

ELLIPSOMETRIC STUDIES OF POLY-3-METHYLTHIOPHENE FILMS. DEPOSITION UNDER DIFFERENT CONDITIONS.

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The generation of conducting organic polymers is usually carried out by the anodic oxidation of suitable monomer species. Despite the number of studies devoted to electropolymerization the mechanism and the initiation of the process is still matter of controversy [1,2].

Studies on the properties of polymer films have shown the dependence on electrochemical deposition conditions [3,4] which can give rise to different morphologies and consequently affect the kinetics of potential switching.

In the present work we have used the ellipsometric technique to characterize and compare the growth of thin poly-3-methylthiophene films on Pt electrodes, by galvanostatic (G.) and potentiostatic (P.) methods. The properties of the deposits were examined subsequently by electrochemical measurements and the evolution of ellipsometric parameters, the phase, Δ and the azimuth, ψ .

Under the chosen conditions - 0.6 M 3-methylthiophene + 0.1M lithium perchlorate in acetonitrile - the evolution of the potential during G deposition ($i = 1 \text{ mA cm}^{-2}$; $Q_g = 50 \text{ mC cm}^{-2}$) presents a peak followed by a plateau as shown in figure 1a.

The lowest required potential to promote P. deposition was found to be of the order of magnitude of that peak, otherwise significant amount of oligomers will be formed in solution and a continuous film is not observed at the electrode surface. Therefore an imposed potential of 1.35 V vs SCE was used and figure 1b compares the rate of electropolymerization for films prepared under the same growing charge, $Q_g = 50 \text{ mC cm}^{-2}$.

The optical response delay, observed for both deposition methods, figure 2, reveals that an initial amount of charge ($\sim 2.5 \text{ mC cm}^{-2}$) is consumed in the formation of oligomers in the solution which agrees with previous report [4]. Also the evolution of the optical parameters during electropolymerization indicates the formation of two layered films.

As seen in figure 3, the transition between the first dense ordered layer and the subsequent polymer thickening is more abrupt when G is used. Due to the high rate of deposition, P is likely to produce films with defects and thus less compact.

Data analysis, figure 4, shows that the intrinsic complex dielectric constant is different for the two layers ; however for thick deposits the optical characteristics seem to be similar.

The penetration of doping ions is expected to be easier for polymers of low density and/or order. In fact the electroactivity (evaluated by the oxidation charge when the redox behaviour is followed by cyclic voltammetry) of PMeT prepared by P is 25% larger than when G is used.

Acknowledgements

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References

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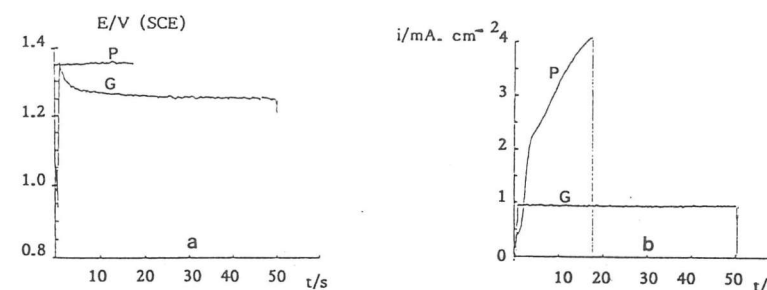


Fig.1 : Potential (a) and current (b) evolution during galvanostatic ($i_g = 1 \text{ mA cm}^{-2}$) and potentiostatic ($E_g = 1.35 \text{ V vs SCE}$) polymerization of methylthiophene. The figure also shows the correspondent values of applied potential and current.

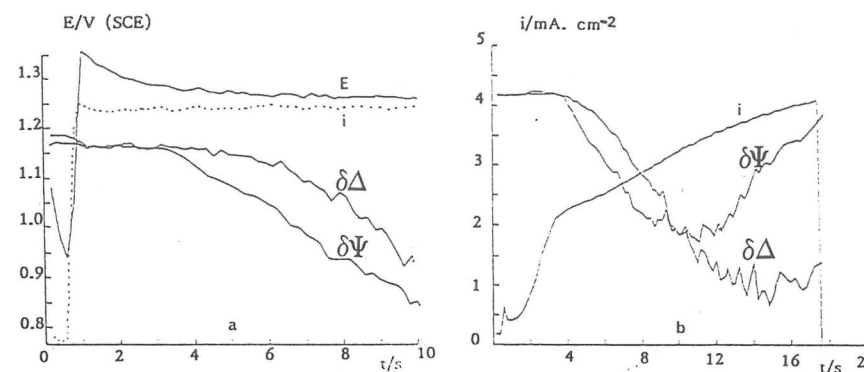


Fig.2 : Changes in Δ and Ψ measured at 725 nm during the first step of MeT polymerization at constant current (a) and constant potential (b).

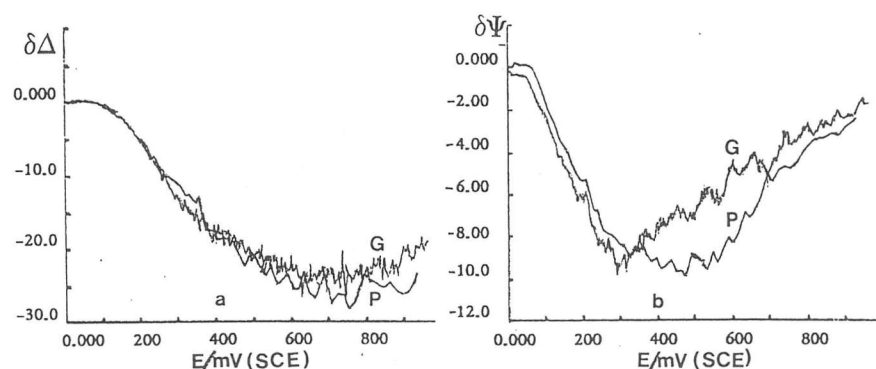


Fig.3 : Comparison of the ellipsometric data, delta (a) and psi (b) measured at 725 nm, during galvanostatic (G) and potentiostatic (P) PMeT growth.

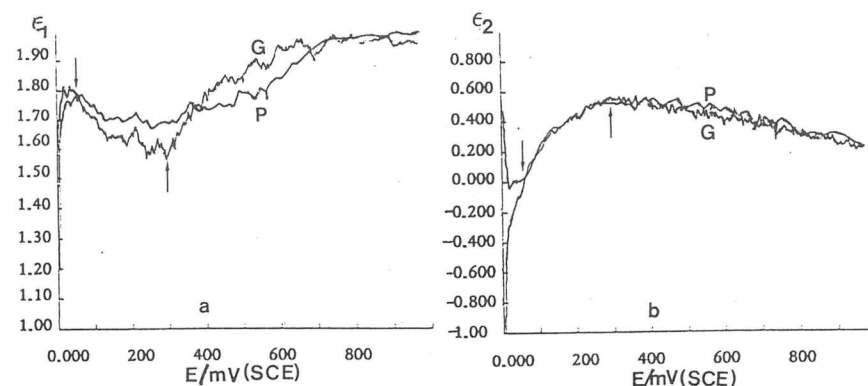


Fig.4 : Real (a) and imaginary (b) part of complex dielectric constant for PMeT (↓) denotes the start of first layer and (↑) the transition for a second layer formation.

THE ROLE OF THE "CHARGING CURRENT" IN THE ELECTROCHEMICAL BEHAVIOUR OF POLYPYRROLE

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In spite of the extensive research in the area of conducting polymers during the past few years, as a result of the interest in potential applications of these materials, the interpretation of some aspects of their electrochemical behaviour is still controversial [1].

In the electrochemical behaviour of different conducting polymers the appearance of current plateaus after the voltammetric peaks is characteristic and was attributed to a double layer charging [2]. The a.c. impedance is used as a technique to evaluate the nature of that current plateau [3], but the expected Warburg behaviour is not observed. As pointed out by Rubinstein *et al* [4], it is not possible to distinguish a non-faradaic double layer capacitance from a faradaic pseudo-capacitance on the basis of electrical measurements alone.

The relationship between electrical and optical a.c. response has been recently discussed [5,6] and the simultaneous analysis of the periodic electrical and optical response of PANI modified electrodes was shown to be related with Faradaic processes [6].

In the present study modulated transmittance was applied to characterize polypyrrole (PPy). Thin PPy films were electrosynthesized on optical transparent electrodes, ITO, from pyrrole in acetonitrile. A typical cyclic voltammogram is shown in figure 1-a) together with the optical absorbance change at 550 nm. The absorbance increase, even after the peak current, varies linearly