Ion-exchange properties of polypyrrole doped by ω-carboxylated polyethyleneoxide

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Abstract

α-Methoxy ω-Na carboxylate polyethylenoxide (f-PEO) has been synthesized and used as counter-ion for the synthesis of polypyrrole (PPy) films. The effect of f-PEO concentration on the kinetics of pyrrole polymerization has been studied. The ion exchange properties of the formed PPy/f-PEO composite have been analyzed in aqueous solution containing various salts (f-PEONa and $LaCl_3$). The incorporation of indigo carmine in this type of composite has also been investigated.

Keywords

Ion-exchange properties; Polypyrrole; Polyethyleneoxide

1. Introduction

Electroactive polypyrrole (PPy) films have been widely studied as components of high-tech polymeric materials. For example, as result of their ion-exchange properties, these films can be used as electroactive membranes in controlled-delivery systems [1]. Much research effort has also been devoted to the study of the ion-exchange triggered by variation of the potential applied to electroactive PPy films [2,3].

Examples are known of ionic polymers used as constitutive components of conductive composites. These composites can be prepared by anodic polarization of solution containing the monomer precursor of the conducting polymer (e.g., pyrrole) and ionic polymers which are the actual dopants. A series of ionic polymers have been successfully used for this purpose, such as polyvinylsulfate [4], sulfonated butadiene-styrene copolymer [5], Nation [6], sulfonated acrylic polymers [5], carboxylic polymers [7] and sulfonated polystyrene [8]. Recently, macromolecular composites based on poly(p-phenyleneterephthalamido)pro-pane sulfonate [9] and polyurethane propane sulfonate [10] have been reported. All these water soluble polyelec-trolytes are potential polymeric counter-ions for conducting polymers.

This paper aims at investigating a new type of water soluble polymeric counter-ion and its ability to shape out new PPy-based composites. Instead of using polyanions, the choice has been made of water-soluble polyethylene oxide (PEO) end-capped by a carboxylate anion at one end (see Scheme 1). It must be noted that only part of the anionic groups of the polyanions act as counter-ions for PPy [11]. The role of the extra groups remains unknown, which can raise problems in the understanding of the ion-exchange phenomena. In order to avoid these possible difficulties, monofimctional PEO has been synthesized. The choice of the fumarate end-group relies on results published by Kuwabata et al. [12], who pointed out that the conductivity of PPy films doped by carboxylate anions decreased as the basicity of the dopant anions was increased. The structure of the carboxylate end-group (fumarate end-group) used in this work is such that the pK_a of the acid is smaller than the critical value of 4 at which the PPy film does not grow significantly.
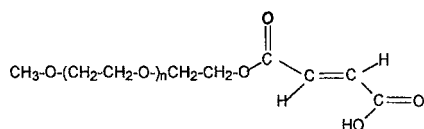
Scheme 1.
The neutralized PEO oligomer shown in Scheme 1 (f-PEO) will be tested as macromolecular electrolyte for the electropolymerization of Py and production of PPy/ PEO composites. The ion-exchange properties of these composites will be studied during redox cycles. In addition to voltammetric experiments, the Quartz Crystal Microbal-ance (QCM) analyzer will be used to record mass variations during potential scannings.

2. Experimental

α-Methoxy ω-hydroxyl polyethylenoxide (PEO) (Sigma) (Mn = 2000; Mw/Mn = 1.15) and fumaryl dichloride (Acros Chimica) were used as received. Toluene was distilled over the purple sodium/berrzophenone complex before use. The H-NMR spectrum was recorded in D_2O at 400 MHz with a Bruker AM 400 spectrometer operating at room temperature. The chemical shifts were referred to the protons of residual solvent. IR spectra were recorded with a Perkin-Elmer 1600 FT spectrometer (KBr pellets).
Pyrrole (Aldrich) was freshly distilled before use. Water was twice distilled and purged with nitrogen before use. NaCl, $LaCl_3$ and indigo carmine (IC) were used without purification.
Electrochemical polymerization and cyclic voltammetry were carried out using an EG&G Princeton Applied Research Model 263A potentiostat/galvanostat. All the electrochemical experiments were performed under nitrogen atmosphere in a closed cell, using platinum plates (1 cm^2) as working electrodes and platinum sheets as counter electrode and pseudo-reference.
The electrochemical QCM [13] was used to measure mass changes of a Pt electrode by monitoring changes in the resonant frequency of an AT-cut quartz crystal (0.2 cm^2) (Inficon) oscillating at 9 MHz. The film morphology was observed by scanning electron microscopy (SEM) (Cambridge Leica). Contact angles were measured by the sessile drop technique with 1 μl of milliQ water.

3. End-functionalization of PEO

A total of 10 g of PEO (5 mmol based on Mn) was dissolved in 100 ml of dry toluene and added dropwise to 100 ml of dry toluene solution of fumaryl dichloride (1.5 g; 10 mmol). This solution was heated at 80°C for 12 h under stirring. It was then cooled down to 0°C, and added with 40 ml of water. Solvent was evaporated and the solid was redissolved in chloroform. The insoluble fumaric acid was eliminated by centrifugation.
In addition to the PEO characteristic peaks, the IR spectrum of the reaction product (Fig. 1) showed two additional bands at 1724 and 1638 cm^{-1} assigned to the ester and the carboxylic acid functions formed as result of the end-capping reaction (Scheme l).
The ^{1}H-NMR spectrum (Fig. 2) measured in D,O showed the protons characteristic of the asymmetric double bond of the fumaryl end-group at 6.71 ppm. The fine structure of this resonance agreed with a second order spectrum, the two doublets of the asymmetric ethylenic end-group being visible. The two peaks of smaller intensity at 6.67 and 6.76 ppm might be due to cis isomer formed upon heating the reaction medium. Integration of the 6.71 ppm region compared to the integration of the most unshielded CH_2 group of PEO at 4.22 ppm (proton 3) agreed with 1.26 CH_2 for 2 CH instead of 1 CH_2 for 2 CH. This observation was consistent with some disubsti-tuted fumaryl units (coupling reaction). Would it be the case, a singlet should be observed at 6.71 ppm for the symmetric CH, which might, however, be hidden in the foot of the most intense central doublet of this pattern. Moreover, comparison of the integration of the CH pattern with the one of the CH_3 observed at 3.19 ppm was in agreement with one CH_3 for two CH. This result reveals the presence of unreacted chains. Although contaminated by coupled and unreacted chains, α-methoxy, ω-carboxylic acid PEO was not purified further, because the contaminating chains will remain inactive in the PPy synthesis being deprived of acid groups.
The carboxylic acid end-groups were neutralized by NaOH aqueous solution. The titration curve did not show residual fumaric acid and indicated the end-functionaliza-tion of 90% PEO chains. An approximate pK_a of 2.95 was also measured for the fumaric acid end-group.
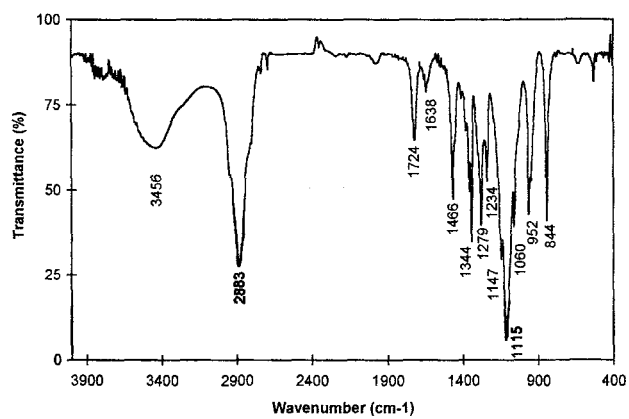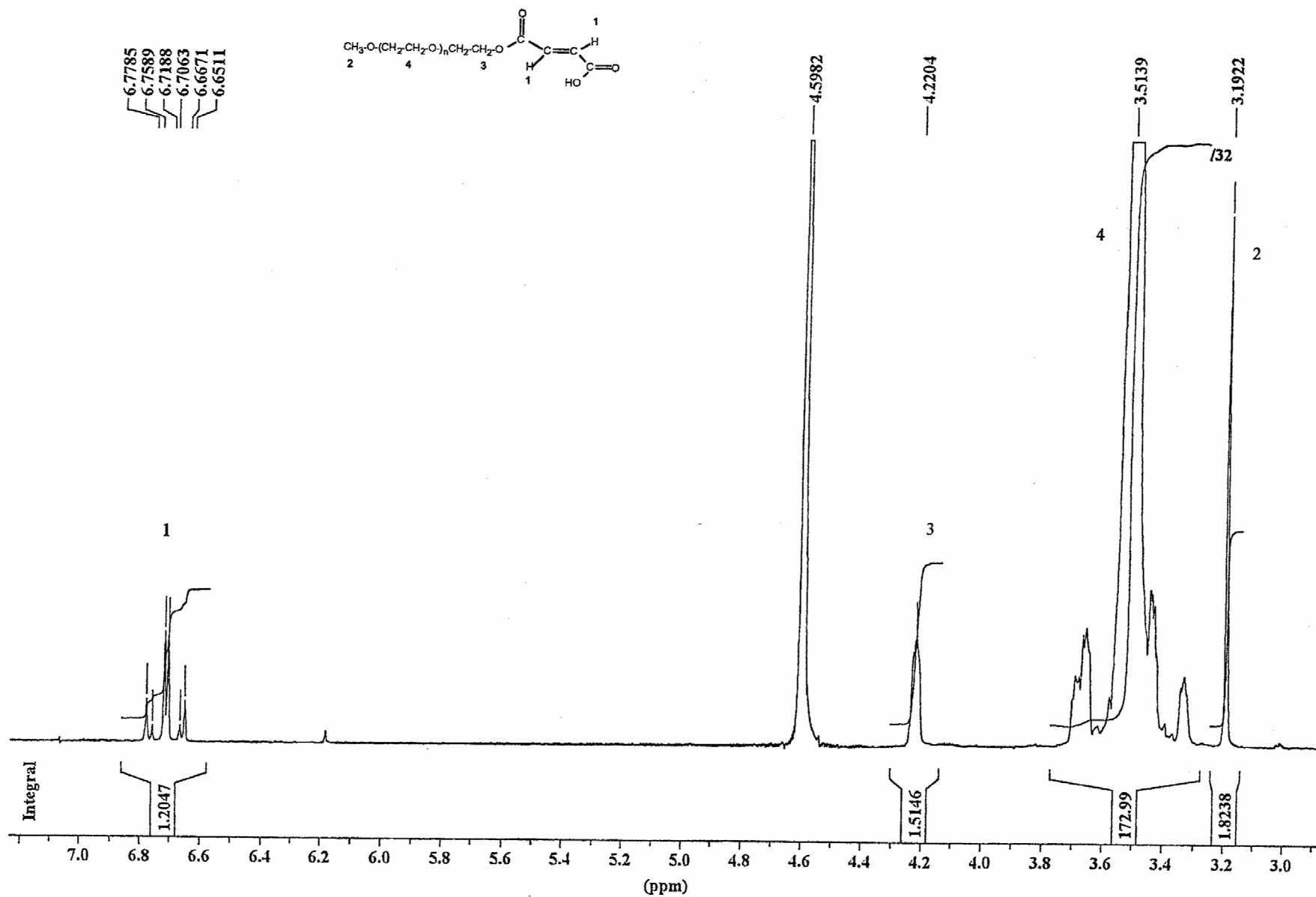
Fig. 1. IR spectrum of f-PEO (KBr pressed pellet).

Fig. 2. ^{1}H-NMR spectrum of f-PEO in D_2O.

4. Results and discussion

4.1. Electropolymerization

Cyclic voltammetry carried out in aqueous solution of Py and Na fumarate terminated PEO (f-PEO) shows an irreversible wave starting at +0.7 V/SCE in parallel to the mass increase of the electrode. A black film observed on the electrode surface confirms the PPy formation.

Fig. 3 shows chronoamperograms measured at constant potential of 0.8 V/SCE (Pt electrode) for different f-PEO concentrations. The rather flat current evolution at constant polarization is noteworthy. The current increase usually observed when conducting polymers are synthesized as result of the increased surface of the conducting electrode is less pronounced when f-PEO is the electrolyte. This observation more likely indicates a lower conductivity of PPy. The electrode is, however, not totally passivated, since the polymer thickness increases slowly with the polarization time.

At low concentrations (from 0.01 to 0.0175 M), the limiting current (measured at 900 s) increases with the electrolyte concentration (Fig. 3), as expected for PCE synthesis [14]. At higher concentrations, the reverse tendency is observed, since only a small increase is reported between curves b (0.0175 M) and c (0.04 M), followed by a sharp decrease when the f-PEO concentration is further increased (curve d, 0.06 M). This effect may be explained by the steadily increasing viscosity of the reaction medium with the concentration of the macromolecular electrolyte. The coupled PEO chains detected by NMR can develop this phenomenon, since they contribute most to the solution viscosity and not at all to the solution conductivity.

The PPy growth in presence of f-PEO has also been compared by the QCM technique with the well-known polymerization of pyrrole in presence of polystyrene sulfonate (Fig. 4). The mass increase of the PPy/f-PEO composite is initially slower and tends to accelerate with the consumption of current (Q). Beyond 3 mC, the slope of the dependence of Δf (Hz) on Q becomes indeed higher for this composite (curve a) compared to the PPy/PSSO$_3$ one (curve b).
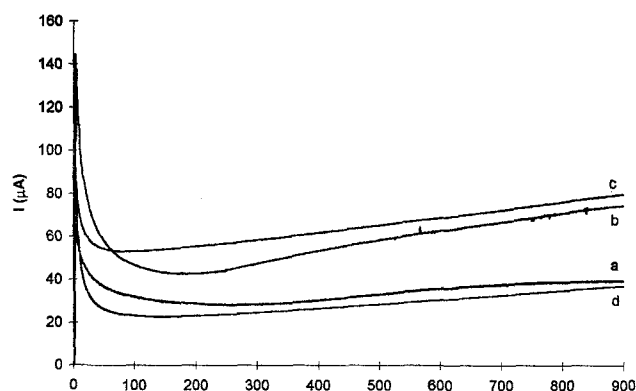

Fig. 3. Chronoamperograms obtained for 900 s polarization (E= 0.8 V) in Py (0.1 M) aqueous solutions of different f-PEO concentrations: (a) 0.01 M; (b) 0.0175 M; (c) 0.04 M; (d) 0.06 M.
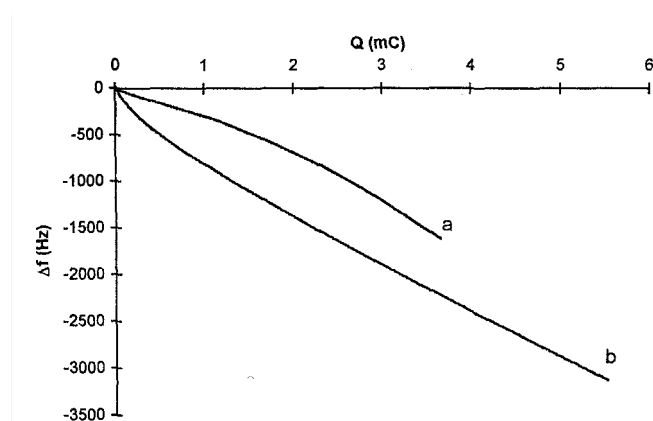

Fig. 4. Electrogravimetric quartz crystal microbalance profile vs. current quantity during potentiostatic polarization (E = 0.8 V/SCE) in aqueous solution of Py (0.1 M) and (a) f-PEO (0.0175 M); (b) PSS0$_3$ (0.1 M).

This observation indicates that more monofunctional f-PEO is incorporated into PPy compared with PSSO$_3$.

Calculated for 1 mC and for doping level of 0.3 (value commonly reported for doped PPy [15]), the theoretical mass increase of the electrode is 3.63 x 10^{-6} g for the PPy/f-PEO film, and 5.40 x 10^{-7} g for the PPy/PSSO$_3$ composite. According to the QCM analysis, the experimental increase is 5.61 x 10^{-7} g for PPy/PSSO$_3$ between the fourth and the fifth consumed millicouloumb (Δf= 500 Hz), in very good agreement with the expected value. In case of PPy/f-PEO, Δf is 650 Hz and corresponds to a mass of 7.01 X 10^{-7} g, i.e., only 20% of the theoretical mass. This apparent disagreement might be reconciled by lower polymerization yield and lower doping of PPy by the monofunctional PEO counter-ion, so leading to less conductive PPy. The charge/time evolution at constant potential of 0.8 V/SCE (Fig. 5) confirms the lower polymerization rate of pyrrole in presence of f-PEO, consistently with the low electrolyte concentration, and the less conductive PPy formed. Moreover, during the polymerization of pyrrole, pH close to the electrode surface has to decrease since two protons are liberated per monomer unit [16] leading to the partial protonation of the f-PEO oligomers which are then facing more difficulty for being incorporated in the film.
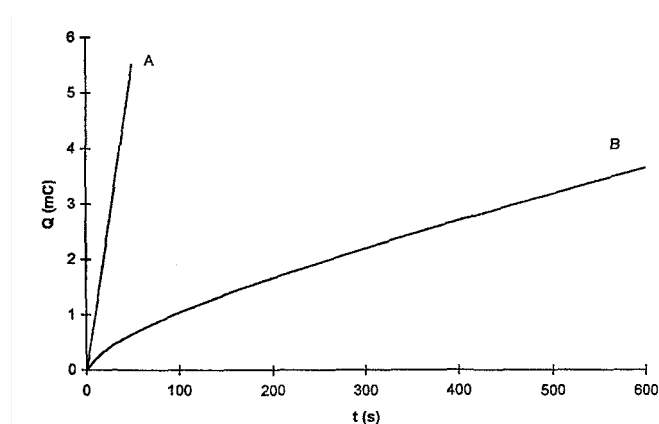

Fig. 5. Charge vs. time curve for constant polarization (E = 0.8 V/SCE) in aqueous solution of Py (0.1 M) and (a) PSSO$_3$ (0.1 M); (b) f-PEO. (0.0175 M).

For sufficiently long polarization time *(E* = 1 V, *Q* = 200 mC, *t* = 900 s), the film is thick enough for SEM observations to get rid of interference with the substrate (Fig. 6). The PPy/PEO film is very smooth similarly to the PPy/PSSOj one and does not show the cauliflower-like structure which is usually observed for PPy doped by inorganic anions [17]. The beam used for SEM observation is imprinted in the scanned area of the film, which is not the case for PPy doped with amorphous polystyrene sulfonate. The melting of the incorporated f-PEO by the electron beam could account for this observation.

Contact angle formed by water on the surface of the PPy/f-PEO and PPy/PSSO$_3$ films has been measured after polarization of these films at +0.6 V vs. SCE (oxidated films) in a monomer free bath, until the current drops to zero. Although a contact angle of 40° has been observed for the PPy/PSSO$_3$ film, the method proved to be not suited to the PPy/f-PEO film since water was absorbed by the composite. This observation is of course indirect evidence for increased hydrophilicity imparted by f-PEO to PPy in comparison with PSSO$_3$.

We have then investigated the ion-exchange during the redox reactions of Ppy.

4.2. Redox reaction of PPy films

The electrochemical activity of the PPy/f-PEO film has first been observed by scanning the potential between — 0.8 V and +0.4 V in aqueous solution of f-PEONa (0.02 M). Fig. 7 shows the accordingly recorded *I/E* and *Af/E* potentiodynamic profiles. Voltammetry does not show any well-defined redox peak in this diluted solution; only a large wave seems to emerge at — 0.3 V. The QCM analysis shows that this redox cycle is accompanied by mass variation of the electrode.

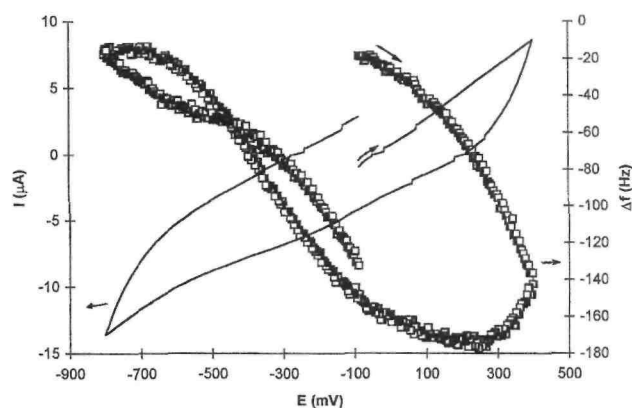*Fig. 6. SEM image of the PPy/f-PEO film deposited onto Pt.*

Fig, 7. Potenfiodynamic i/E and Δf/E profiles for the PPy/f-PEO film in f-PEONa (0.03 M) aqueous solution.

Mass is indeed increased during oxidation, while it decreases upon film reduction. This observation indicates that when PPy is reduced, i.e., when the positive charges on the PPy backbone disappear, oligoanions are released from the film rather than cations to be inserted. The PPy/f-PEO composite thus behaves as an anion-exchange resin.

This behavior has been confirmed in 0.1 M $LaCl_3$ aqueous solution that shows similar *I/E* and Δ*f/E* profiles (Fig. 8). Better defined reduction process (— 0.65 V) and corresponding oxidation wave (-0.25 V) are observed in this more concentrated solution. Decrease in mass is still observed parallel to the reduction process, which is evidence of the role played by the anions in the redox process. When the potential sweep is reversed, the change in mass is also reversed.

These observations are in contrast to previously reported results [18] about PPy doped by anions of long alkyl sulfate chains, such as dodecyl sulfate. In this case, alkyl chains longer than C10 are irreversibly trapped in PPy and only cations participate to the redox process. Since PEO oligomers used in this study have Mn = 2000, they are expected to be long enough to be entangled with the PPy chains. However, neutral PPy is typically hydrophobic and is expected to have more affinity for alkyl chains than for hydrophilic f-PEO, so that polymer immis-cibility may result. However, oxidized PPy is a polycation prone to electrostatic interactions with the anionic end-group of f-PEO. Upon reduction of PPy, the positive charges disappear, and f-PEO is no longer immobilized by PPy, so that this water soluble component is extracted from the insoluble PPy film in aqueous $LaCl_3$ solution.
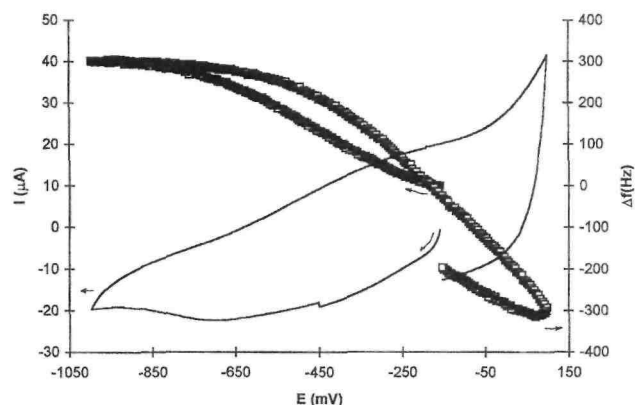
Fig. 8. Potentiodynamic i/E and Δf/E profiles for the PPy/f-PEO film in LaCl$_3$ (0.1 M) aqueous solution.

4.3. Application to anion-exchange

Since the PPy/f-PEO film behaves as anion exchanger, its ability to exchange large size anions has been investigated. Some authors [19] have reported that the addition of inert polyethylene glycol (PEG) to the electropolymeriza-tion solution provides the as-prepared PPy films with higher permeability. Then PEG is actually a 'co-solvent', which is not incorporated in PPy as counter-ion. In order to know whether f-PEO also influences the permeability of PPy, the exchange of IC (MW 466.36 g/mol) as model for large size anion, has been studied.

The mass evolution noted as result of the redox reaction of PPy/f-PEO dipped in 0.01 M IC aqueous solution (pH = 5) is reported in Fig. 9. At this pH, the IC reduction starts at - 0.55 V and peaks at - 0.9 V. The maximum of the reoxidation wave appears at — 0.3 V. The redox activity of the PPy film is, however, not clearly observed. The Δf/E curve shows that the mass decreases regularly during the cathodic scanning down to — 0.55 V in agreement with release of f-PEO from the PPy film. For further reduction until -0.9 V, the cyclic voltammogram shows mass increase simultaneous to increase in current intensity. During reverse scan, a loss of mass is observed between -0.8 and -0.15 V followed by a mass increase.

These observations can be explained as follows. When the PPy/f-PEO film is immersed in the IC solution, some anion-exchange is expected to occur rapidly between f-PEO in the film and IC, since PPy must have better affinity for IC than for f-PEO. During the cathodic scanning, PPy becomes neutral and f-PEO is released. At $E = — 0.5$ V, the major part of f-PEO is extracted and the anions in PPy are IC.
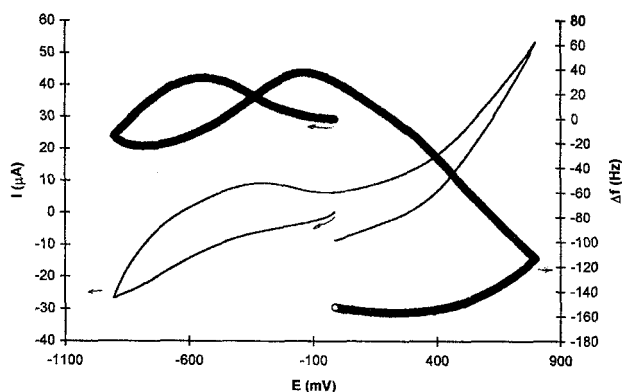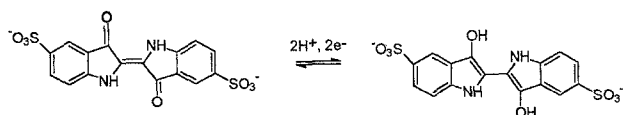

Fig. 9. Potentiodynamic i/E and Δf/E profiles for the PPy/f-PEO film in IC (0.01 M) aqueous solution.

Scheme 2.

Since these molecules are dianions of large size, their extraction from PPy is slow and cations have to be inserted for obvious electroneutrality arguments. Moreover, at this potential, IC reacts electrochemically, the mechanism of the redox reaction [20] being shown below (Scheme 2).

This reaction requires the insertion of two protons, that also contributes to the increase of the mass of the electrode.

In the reverse process, the mass decrease is explained by release of cations upon reoxidation of IC and initial reoxidation of PPy. Then IC is importantly incorporated in the film between - 0.2 V and + 0.8 V as result of the PPy reoxidation.

The Δf vs. potential curve of PPy doped by chloride anions (synthesis conditions: 0.1 M Py, 0.1 M NaCl, bidistilled water, $E = 0.5$ V) in the IC solution is shown in Fig. 10 for the sake of comparison with the PPy/f-PEO film (Fig. 9).

There is no important mass evolution in the cathodic regime, no mass increase being observed when the potential is scanned down to —0.8 V; only a small mass increase is observed during oxidation above +0.15 V. Apparently, the porosity of the PPy/Cl film is not large enough for IC anions to be incorporated.

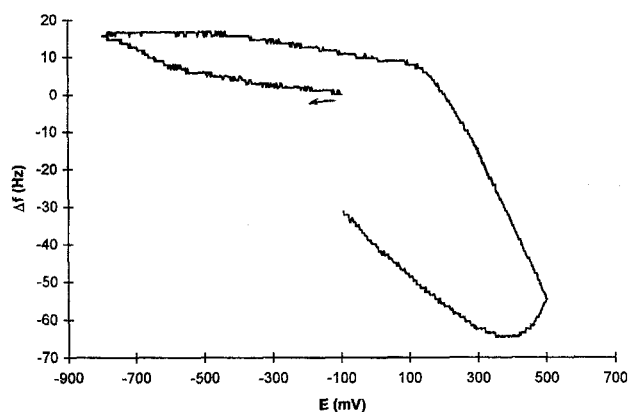This preliminary investigation has thus proved the ability of a prereduced PPy/f-PEO film to incorporate IC.

Fig. 10. Potentiodynamic $\Delta f/E$ profile for the PPy/Cl film in IC (0.01 M) aqueous solution.
This incorporation is, however, partly irreversible leading to some cation exchange in the cathodic region.

5. Conclusion

PEO oligomers ended by one Na carboxylate end-group (f-PEO) have been synthesized by esterification of the α-methoxy, ω-hydroxyl precursor by fumaryl dichloride. This type of oligomer has been used as dopant for the preparation of PPy films of low conductivity and some electroactivity, so leading to films with anionic exchange properties.

In contrast to the composites listed in the introduction, no cation exchange occurs during the redox process when carried out in aqueous solutions of α-mefhoxy, ω-Na carboxylate PEO and LaCl₃.

Nevertheless, the PPy/f-PEO has the capability of incorporating large size anions, such as IC. Further experiments will be carried out to take advantage of this opportunity and to analyze in more detail, the increase of permeability of the PPy/f-PEO film. This kind of low conductive but highly permeable PPy film is indeed very promising as biosensor, whose the key problem is too slow mass transfer in the polymer matrix.

Acknowledgements

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