



## CHARACTERIZATION OF ELECTROCHEMICAL PROPERTIES OF POLY(3,4-ETHYLENE DIOXYTHIOPHENE) – POLY(N, N-DIMETHYL ANILINE) AND COPOLYMER

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Homopolymerization of 3, 4-ethylene dioxythiophene (PEDOT) and copolymerization with N,N-dimethyl aniline (PDMA) were performed onto a platinum electrode. The synthesis was performed using potentiodynamic electrodeposition modes from LiClO<sub>4</sub> solution containing 1:1 monomer ratio, in case of copolymer. The influence of sodium dodecyl sulphate (SDS) as a wetting agent was studied. The resulting copolymer films were characterised using cyclic voltammetry and EIS measurements in neutral phosphate buffer solutions. The results confirmed the obtainment of a new material by copolymerizing 3,4-ethylene dioxythiophene with N,N-dimethyl aniline with different properties than the corresponding homopolymers. SEM measurements showed that SDS surfactant had a marked influence on the films porosity. The specific capacitance of the PEDOT-PDMA copolymer was calculated and it showed good stability during cycling in PBS solution.

### INTRODUCTION

Electroactive materials based on conducting organic polymers and their composites have been intensively studied in recent years.<sup>1-4</sup> Poly(3,4-ethylene dioxythiophene) (PEDOT) is one of the most successful polythiophene derivative because of its interesting properties: high conductivity, unusual electroactivity and a relative environmental stability.<sup>5-7</sup>

PEDOT proved a better aqueous stability and biocompatibility than polypyrrole and polyaniline and therefore it is considered a promising polymer appropriate for continuous sensing and even *in vivo* implantation.<sup>8-9</sup> It can be produced electrochemically in a variety of solvents. It has been showed that the electrochemical and physical properties of polymers are greatly influenced by the nature of dopant and electrolyte during the polymeric process.<sup>10, 11</sup> In this study, sodium

dodecyl sulphate (SDS) was used as dopant in the synthesis and also as the ionic surfactant.

On the other hand, it is well known that the simplest representative of poly(N-alkylanilines), poly(N-methylaniline), shows well expressed electrochemical redox activity and relatively high electric conductance even at pH 7 or 8, whereas PANI losses its activity at pH above 4.<sup>12</sup> When considering N,N-dialkylanilines as monomers for electropolymerization, some problems arise as polymerization of N,N-dialkylanilines due to impeding  $\pi$ -electron conjugation in resulting oligomers or polymers. Therefore, no electric conductivity and usual redox properties should be expected for the resulting polymers. Despite of this, there is a number of publications on electrogenerated polymers derived from N,N-dialkylanilines. Electropolymerized layers of N, N dimethyl aniline (DMA) attracted some attention mostly due their anion-exchange properties.<sup>13</sup>

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Our studies revealed that the electrochemically synthesized PEDOT is stable in phosphate buffered solutions, which makes the former polymer an excellent candidate for application in biosensors. Moreover, the copolymerization of 3,4-ethylenedioxythiophene with N, N dimethyl aniline (PEDOT:PDMA) was studied as a function of SDS concentration. This paper reports the detailed results on the electrochemical stability of PEDOT and PEDOT: PDMA modified electrodes under physiological conditions by means of cyclic voltammetry measurements, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

## EXPERIMENTAL

3,4-Ethylenedioxythiophene (EDOT) and N,N dimethyl aniline were purchased from Aldrich. All other reagents used were of analytical grade and used as received.

The electrochemical measurements were performed using a Voltalab 40 potentiostat. The electrochemical cell was a conventional three electrodes system with a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. PEDOT films were synthesized by means of potentiodynamic deposition mode in 0.1 M LiClO<sub>4</sub> supporting electrolyte containing 10 mM monomer. The films were electropolymerized at the surface of bare platinum electrode by cyclic voltammetry in the -0.4 V and 1.2 V potential windows at a scan rate of 20 mVs<sup>-1</sup>. Various concentrations of SDS were added as dopant to the electrolyte. The PEDOT: PDMA copolymer was synthesized employing a 1:1 molar monomer ratio in LiClO<sub>4</sub> supporting electrolyte in absence and presence of SDS.

All assessment measurements for the obtained films were performed in 0.1M phosphate buffered saline (PBS) solutions (pH 7) and the potentials are given against SCE, unless stated otherwise. Cyclic voltammetry (CV) was used to assess the cycling stability of the PEDOT homopolymer and PEDOT: PDMA copolymer films. The modified electrodes were

subjected to successive cycles CV test at a scan rate of 25 mVs<sup>-1</sup> and the corresponding CV curves were measured. Electrochemical impedance spectroscopy (EIS) was further employed to assess the properties of PEDOT and PEDOT: PDMA films by using the Voltalab 40 equipment. Morphologies of the polymer-coated electrodes were examined using a Philips SEM-500 scanning electron microscope at an accelerating voltage of 12 kV and a Nicolet FT-IR spectrophotometer was employed to assess the formation of PEDOT film.

## RESULTS AND DISCUSSION

Electropolymerization of PEDOT homopolymer and PEDOT: PDMA copolymer films were studied as a function of dopant concentration in the polymerization electrolyte. Firstly, the corresponding homopolymers were electrosynthesized in absence of dopant as it can be depicted in Fig. 1. The copolymerization of EDOT and DMA was attempted under similar conditions. A 1:1 monomer feed ratio of EDOT and DMA, respectively, was taken in order to obtain the electrogenerated copolymer film of PEDOT: PDMA via cyclic voltammetry and then the results were compared with homopolymers, which were obtained by repetitive cycling.

It can be seen from Fig. 1 that, in absence of dopant, the current corresponding to PEDOT formation increases sharply when the applied potential is larger than 0.7 V, which reveals the formation of the radical cations.<sup>14</sup> The increased current implies that the PEDOT radical cations start to electropolymerize onto the platinum electrode. The current is increasing upon continuous cycling, being indicative for a conductive film formation.

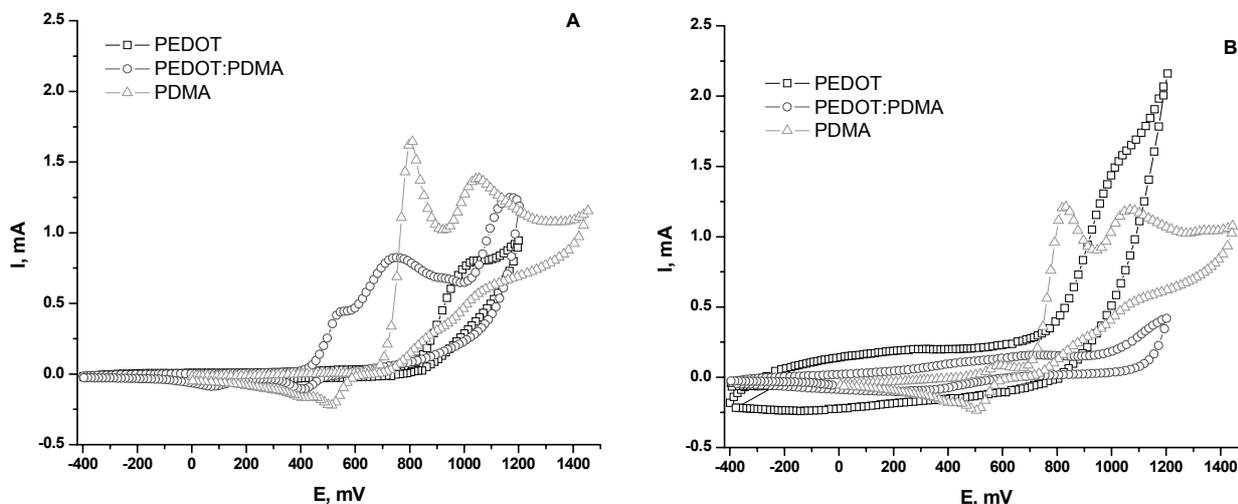


Fig. 1 – The cyclic voltammograms of EDOT, DMA and EDOT: DMA polymerization at a scan rate of 20 mVs<sup>-1</sup> in absence of SDS: A) 1<sup>st</sup> cycle and B) 10<sup>th</sup> cycle.

In case of PDMA formation, the voltammograms shows several oxidation peaks: two anodic peaks, located at 0.81 and 1.05 V, appear in the first scan; in the back potential scan, the cathodic peak at 0.52V is observed. Most probably, the two oxidation peaks correspond to two one-electron oxidation steps of DMA, leading consecutively to cation radical and dictation of DMA. By repeating of cyclic potential scans, all anodic and cathodic peaks intensities decrease, especially the first anodic peak located at 0.81V, whereas the third anodic peak at 1.36V forms (Fig. 1B). This indicates probably that the electrode surface is covered gradually by the products of anodic oxidation of DMA, which retard the electrooxidation of this monomer. At the same time, a new anodic peak appears at 0.58 V. It grows in the first 10 potential scans. The comparison of repetitive cyclic voltammogram of copolymer and homopolymers PEDOT and PDMA, respectively, clearly showed striking differences. The anodic

and cathodic peaks corresponding to PDMA seem to be shifted to more negative values whereas the peak at 1.1 V can be attributed to PEDOT formation. The current intensities are lower in case of copolymer than with respect to PDMA homopolymer and they decrease upon continuous cycling as it can be seen from flattened voltammogram in Fig. 1B.

Further, the SDS effect on the electropolymerization process of EDOT has been studied as it can be seen in Fig. 2. Only few characteristic values for SDS concentration are represented graphically. It is observed in Fig. 2A that the current response of doped PEDOT films increases as the dopant concentration increases to 10 mM, after which the doped PEDOT films exhibits much lower current responses. Moreover, the current increases with continuous cycling in the potential range as seen in Fig. 2B and the best electrochemical behaviour is presented by PEDOT doped with 10 mM SDS.

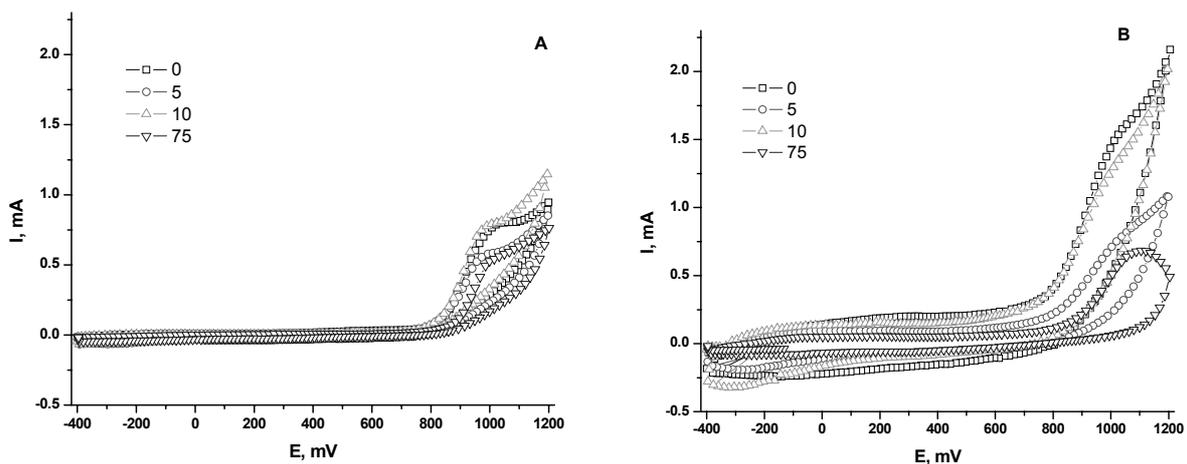


Fig. 2 – The cyclic voltammograms of EDOT polymerization at a scan rate of  $20 \text{ mVs}^{-1}$  in presence of different concentrations of SDS (mM): A) 1<sup>st</sup> cycle and B) 10<sup>th</sup> cycle.

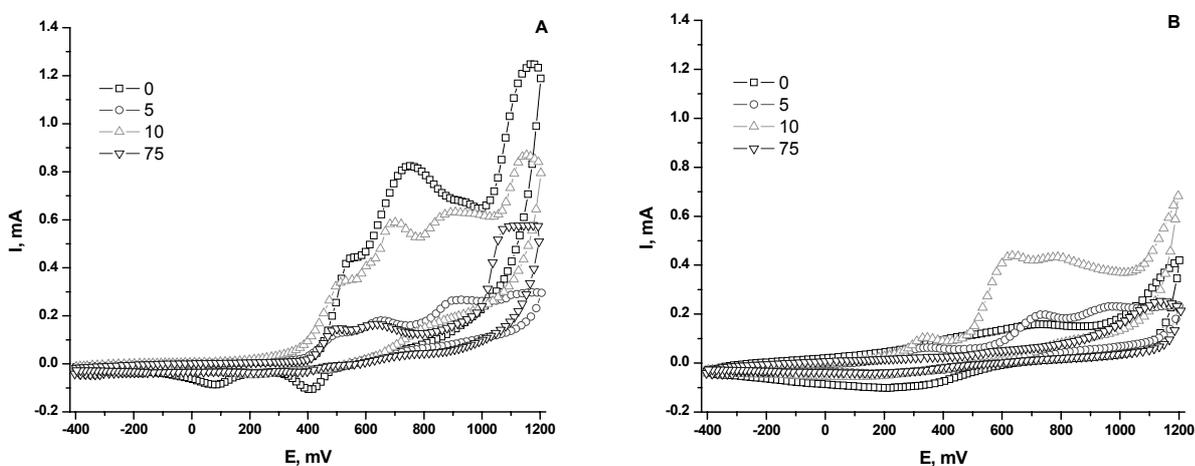


Fig. 3 –The cyclic voltammograms of EDOT: DMA polymerization at a scan rate of  $20 \text{ mVs}^{-1}$  in presence of different concentrations of SDS (mM): A) 1<sup>st</sup> cycle and B) 10<sup>th</sup> cycle.

Next, the study on the SDS effect on the electropolymerization process of EDOT: DMA was performed as depicted in Fig. 3. The dopant influences the copolymerization of EDOT: DMA in similar way as for EDOT meaning that the current response of doped PEDOT: PDMA films increases as the dopant concentration increases to 10 mM, reaching the value corresponding to PEDOT: PDMA formation in absence of SDS, after which the doped PEDOT: PDMA films exhibit lower current responses. Instead, in comparison to PEDOT behaviour upon continuous cycling, the current response for PEDOT: PDMA showed a decrease as seen in Fig. 3B, suggesting a less conductive film formation. The best

electrochemical behaviour is presented by PEDOT: PDMA doped with 10 mM SDS.

The choice of the electrochemical synthesis method has an influence on the morphology, appearance and adhesion of the polymer.<sup>15</sup> Generally, films obtained by alternating polarization are more adhesive and smoother than the ones obtained at constant current or potential. The electrochemical behavior of PEDOT and PEDOT: PDMA films deposited from aqueous solution in absence and presence of SDS was characterized further using cyclic voltammetry. These films can be cycled repeatedly without significant decomposition of the material, which is consistent with the results reported in the literature.<sup>16</sup>

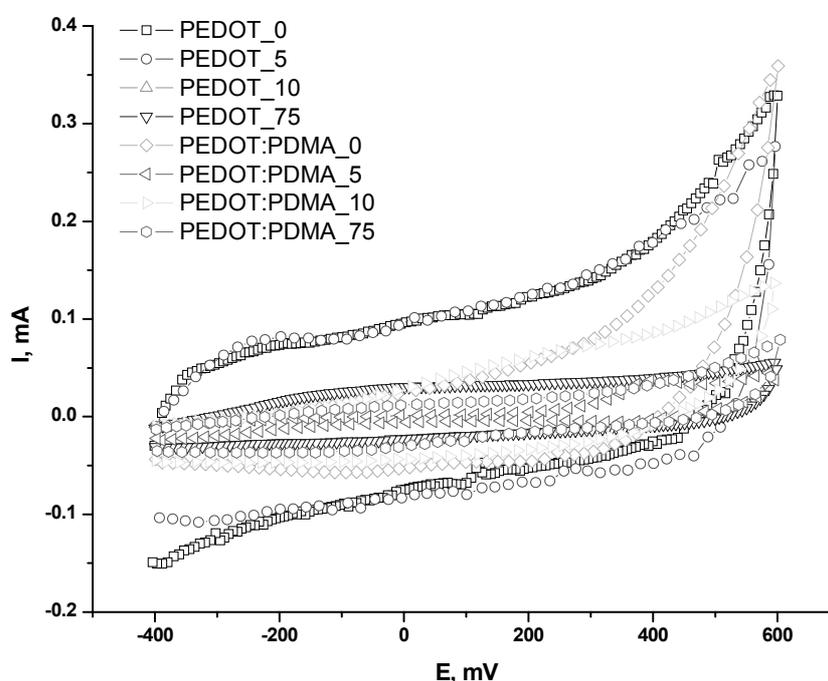


Fig. 4 – Voltammetric behavior of the PEDOT and PEDOT: PDMA films in 0.1M PBS solutions at  $25 \text{ mVs}^{-1}$  in absence and presence of SDS (mM).

The current–voltage characteristic of SDS doped PEDOT and PEDOT: PDMA films in the potential range of  $-0.4$  to  $0.6$  V in  $0.1$  M PBS solution (pH 7) is shown in Fig. 4. As it can be seen, the curves of the PEDOT polymer films have nearly rectangular shape, which is typical of the pure capacitive behaviour of the tested object.<sup>17</sup> However, the current response of PEDOT films obtained in presence of 75 mM SDS is nearly 3 times less than the film without dopant, which proves that SDS can hinder the polymer electroactivity after a certain concentration, this being the value of 10 mM in the case of our studied system. In case of PEDOT:PDMA film, the

curve rectangularity is less pronounced than for PEDOT and the current responses is lower than for PEDOT films. It can be concluded that not only SDS but also PDMA influences the capacitive behaviour of the copolymer films.

Electrochemical impedance spectrometry is a more reliable technique than cyclic voltammetry for measuring the capacitance with minimised effect from non-capacitive Faradaic contributions.<sup>18</sup> Therefore, the doped and pure homopolymer/copolymer films were studied by EIS. The resulting Nyquist plots for PEDOT and PEDOT: PDMA films in absence and presence of SDS are shown in Figs. 5A and 5B. The Nyquist

plot for PEDOT film is featured by a vertical trend at low frequencies, indicating a capacitive behaviour according to the equivalent circuit theory. The semicircle appeared at high frequencies is considered to owe to the charge transfer resistance, which originates from the interface structure between the porous electrode surface and the electrolyte.<sup>19</sup>

In presence of SDS, it can be observed that the capacitive behaviour was replaced by the more inclined diffusion line as the SDS concentration increased. It can be said that increasing SDS concentration leads to an increasing diffusive behaviour, observation corroborated with the changed morphology of doped PEDOT film in Fig. 6. In case of PEDOT:PDMA, the dopant has a strong influence as its concentration increases, sweeping from a diffusive to a capacitive

behaviour and back at the flexion point of 10 mM SDS. The capacitances of the electrode materials were calculated according to the equation  $C = -1/(2\pi f Z''')$ , where  $f$  = frequency;  $Z'''$  = imaginary impedance, from the slope of the linear correlation between the imaginary impedance and the reciprocal of the frequency at low frequencies. One can observe the decrease of capacitance value for SDS-doped PEDOT film with respect to undoped PEDOT, as smaller as the SDS concentration increases (see Table 1). The SDS leads to increased capacitance value but only if added up to 10 mM concentration to the polymerization electrolyte. In case of PEDOT:PDMA film, the capacitance is lower than for PEDOT homopolymer, and it decreases in presence of SDS. The highest capacitance values are obtained at low values of added dopant.

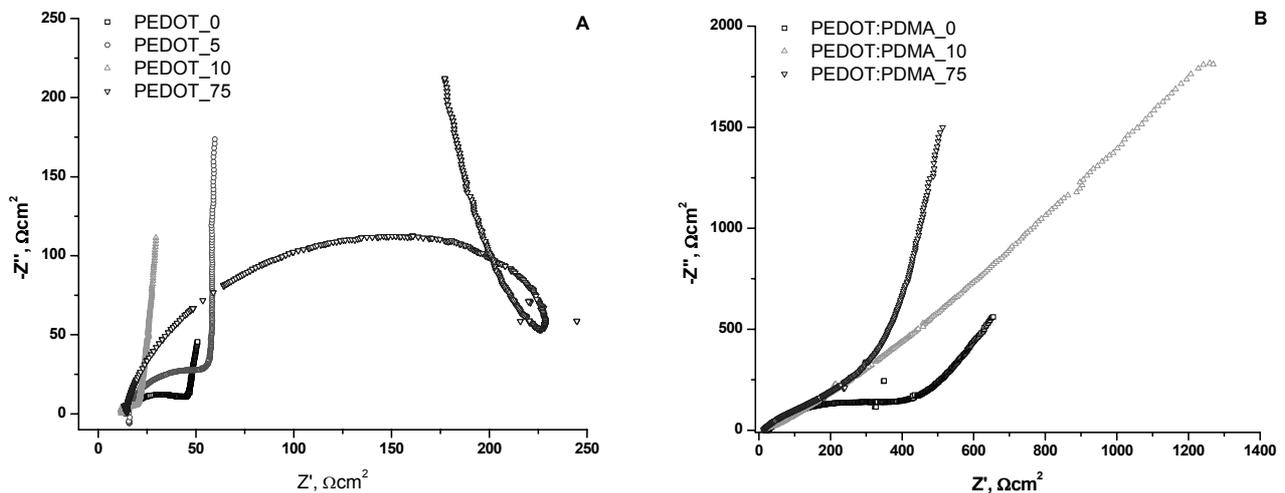


Fig. 5 – Nyquist plots for A) PEDOT and B) PEDOT:PDMA films as a function of SDS concentration.

Table 1

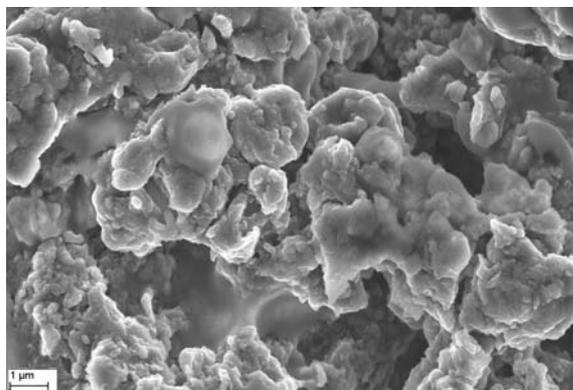
Capacitance values of PEDOT and PEDOT:PDMA films as a function of SDS concentration

Film	[SDS], mM	Slope values obtained from graph $-Z''' = f(1/2\pi f)$	$C, Fcm^{-2}$
PEDOT	0	100	0.0099
PEDOT	5	149.79	0.0066
PEDOT	10	97	0.0103
PEDOT	75	270.99	0.0037
PEDOT:PDMA	0	447	0.0022
PEDOT:PDMA	5	1049	0.0009
PEDOT:PDMA	10	942	0.0010
PEDOT:PDMA	75	1200	0.0008

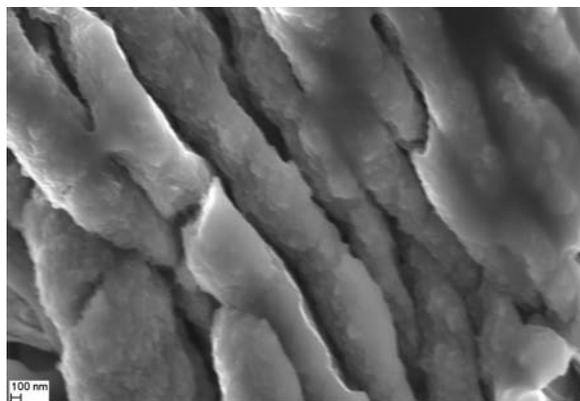
This is in agreement with the SEM results presented below (Fig. 6) that suggested much higher porosity in the SDS-doped PEDOT films than in the undoped polymer counterparts. In

Fig. 6A a nodular accumulating structure is evidenced. The size of the nodules ranged a few hundred nanometers in diameter and they aggregate to form goblets. In Fig. 6B, the effect of

high concentration of SDS on the morphology of PEDOT film can be observed: lamellar structure with almost vertical orientation to the substrate. It is evident that SDS dopant changes the



a)



b)

Fig. 6 – SEM images of the film surface of A) undoped PEDOT and B) PEDOT doped with 75 mM SDS.

FT-IR studies showed that the PEDOT homopolymer was formed after only 5 min of polymerization. The spectrum shows several bands of which the band at  $819\text{ cm}^{-1}$  is assigned to the symmetric C-S-C deformation, and the band at  $1053.91\text{ cm}^{-1}$  is assigned to the symmetric C-O-C ether bond.<sup>20</sup> Thereafter no major changes were observed. It can be noted that the signal at  $800\text{ cm}^{-1}$  disappeared and signals at  $1640\text{ cm}^{-1}$  and in the  $3000\text{--}4000\text{ cm}^{-1}$  region appear. The first signal can be assigned to an aromatic CH out-of-plane swing vibration of the terminal thiophene group, which will decrease as the reaction proceeds.<sup>21</sup>

## CONCLUSIONS

Pure and SDS-doped PEDOT and PEDOT:PDMA films were electrodeposited potentiodynamically onto a Pt surface. The current response of doped PEDOT films decreased as SDS concentration increased, the value of 10 mM SDS being the one at which the SDS-PEDOT and SDS-PEDOT:PDMA behaviour changed. A more porous and lamellar structure was obtained when adding SDS in a concentration higher than 10 mM. Nearly rectangular shaped CVs are obtained for all PEDOT films suggesting that charge and discharge reversibly occur at the electrode/electrolyte interface. Higher capacitance values were exhibited by pure PEDOT and PEDOT doped with SDS up to 10 mM. Lower capacitance values were obtained in the case of PEDOT:PDMA film. The

morphology of PEDOT film into a more porous structure with higher interface area and in conclusion also the morphology of the PEDOT:PDMA film.

obtained results can be employed to get the desired value of the capacitance by choosing the adequate preparation method and so, by controlling the microstructure of the composites. Ongoing work is being carried out.

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