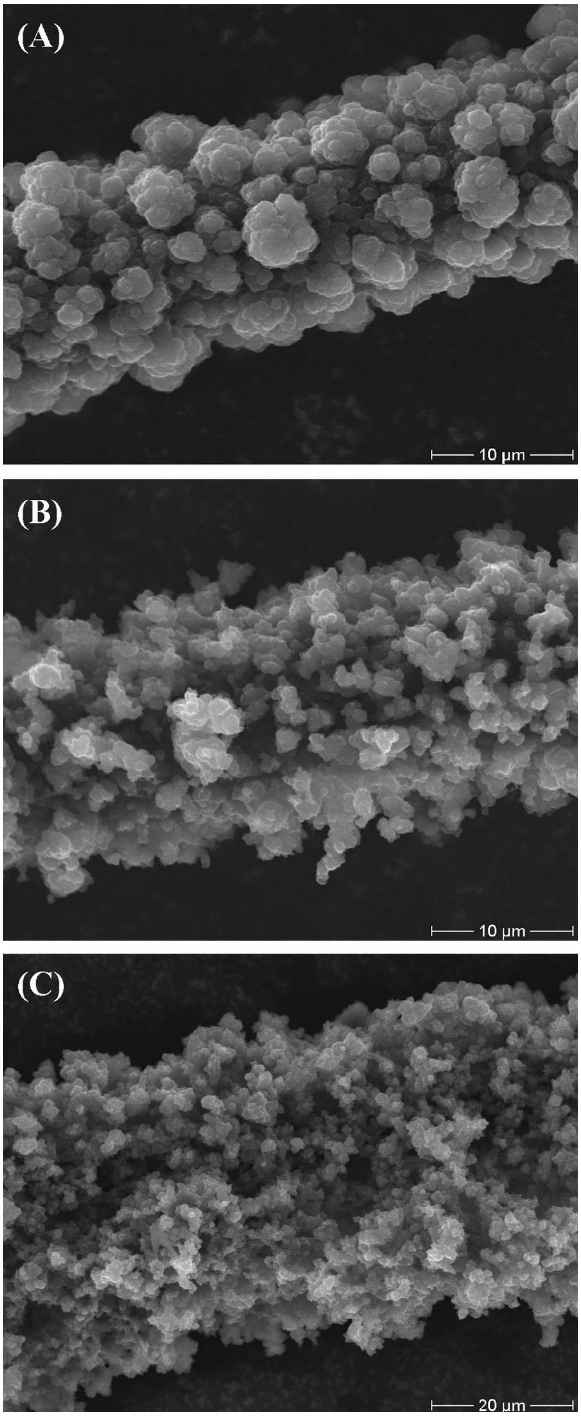

Fig. 8. SEM pictures of (**a**) PPy ($X_E = 0.0$), (**b**) P(Py-EDOT) ($X_E = 0.925$) and (**c**) PEDOT ($X_E = 1.0$) films on the CFMEs. Each film was prepared by potentiodynamic deposition after 15 cycles using 0.1 M $LiClO_4$/PC solution containing monomers. (Scan rate 50 mV s^{-1}.)

3.5. *Morphology*

The polymers of Py, EDOT and Py-EDOT on the CFME were grown by potentiodynamic depositions (15 cycles) from the solution of 0.1 M $LiClO_4$/PC containing a total monomer concentration of 10^{-2} M. The morphologies of the oxidized PPy, PEDOT and P(Py-EDOT) on CFMEs were investigated comparatively by scanning electron microscopy (SEM) (Figure 8). A globular structure resulting from a three-dimensional nucleation growth is observed in all cases. The SEM picture of PPy film shows clusters of globules (dia. $\sim$4 μm) with a void space in between (Figure 8A). The morphology of PEDOT is quite different from PPy. For example, the globules are smaller (dia. $< \sim 2$ μm), dispersed and void spaces between globules are smaller than PPy. This structural difference helps us to follow the incorporation of both monomers to the structure when they make a copolymer (P(Py-EDOT)). Copolymers of pyrrole and EDOT on the CFMEs have been prepared with different mole fractions ($X_E = n_{EDOT}/n_{EDOT} + n_{Py}$) of the monomers. SEM pictures of these films have shown that incorporation of the EDOT to the resulting copolymer is achieved at high concentration of this monomer (starting from the mole fraction of EDOT more than 0.90) and the most homogeneous mixture of the components in the resulting polymer have been observed when the mole fraction is selected as $X_E = 0.925$. The SEM picture of the polymer prepared at this mole fraction ($X_E = 0.925$) is given as an example in Figure 8B. This coincides with the results obtained from CV and spectroelectrochemistry of the polymers (Figures 5 and 6).

4. Conclusions

In summary, polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and copolymers of pyrrole and 3,4-ethylenedioxythiophene films have been synthesized electrochemically on carbon fibre microelectrodes (CFME). Deposition conditions on the carbon fibre and the influence of the monomer concentrations on the resulting copolymer have shown that very homogenous copolymers can be synthesized with a mole fraction of EDOT of 0.925. The electroactivity and well defined electrochemistry of both polymers PPy and PEDOT, and their copolymer on CFME as well as on Pt suggests the possibility of using these coated electrodes for bioapplications. A high level of stability to overoxidation has also been observed for PEDOT as the polymer on this CFME substrate shows limited degradation of electroactivity at potentials 1.2 V above the half-wave potential.

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