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## Electrosynthesis and characterization of poly(3-methylthiophene) on different substrates

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**Abstract** We report on the study of the electropolymerization of 3-methylthiophene onto Pt, p-Si and indium-tin oxide deposited on polyester using quartz crystal microgravimetry, electrochemical and spectroelectrochemical measurements. We observe that potential variation during the galvanostatic electrodeposition is correlated with the nucleation process. The mass variation of poly(3-methylthiophene) is linear with the amount of the electrochemical charge whereas the absorbance variation curve shows two distinct slopes. The latter result has been explained in terms of conjugation length variation during polymer growth. Scanning electron microscopy analysis allowed the detection of morphological changes from a dense and compact structure to an open morphology when the poly(3-methylthiophene) film thickness increases. The roughness of the films did not change considerably with the substrate, as observed by atomic force microscopy. Absorption and photocurrent spectra at different film thicknesses show a shift of the peaks to lower wavelengths when the thickness increased, thus confirming the decrease of mean conjugation length in thicker films.

**Key words** Poly(3-methylthiophene) · Electrosynthesis · Photocurrent spectra

### Introduction

Conducting polymers are widely studied with the aim of testing their performance in applications as modified

electrodes or electronic devices [1]. A further development in these directions is conditioned to the attainment of polymer films with a controlled structure and defined properties.

Optimization of the electrochemical synthesis conditions can lead to a better control of the polymer properties with a better understanding of the polymer deposition mechanism. Indeed, despite the well-established electropolymerization mechanism for aromatic and heteroaromatic compounds [2], the formation of a polymer on the electrode still represents an open question in various cases [3]. Photocurrent spectroscopy of conducting polymers is a suitable technique for monitoring the initial steps of electrodeposition [4]. It has been shown that the initial stages of poly(3-methylthiophene), PMeT, deposition onto indium-tin-oxide (ITO) involved polymeric chains with a large conjugation length [4, 5]. Moreover, photocurrent spectroscopy allowed the observation that short chains are deposited when ITO electrodes are covalently modified with thiophene-containing compounds [5, 6]. In fact, a video recording of PMeT electrodeposition showed enhancement of the nucleation kinetics by ITO surface modification [7]. In situ characterization of the growing film can provide substantial information on the first stages of the electrodeposition process. The mechanism of PMeT growth has been also characterized with in situ spectroelectrochemical and kinetic measurements [8]. Other suitable techniques are Fourier transform infrared spectroscopy [9] and Raman scattering [10] for determination of the structural properties of polymer chains, and the scanning-probe techniques, e.g. scanning tunneling microscopy (STM) and atomic force microscopy (AFM), for the detection of the spatial distribution in early polymer deposits [11–14]. Moreover, the combination of two in situ techniques represents a suitable approach for the study of conducting polymer electrodeposition, like the simultaneous spectroscopic ellipsometry and quartz crystal microgravimetry (QCM) characterization of polyaniline and polynaphthylamine formation [15, 16].

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The formation of a conjugated double bond chain occurs by  $\alpha$ - $\alpha$  coupling of the heterocyclic rings. The occurrence of  $\alpha$ - $\beta$  coupling during electrochemical polymer synthesis interrupts the electronic conjugation of the polymeric chains, with undesirable consequences on the optical properties and electric transport of the resulting polymer [17]. The number of such defects should increase with the extent of electropolymerization [18]. Yassa et al. [19] showed that the efficacy of conjugation was higher for thinner electropolymerized PMeT films, as demonstrated by conductivity measurements and optical spectra at different film thicknesses. Moreover, absorption spectra of polymer films can also reflect the distribution of the effective conjugation lengths, showing the degree of conformational disorder in the polymer structure [20]. The relevance of the latter parameter on PMeT electronic properties has been stressed in the analysis of the photovoltaic response of the CdS(AI):PMeT junction [21].

In a previous study we characterized the photoelectrochemical processes at the PMeT/electrolyte interface and it was observed that the photocurrent had a maximum when the PMeT film thickness was  $0.7 \mu\text{m}$  [22]. Such results outlined how the definition of electrodeposition parameters is important for the optimization of the transport properties in polymer films. In this work we report on the study of PMeT electropolymerization with QCM and UV-visible spectroscopy during PMeT galvanostatic synthesis. Moreover, we present the characterization of PMeT films of different thicknesses with SEM, AFM, UV-visible and photocurrent spectroscopy.

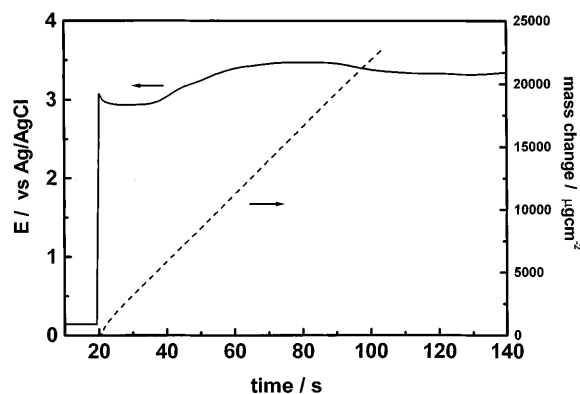
## Experimental

PMeT films were galvanostatically deposited on ITO-polyester (ITO-PET resistance  $60 \Omega$ , Innovative Sputtering Technology), Pt and p-Si (Semimetrics, resistivity  $10 \Omega \text{ cm}$ ) in a single compartment cell. The electrolyte was  $0.1 \text{ M}$  3-methylthiophene (Aldrich),  $(\text{C}_4\text{H}_9)_4\text{NBF}_4$   $0.01 \text{ M}$  (Sigma) in dry distilled acetonitrile (Carlo Erba). The applied current density was  $3.75 \text{ mA cm}^{-2}$ . Electrochemical measurements were accomplished with an EG&G PAR potentiostat model 362. The monitoring of the mass variation during galvanostatic synthesis was made with a quartz crystal microbalance (Seiko-EG&G model QCA 917). The resonance frequency of the quartz crystal was  $9 \text{ MHz}$  and the working Pt electrode area was  $0.3 \text{ cm}^2$ . The in situ determination of absorbance during PMeT electrosynthesis and the absorption spectra of the PMeT films were made with a 8452A HP-diode array UV/Vis spectrophotometer. The morphology of the PMeT films was analyzed with a SEM JXA-840 operating at  $20 \text{ kV}$  (magnification  $7500$ ). AFM images were run with a TopoMetrix TMX 2010 AFM instrument and the roughness was estimated from the standard deviation values. Film thickness measurements were done with an Alpha-Step 200 Tencor Instrument. Absorption and photocurrent spectra of PMeT films were run inside a single compartment cell with optically transparent windows. The electrolyte was  $0.1 \text{ M}$   $(\text{C}_4\text{H}_9)_4\text{NBF}_4$  in acetonitrile. A Pt wire was used as the counter electrode and an Ingold Ag/AgCl as a reference electrode (the salt bridge was made with the organic solvent). Photocurrent spectra of PMeT films were run with an ORION halogen lamp ( $100 \text{ W}$ ). The monochromator (Applied Photophysics, model F34) was controlled by a Stepping Motor Control Unit (Applied Photophysics,

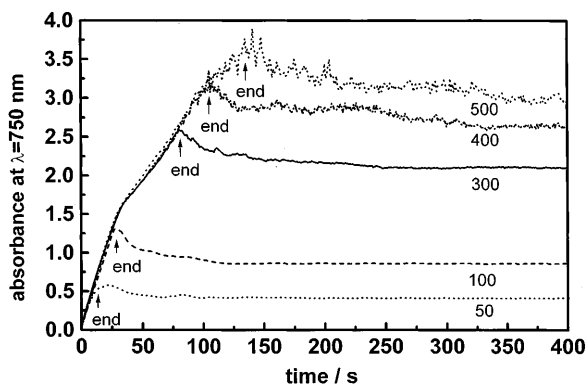
model 7602) and a HMS Light Beam Chopper model 230 was used at the working frequency of  $15 \text{ Hz}$ . The lock-in amplifier was a Stanford Research Systems SR 530 instrument. The experimental data were acquired with a Labview 3 system from National Instruments.

## Results and discussion

The growth of PMeT films on ITO-PET was analyzed by measuring the potential during the galvanostatic polymerization. The slight potential variations during the galvanostatic polymerization (full line in Fig. 1) were associated with the nucleation process on the electrode. The chronopotentiogram shows an initial spike at  $3.4 \text{ V}$  versus Ag/AgCl for the onset of monomer oxidation in the solution. The slight increase of potential with time was ascribed to the formation and growth of a polymeric film with good conducting properties [23–26]. The electrode mass variation was also analyzed during the galvanostatic synthesis of PMeT using QCM (dashed line in Fig. 1). We observe that the electrode mass increases linearly with time and charge. In the same experimental conditions the in situ monitoring of absorbance at  $\lambda = 750 \text{ nm}$  was done at different final values of the charge density (Fig. 2). All measurements showed a linear increase of absorption during the first  $30 \text{ s}$  of galvanostatic synthesis, followed by a change of the slope. This result shows that the amount of deposited polymer is linear during the synthesis (dashed line in Fig. 1), whereas the linear increase of absorbance occurs only for films with deposition charge density  $\leq 100 \text{ mC cm}^{-2}$ . This change of slope could indicate an abrupt modification of the electrode surface. In accordance with Bock et al. [20], the dependence of absorption spectra on film thickness is ascribed to morphology changes during film growth. The mean effective conjugation length could also vary during such morphological



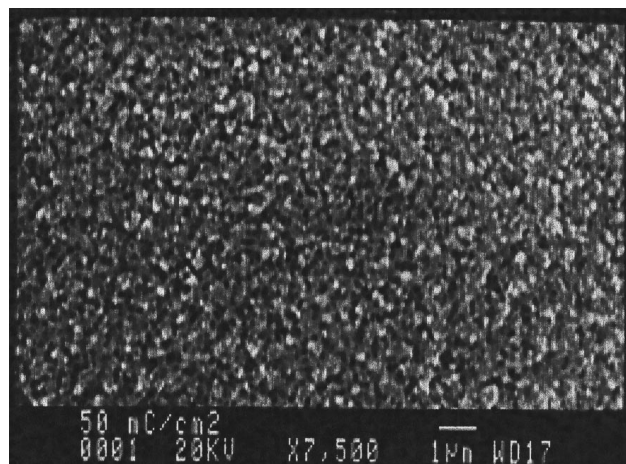
**Fig. 1** Full line: potential change ( $E$  vs. Ag/AgCl) during the galvanostatic polymerization of PMeT film onto ITO-PET;  $j = 3.75 \text{ mA cm}^{-2}$ ,  $[3\text{-MeT}] = 0.1 \text{ M}$ . Dashed line: in situ mass variation of the electrode during the electropolymerization of 3-MeT onto Pt under the same conditions mentioned above,  $Q \leq 300 \text{ mC cm}^{-2}$



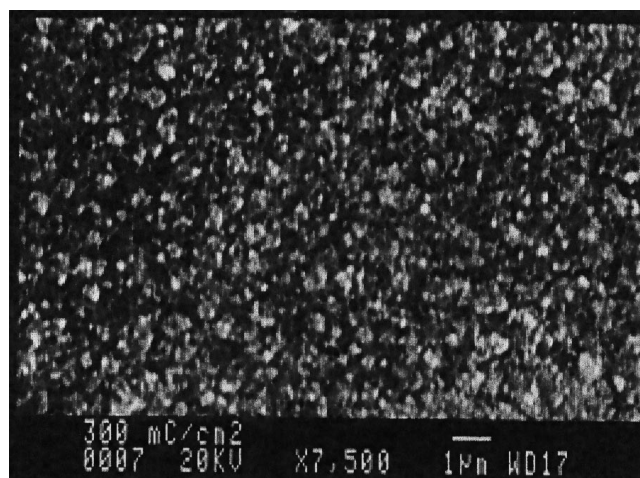
**Fig. 2** In situ variation of absorbance at  $\lambda = 750$  nm as a function of the time during the synthesis of PMeT. The *arrows* indicate the end of the synthesis and the charge density is given on the figure ( $\text{mC cm}^{-2}$ )

changes with a possible decrease in thicker films [20]. In Fig. 2 we can see a steep increase of absorbance within the first 30 s of synthesis (charge density  $Q = 112 \text{ mC cm}^{-2}$ ), which indicates a defined value of the conjugation length. At longer times it shows a slower variation, which is assigned to the decrease of polymer density. The changes of film morphology with thickness have been visualized with SEM (Fig. 3). When  $Q$  did not exceed  $100 \text{ mC cm}^{-2}$  (measured thickness  $\tau \cong 0.2 \mu\text{m}$ ), the polymer films show a quite homogeneous and compact surface, characterized by the presence of small globules (Fig. 3a). Above this limit, PMeT films showed a lower density with the increase of globule size ( $Q = 300 \text{ mC cm}^{-2}$ , measured thickness  $\tau \cong 0.7 \mu\text{m}$ , Fig. 3b). Yassar et al. [19] showed that the progress of the electropolymerization produced an analogous morphological variation, resulting in a steep decrease of polymer conductivity. The conductivity can reach values on the order of magnitude of  $2 \times 10^3 \text{ S cm}^{-1}$  if the polymer film is few nanometers thick [19]. The progress of the polymerization can involve cross-linking between different chains and  $\alpha$ - $\beta$  coupling, which noticeably modify the mean conjugation length in PMeT. Santos and Brédas [17] have presented a detailed theoretical investigation about the role of  $\alpha$ - $\beta$  bonds on the electronic structure and conjugation length of polythiophene chains.

STM and AFM studies showed that polymer islands are formed at preferential locations on the electrode surface; then nuclei grow in three dimensions, with resulting overlap [6, 11]. The role of the substrate on PMeT film morphology and roughness was studied with AFM. ITO-PET presents a rough surface and p-Si a smoother surface. We synthesized a thin film (measured thickness  $\tau \cong 0.1 \mu\text{m}$ ) on these substrates and observed that the film surfaces were similar (Fig. 4) and with comparable roughness values (60 nm for ITO-PET substrate and 65 nm for p-Si substrate). These results show that PMeT growth does not strictly depend on the substrate. Moreover, PMeT films with measured thickness  $\tau \cong 0.1 \mu\text{m}$  possess a surface with porous features



(a)



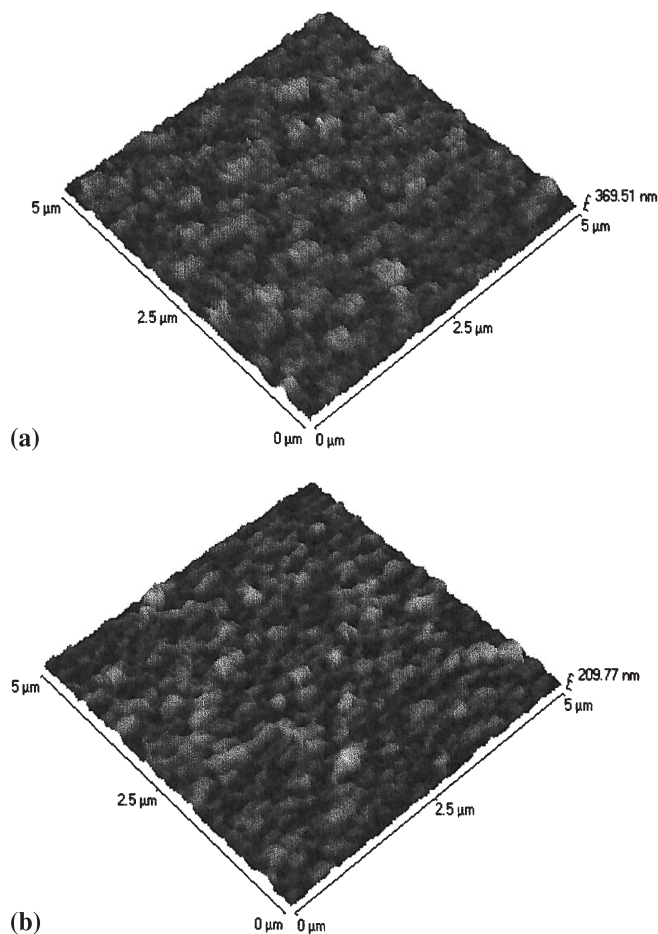
(b)

**Fig. 3** Scanning electron micrographs of PMeT films prepared with different charge densities: **a**  $50 \text{ mC cm}^{-2}$ ; **b**  $300 \text{ mC cm}^{-2}$ . Substrate: ITO-PET. Magnification:  $7500\times$  (bar indicates  $1 \mu\text{m}$ )

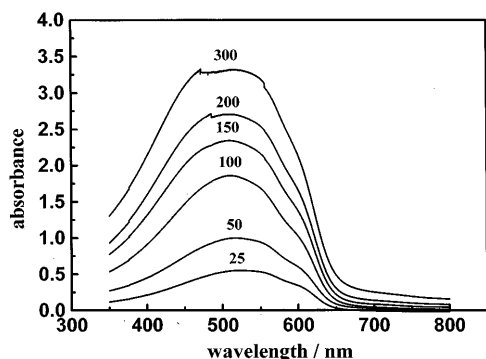
characterized by the presence of small globules. Some studies show also that electrode surface pretreatment, e.g. chemical treatment with sulfurated species, can make the grafting easier with a marked improvement of film uniformity [27]. The variation of polymer structure during the electropolymerization was characterized with absorption spectra taken at different PMeT deposition charges (Fig. 5). From these spectra we observe a shift of the absorption maximum toward lower wavelengths of ca. 10 nm (from 522 to 508 nm) with the charge density used in the polymerization. Such a tendency can be associated with the decrease of the mean conjugation length in the polymer film when the thickness increases. Yassar et al. [19] analyzed the variation of the electrochemical and spectroscopic properties of PMeT as a function of film thickness, showing that the anodic current peak shifts by ca. 100 mV toward less positive values whereas the absorption maximum shifts approximately 40 nm to longer wavelengths with the decrease

of thickness. This is a further confirmation of the more extended conjugation length in thinner PMeT films.

The full line in Fig. 6 shows the variation of the energy corresponding to the absorption maximum,  $E_{\max}$ , at various PMeT film thicknesses. The largest shift of  $E_{\max}$  is reached when  $\tau \leq 0.2 \mu\text{m}$ . These results are



**Fig. 4a, b** Atomic force micrographs of PMeT ( $\tau = 0.1 \mu\text{m}$ ). Substrate: **a** ITO-PET; **b** p-Si (scanned area  $5 \times 5 \mu\text{m}$ )

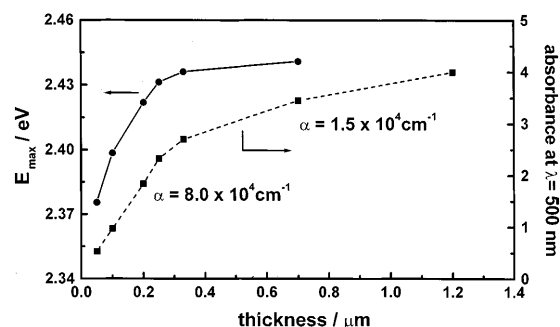


**Fig. 5** Absorption spectra of neutral PMeT films ( $E = -0.2 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ ); the films were deposited onto ITO-PET with  $j = 3.75 \text{ mA cm}^{-2}$  at different charge densities as indicated in the figure ( $\text{mC cm}^{-2}$ )

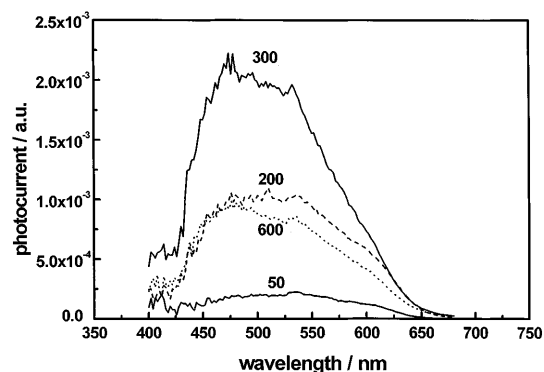
consistent with a more extended delocalization of the  $\pi$ -electrons in thinner films. Generally, the absorption coefficient,  $\alpha$ , increases with the conjugation length. We calculated  $\alpha$  as the slope of the curve of absorbance, at  $\lambda = 500 \text{ nm}$ , versus film thickness (dashed line in Fig. 6) from the spectra in Fig. 5. We noted that the highest value of  $\alpha$  is obtained for films prepared with  $Q \leq 150 \text{ mC cm}^{-2}$  (measured thickness  $\tau \cong 0.3 \mu\text{m}$ ,  $\alpha = 8.0 \times 10^4 \text{ cm}^{-1}$ ) and it indicates that the more effective conjugation is in thinner films. The latter value of  $\alpha$  is in good agreement with the literature [28]. The photocurrent spectra have been also measured for characterization of the conducting polymers electrodeposition. Figure 7 shows the photocurrent spectra of PMeT films at different values of deposition charge. The photocurrent spectra resemble the trend of the absorption spectra (Fig. 5). If  $Q > 300 \text{ mC cm}^{-2}$  we observe a decrease of photocurrent intensity. This result was ascribed to the onset of coupling reactions which depressed the charge transport. The photocurrent spectra showed also an analogous shift of  $\lambda_{\max}$  toward shorter wavelengths (from 520 to 480 nm) with the increasing of  $Q$ . This shift is higher than the corresponding shift in the absorption spectra because the photocurrent response is more sensitive to properties of the external layers and the photocurrent is generated at the polymer/electrolyte interface.

## Conclusions

We monitored the galvanostatic electropolymerization of 3-methylthiophene onto different substrates, e.g. ITO-PET, Pt and p-Si, with the in situ measurements of potential, mass and absorbance. We observed that the potential variation during electrodeposition could be associated with a nucleation process. QCM measurements showed that the amount of polymer deposited is linear with time whereas the absorbance shows an inflection, i.e. an alteration of curve slope after only 30 s of synthesis ( $j = 3.75 \text{ mA cm}^{-2}$ ). This change indicated the onset of a process limiting the effective conjugation



**Fig. 6** Full line: variation of  $E_{\max}$  for PMeT films as a function of thickness. Dashed line: variation of absorbance at  $\lambda = 500 \text{ nm}$  as a function of film thickness.  $\alpha$  indicates the absorption coefficient



**Fig. 7** Photocurrent spectra of PMeT films in the neutral state ( $E = -0.2$  V vs. Ag/AgCl). The films were deposited onto ITO-PET with  $j = 3.75$  mA cm<sup>-2</sup> at different charge densities as indicated in the figure (mC cm<sup>-2</sup>). Curves were normalized with respect to the lamp spectrum

length. We also studied by SEM the surface morphology changes of PMeT films as a function of deposition charge. We observed modifications of morphology from a compact to a more open structure with the increase of PMeT thickness. The progress of the polymerization could involve defects such as cross-linking and  $\alpha$ - $\beta$  coupling. These structural defects modify the mean conjugation length of the PMeT chains. AFM showed that PMeT film roughness did not depend on the nature of the substrate. Absorption and photocurrent spectra of PMeT showed a shift of the peaks toward lower wavelengths when the PMeT film thickness increased. Moreover, the absorption coefficient was larger for thinner films. These results are consistent with a decrease of the mean conjugation length when the polymer film thickness increases. The decrease of the photocurrent with PMeT film thickness above  $0.7$   $\mu$ m (measured thickness) is probably due to the occurrence of reactions blocking the extension of the electronic conjugation. Therefore, thin films of PMeT (measured thickness  $\tau < 0.2$   $\mu$ m) have a longer mean conjugation length due to a lower number of defects at the beginning of the polymerization process. In these conditions, PMeT showed a more homogeneous morphology.

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