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'Stuffed' conducting polymers

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Abstract

Conducting polymers (CP) obtained by oxidative polymerization using iron(III) salts shrink when Fe(II) and the excess counter ions are washed out after polymerization. This phenomenon can be used to incorporate active molecules into the CP matrix via their addition to the wash liquid. In the present work we demonstrate this principle on three different CP's: polypyrrole (PPy), poly-terthiophene (PTTh) and poly(3,4-ethylenedioxy thiophene) (PEDT), using ferrocene as a model molecule to be trapped in the polymer films.

Keywords: Polymer science and technology; Polymer materials; Polymer composite materials

1. Introduction

Since, the appearance of conducting polymers (CP's) in 1977 [1], much attention has been paid to the development of protocols for entrapment of functional molecules either for applications as diverse as biosensors [2–5], polymer-based energy storage devices [6–8], plastic solar cells [9, 10], or corrosion protection [11,12]. In the present paper an alternative route to the preparation of CP films loaded or 'stuffed' with active molecules is presented. This method avoids the sometimes harsh conditions present on the surface during oxidative polymerization.

It is well known that mesoscopic and nanometric materials can have physical properties differing from bulk materials, which is the basis for numerous technological and commercial applications. To prepare nano materials, template synthesis within porous membranes is a good alternative to lithographic techniques. This method has already been used to prepare fibers of magnetic or non-magnetic metals and semiconductors [9–15].

Conjugated polymers prepared by oxidative polymerization using ferric salts shrinks considerably when Fe(II) and the excess counter ions are washed out after the polymerization.

Volume contraction during rinse of 3,4-ethylenedioxy thiophene (EDT) polymerized using ferric toluenesulfonate (Fe(III) tosylate) as oxidant was reported by Aben et al. [16] from Philips Display Company in 1998. They made use the phenomena to replace Fe(II) and excess of tosylate with tetraethyl-*o*-silicate (TEOS), that in a later heating step was converted to SiO_2. They reported a shrinkage of the PEDT film to 5% of its original thickness during the washing step without TEOS, and managed to incorporate over 75% TEOS by volume in the films by rinsing with a 20% TEOS solution in ethanol.

In previous works [17,18] we have shown new routes to achieve well-controlled, coherent film of polypyrrole (PPy), poly-terthiophene (PTTh) and poly(3,4-ethylenedioxy thiophene) PEDT by vapor phase polymerization (VPP) using Fe(III) tosylate as oxidant. Here we present the possibility to using the shrinkage phenomenon, previously reported for PEDT, to incorporate active molecules into these VPP films.

2. Experimental

3,4-Ethylenedioxythiophene (Baytron M) and Fe(III) tosylate (40% solution in butanol, Baytron C) was received from Bayer AG. All other chemicals were obtained from Aldrich and used as received.

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The polymerization of PPy, PTTh and PEDT by vapor phase polymerization (VPP) was carried out as earlier reported [17,18] using Fe(III) tosylate as oxidant. Glass slides or Pt coated PET foils were used as substrates for vapor phase polymerization.

Some films were washed twice in ethanol and the thickness of the films was measured by a DekTak profilometer (Veeco DekTak 3030) before and after wash to determine the shrinkage. Other samples were washed in 5% solutions of ferrocene (in a 50% ethanol, 50% toluene mixture) for 10 min. After drying, the samples were washed 10 s in ethanol to remove excess ferrocene crystals from the surface of the films. The thickness was measured before and after this treatment to estimate the amount of ferrocene trapped in the films.

PEDT films on Pt-coated PET foil washed either with ethanol or the ferrocene solution were characterized by cyclic voltammetry (CV) in a standard three-electrode cell with an aqueous 1.0 M $NaNO_3$ solution as electrolyte and Ag/AgCl as reference electrode.

The conductivity of the samples was measured using a four-point probe from Jandel Engineering Ltd connected to a Keithly 2400 source meter. UV–vis spectroscopy (Shimadzu UV1700) was preformed on samples coated on glass.

Also larger molecules were washed into PEDT, among them poly-ethyleneglycol 600 dicarboxylic acid (PEG600DCA). Five percent solutions in ethanol were used.

3. Results and discussion

The CP films (PEDT, PTTh and PPy) made by VPP all shrank during wash in ethanol or in the ferrocene/ethanol/toluene solution. The results of the profilometry measurements are shown in Fig. 1, calculated as the ratio between the thicknesses of the washed films relative to the pristine films. PEDT washed in ethanol shrank to 5% of its original thickness, which corresponds well with what was reported from the Philips group [16]. Also the amount of ferrocene washed into the PEDT film fits with these results, where 50% TEOS in the films was reported after wash with a 6.5% solution of TEOS. In our case 52% by volume ferrocene was trapped in the film, when washed with a 5% solution of ferrocene. The PPy films shrank to 7.2% of the original thickness by wash with ethanol and the amount of ferrocene trapped in the washed films was 26% by volume.

The PTTh samples in this test were both thinner and with a much more uneven surface than the PEDT and PPy film, making the results less accurate. Nevertheless the PTTh samples clearly shrank by wash in ethanol (to ∼18%) and is was possible to trap ferrocene inside these films as well. The lower shrinkage is not surprising, because the relative weight (and volume) of oxidant required per thiophene unit is approximately three times less than the weight of oxidant per monomer unit for PPy and PEDT.

As demonstrated above, it is possible to incorporate considerable amounts of ferrocene in all three conducting polymers investigated. The shrinkage of PPy by wash in ethanol is fitting well with expectations: The PPy films should theoretically shrink to 7.8% of the original thickness when iron(II) and excess of tosylate is removed and actually shrank to 7.2%. The theoretical value is estimated under the assumptions that 2.25 mol iron(III)tosylate is used to oxidize 1 mol pyrrole and only 0.25 mol tosylate remains in the polypyrrole as dopant after wash and that the density of the reactants is unity.

Contrary to this, the large shrinkage for PEDT cannot be explained only by the fact that iron(II) and excess of tosylate is removed. For PEDT the volume should theoretical shrink to 13% but the measured shrinkage is to 5% of the original volume. SEM pictures of a PEDT

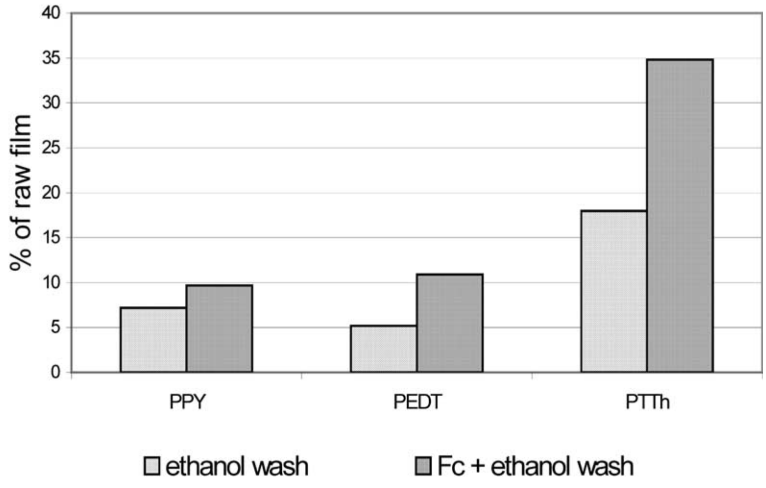

Fig. 1. Thickness of conjugated polymer (CP) films after wash relative to the thickness of the as-prepared films. Left columns show CP films washed in ethanol, right columns CP film washed in 5% ferrocene in a 1:1 toluene/ethanol solution.

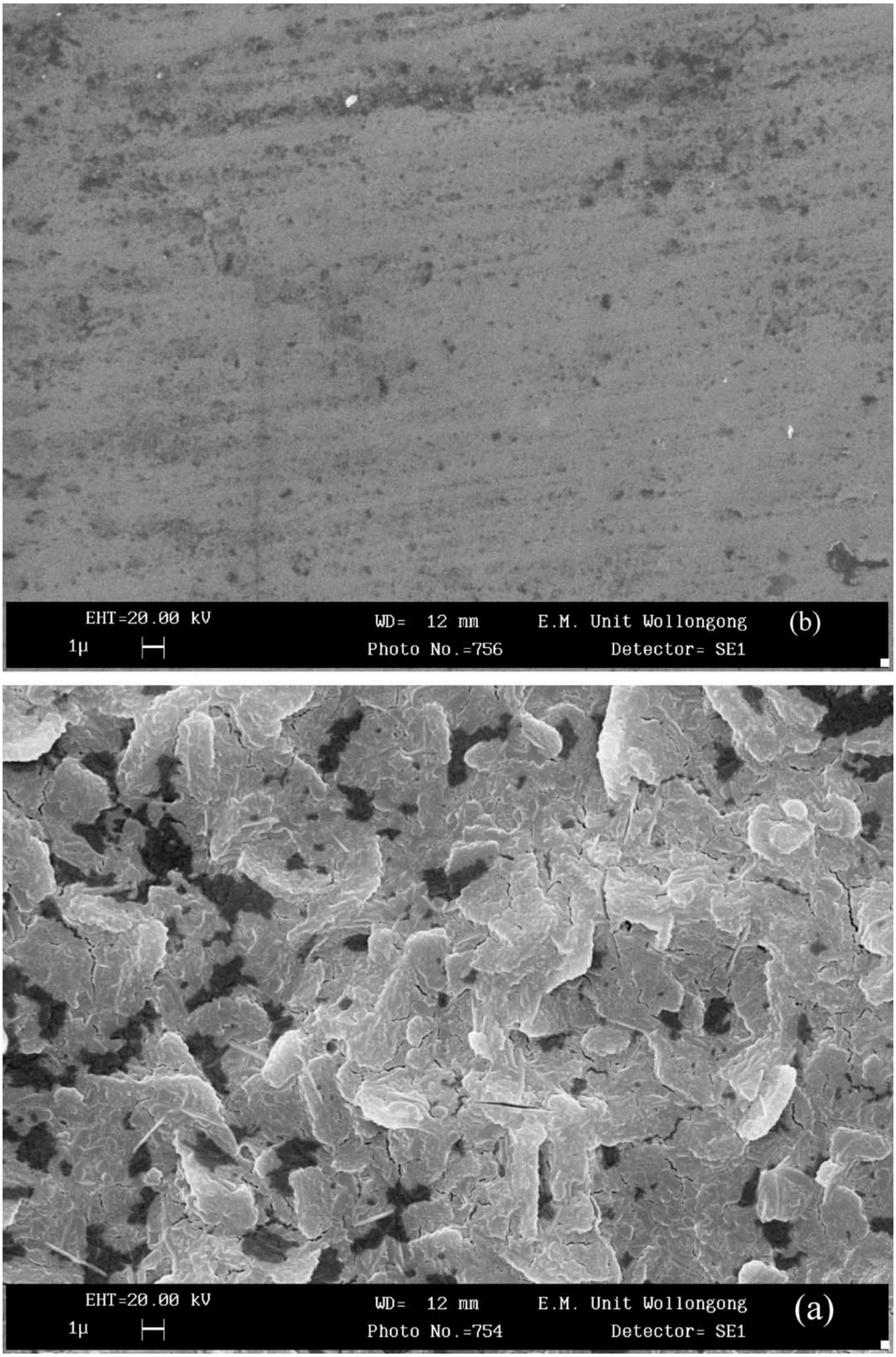

Fig. 2. SEM micrographs of PEDT before (a) and after (b) wash in ethanol.

surface before wash (Fig. 2(a)) shows a very open structure with 'pore' of micrometer size. With washing this structure seems to collapse (Fig. 2(b)). This phenomenon is not seen in PPy samples, and this may explain the unexpected large shrinkage as well as the ease whereby relative large molecules like PEG600 dicarboxylic acid are incorporated into PEDT films during washing.

3.1. Cyclic voltammetry of PEDT/ferrocene

In Fig. 3(a) the CV of PEDT/ferrocene is shown compared to neat PEDT. The ferrocene oxidation and reduction peaks are clearly visible at 0.31 V ('A') and 0.17 V vs Ag/AgCl ('B'). Upon repeated cycling, however, the ferrocene signal disappears as seen on Fig. 3(b). Ferrocene is known to be water soluble in the oxidized state, and during cycling the dissolved ferrocene elutes from the polymer films.

PEDT/ferrocene samples stored at room temperature in the laboratory also lose the ferrocene content over a few days by sublimation (as would a solid ferrocene sample).

3.2. Cyclic voltammetry of PEDT/ferrocene with a PPy overlayer

To prevent ferrocene escaping from the PEDT films, a second PEDT layer was polymerized on top of the ferrocene washed PEDT, either by vapor phase polymerization or by electro polymerization. Both methods decreased the rate at which ferrocene was elucidated, but did not completely stop the loss. Polypyrrole (PPy) polymerized by electro-chemically methods is known to be dense and have good barrier properties [19]. A layer of PPy was electro-polymerized on top of the PEDT/ferrocene film (polymerization conditions: +0.6 V vs Ag/AgCl for 30 s in an aqueous solution of 0.1 M *p*-toluene-sulfonic acid sodium salt (Na-pTs) and

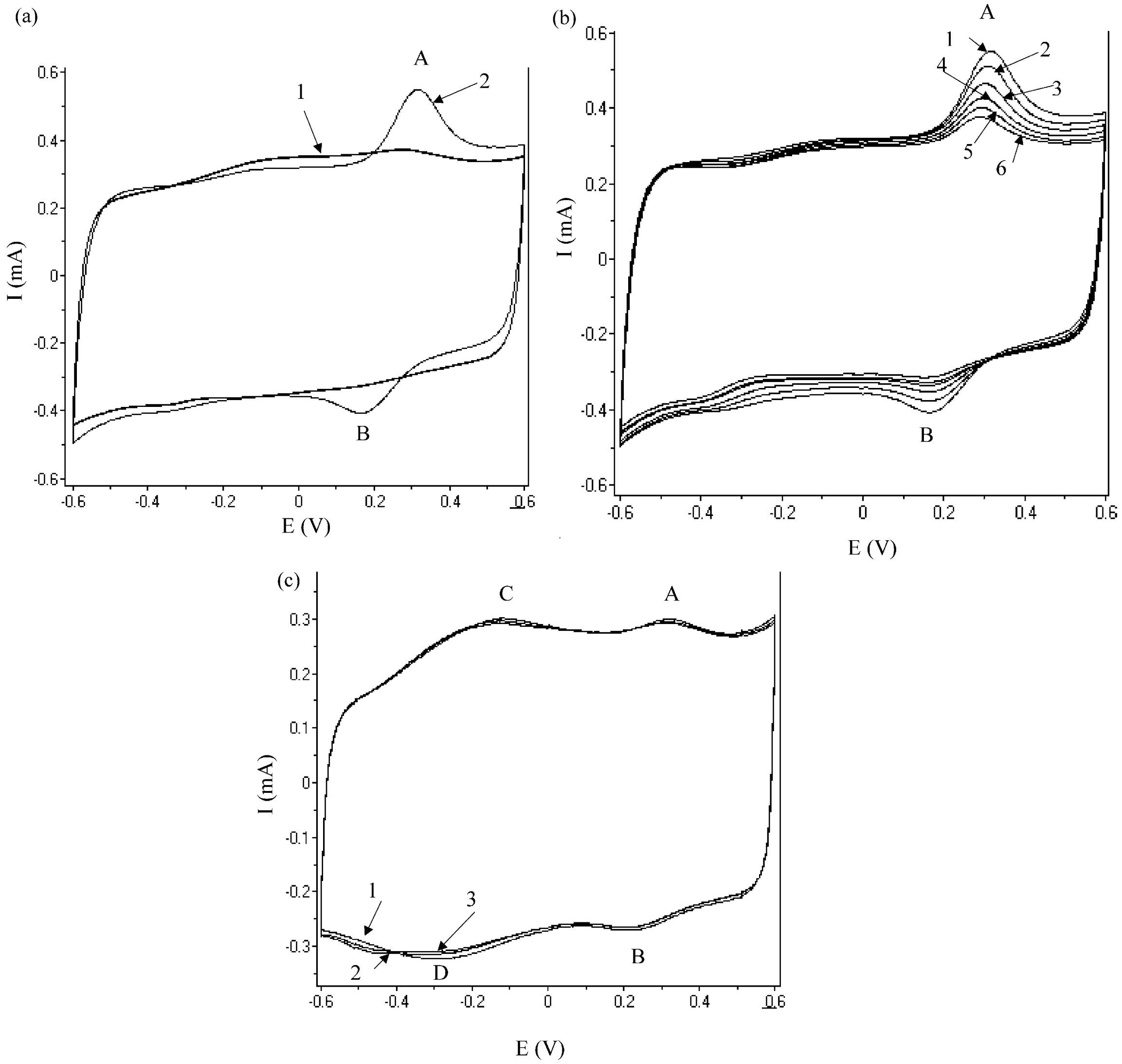

Fig. 3. (a) Post-polymerization CV of PEDOT, which was washed in ethanol (1) or in 5% ferrocene/toluene/ethanol solution (2), in 1.0 M $NaNO_3$. Scan rate: 100 mV s^{-1}, reference electrode: Ag/AgCl. (b) Post-polymerisation CVs of PEDOT washed with 5% ferrocene/toluene/ethanol solution, in 1.0 M $NaNO_3$. Scan rate: 100 mV s^{-1}, reference electrode: Ag/AgCl. 1: cycle No. 1; 2: cycle No. 5; 3: cycle No. 10; 4: cycle No. 20; 5: cycle No. 30; 6: cycle No. 50. (c) Post-polymerisation CVs of PEDOT loaded with ferrocene and covered with a PPy-pTs layer. 1: cycle No. 1; 2: cycle No. 20; 3: cycle No. 40. Electrolyte: 1.0 M $NaNO_3$, scan rate: 100 mV s^{-1}, reference electrode: Ag/AgCl.

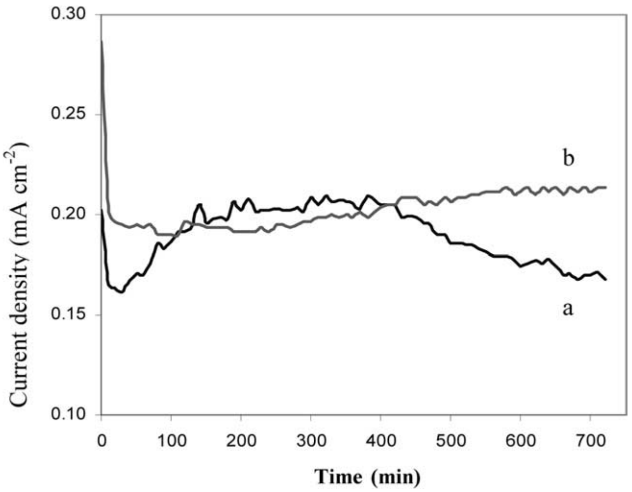

Fig. 4. Current density–time plot for hydrogen generation when poised at −0.44 V vs Ag/AgCl (3 M NaCl) in 1.0 M H_2SO_4 of Pt coated PET foil (a) and PPy-pTs (30 s)/PEDOT-Fc modified Pt coated PET foil (b).

0.2 M pyrrole). The film was then cycled 50 times from −0.6 to 0.6 V without any lose in the ferrocene signal (Fig. 3(c)). The ferrocene peaks did decrease initially after addition of the extra PPy layer. It is possible that some of the ferrocene was lost during electro polymerization of the PPy layer.

In a further study, the catalytic properties of a Pt coated PET foil were compared with a similar foil modified with a PEDOT layer loaded with ferrocene and covered with a PPy-pTs layer. The electrodes were kept at −0.44 V vs Ag/AgCl in 1.0 M H_2SO_4 for 12 h while the current density for hydrogen evolution was monitored, see Fig. 4. With the unmodified Pt coated PET foil, the current density was found to increase in the first 2 h, stabilize for the next 5 h, and then decrease to 0.17 mA cm^{-2} after 12 h (Fig. 4). Using the same conditions, the modified ferrocene-containing electrode gave a more stable current density for hydrogen generation slowly increasing up to 0.21 mA cm^{-2} after 12 h (Fig. 4), which is 27% higher than that of the unmodified Pt coated PET foil. This is consistent with our previous catalytic results on hydrogen generation obtained with other ferrocene containing materials [20].

3.3. Incorporation of PEG600 dicarboxylic acid

To demonstrate that also larger molecules can be incorporated in the washing step, PEG600 dicarboxylic acid (PEG600DCA) was washed into PEDT.

Unwashed samples on glass of vapor-phase polymerized PEDT on Fe(III)tosylate with a thickness of 8–10 μm was washed in a 5% solution of PEG600DCA in ethanol. After wash the thickness of the PEDT films were 12.0–1.35 μm or 13.5–14% of pristine films. Over night storage on a 60 °C hotplate did not change the thickness. Control samples of PEDT films washed with ethanol shrank to 7.5% of the pristine films. This means that ∼45% (volume) of PEG600DCA was trapped in the PEDT/PEG600DCA films. The UV–vis spectra (Fig. 5) of PEDT washed with ethanol and a 5% PEG600DCA solution in ethanol shows a difference in absorbance over ∼800 nm. The difference must be due to changes in the absorbance of PEDT when mixed with PEG600DCA, because PEG600DCA have no absorbance in this region. Similar changes in the UV–vis characteristics have been observed when PEDT has been exposed to environments with neutral pH [21]. These changes are connected to changes in the doping level of the PEDT [21] that normally leads to reduced conductivity of PEDT, but in the case with PEG600DCA, no major decrease was observed; The PEDT control samples had a

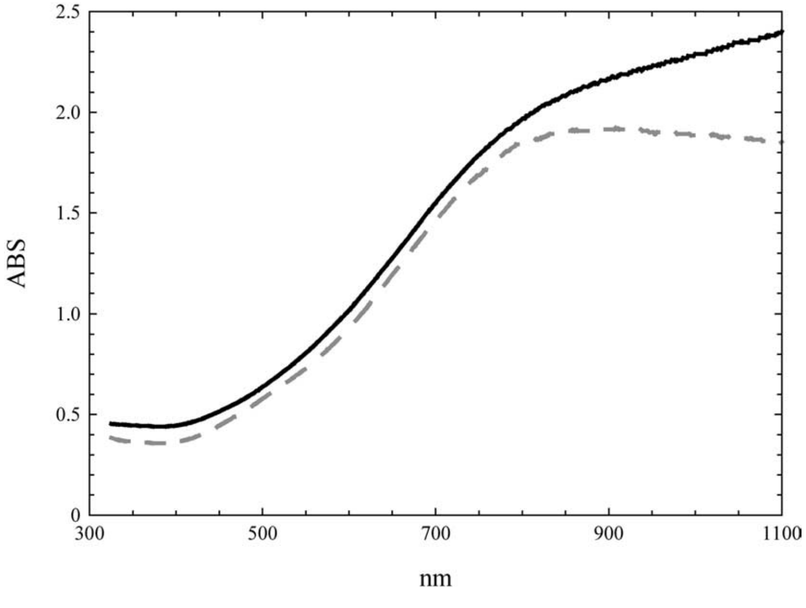

Fig. 5. UV–vis spectra of PEDT (full black line) and PEDT/PEG600DCA (dashed gray line) coated on glass substrates.

conductivity of 990 S/cm and the PEDT/PEG600DCA films had 910 S/cm when normalized to PEDT content.

When PEDT/PEG600DCA film was stored in pure ethanol for 1 h they shrank to 8.2% (volume) of the pristine films. It means that ∼90% of the PEG600DCA was easily removed from the PEDT film. This underlines the need for some kind of bonding of the trapped molecules to keep them within the films when exposed to an appropriate solvent.

4. Conclusion

Conducting polymer coatings polymerized using Fe(III) tosylate as oxidant shrink dramatically when Fe(II) and excess tosylate is washed out after the polymerization step. This can be used to load the polymer film with a quite high density of foreign molecules if these molecules are present in the rinsing fluid used in the washing step. The foreign molecules are not chemically bound to the polymer host, but trapped mechanically when the polymer matrix collapses, and the added molecules can subsequently be leached out using proper solvents. The confinement of the trapped molecules can be improved by polymerizing a more dense overlayer on top of the ‘stuffed’ coating. In the present paper this was demonstrated using electro-polymerized thin dense polypyrrole layer.

The maximum possible size of the molecules that can be loaded into a conjugated host polymer by this method is not known, but PEG600DCA has been incorporated without difficulties. Because of the collapse of the initially very porous structure, PEDOT will probably be able to incorporate cells or nano-particles during the washing step.

This method avoids the sometimes harsh conditions present on the surface during oxidative polymerization, and may be used as an approach to incorporate vulnerable bio-molecules (such as proteins, enzymes or even whole cells) onto the surface of sensor devices. This phenomenon can also be used to trap nano particles or nano fibers in the CP matrix by adding these nano materials to the washing solvent.

Acknowledgements

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