Electrochemical grafting of poly(methylthiophene) onto platinum in acetonitrile

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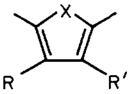
The first steps of the electropolymerization of methylthiophene on a platinum electrode have been analysed, using a differential ellipsometry technique. The results show that the first step is concerned with the formation of oligomers in solution which precipitate onto the electrode surface. The polymer chain growth follows by a coupling reaction to newly formed radical ions. Electrode surface pretreatment, either chemical or electrochemical confirmed the importance of the surface state of the electrode on the electrochemical and morphological properties of the polymer films.

(Keywords: electrochemical grafting; poly(methylthiophene); platinum; acetonitrile)

INTRODUCTION

In the last few years, the interest in electrochemically synthesized doped conducting polyheterocycles of the type



($X = N$, S, O, Se; R, $R' =$ alkyl, halogen, H) has been increasing in the theoretical field and in applications[1-3]. These polymers can be grafted onto weakly oxidizable metals (Pt, Au...) or semiconductors (Si, GaAs)[4] in various solvents (CH_3CN, $C_6H_5NO_2$). Among these polymers, polymethylthiophene (PMT), which has been shown to be chemically and electrochemically stable, appears to be one of the most interesting[5]. Its conductivity and electrochemical reversibility have been optimized by varying the synthesis conditions[6,7], especially the monomer concentration, the nature of the supporting electrolyte and solvents, the current density and the temperature. However, only a few studies[8-12] have been devoted to the first steps of the grafting of these aromatic polyheterocycles. In this paper, we will show, using *in-situ* differential ellipsometry and electrochemical techniques, that the first species generated at the electrode can be characterized. By electrochemical and chemical pretreatments of the platinum electrode, the influence of the electrode surface chemical state on the electrochemical properties of the films as well as on their homogeneity, uniformity and adherence will be demonstrated.

EXPERIMENTAL

The cell and platinum electrode used in the optical experiments have been previously described[12-14]. For purely electrochemical experiments, the glass compartment cell involves a platinum counter-electrode and a platinum (99.999%) electrode which is made of a wire melted at its end and then mechanically flattened out ($S = 0.1\ cm^2$). Before each experiment, the electrode is thermally treated in a gas-oxygen flame ($T > 600°C$), then immediately immersed in ultra-pure water ($18\ M\Omega.cm$)[15] and rinsed out with acetonitrile (Aldrich, HPLC: 99.9% used without any further purification) before being transferred into the cell. The electrode surface is then covered (40 to 50%) with thermally adsorbed oxygen.

The methyl-3-thiophene (Aldrich) is twice distilled, the anhydrous $LiClO_4$ (EGA) supporting salt is used without any further purification, but dried for 10h at 80°C. The supporting salt and monomer concentrations in acetonitrile are respectively 0.2 M and 0.6 M (except in experiments using a rotating disc electrode (see later)). In our conditions, the water concentration, titrated by the Karl–Fisher method, is $\sim 5.10^{-3}$ M. The reference electrode is a silver wire immersed in an $AgNO_3$ (0.1 M) solution, its potential being well defined and near +0.29 V/SCE.

We have correlated the electrochemical measurements with an *in situ* interface study technique namely ellipsometry with phase- and azimuth-modulation[16]. The method consists of measuring and interpreting the change in polarization state that occurs when a polarized monochromatic light beam is reflected at non-normal incidence from a sample surface. The intensity of the luminous flux through the phase (Δ) and azimuth (Ψ)-modulated ellipsometer, can be expressed by:

$$I = I_u(\alpha, \Delta, \Psi) + I_{\Omega 1}(\Delta) + I_{\Omega 2}(\Psi) + \dots$$

with:

$$I_u(\alpha, \Delta, \Psi) = I_{\text{unmodulated}} = I_0 \times g(\Delta, \Psi) 10^{-\alpha c d} \qquad (1)$$

where I_0 is the light flux intensity, $g(\Delta, \Psi)$ is an absorption characterizing function, α is the solution absorption coefficient, c is the concentration of absorbing species, d

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the optical path length of the light. The wavelength was $\lambda = 600$ nm.

The parameters Δ and Ψ, which are related to the constants of the film, can be derived from the dielectric currents $I_{\Omega 1}(\Delta)$ and $I_{\Omega 2}(\Psi)$[17].

FIRST STEPS IN POLYMETHYLTHIOPHENE ELECTROPOLYMERIZATION

There are two hypotheses concerning the first steps of the poly(methylthiophene) grafting. It seems to be accepted that, except in some very particular cases[12], the monomer is first oxidized to a radical cation[3,11]. According to a first hypothesis, after the adsorption of one of these two species at the electrode, growth occurs by the fixation of radical cations or oligomers[8]. According to a second hypothesis, the first step could involve a prepolymerization in solution, followed by a precipitation of oligomers[18]; in this case, it seems unlikely that the monomer or the radical cation would be adsorbed. In the following, results will be presented which argue strongly for the second hypothesis. Furthermore, it will be shown that the monomer is not adsorbed onto the metal surface in acetonitrile solution, in agreement with other experimental data[19,20].

Optical study of grafting

It has been observed that in all potential measurement programmes, a linear scan of the potential is followed by a plateau (*Figure1*) or potential step (*Figure 2*), an important delay exists between the optical signals and the electric current. In the first case (*Figure 1*, curve B) the monomer is significantly oxidized without any optical or electrochemical modification of the electrode (neither variation of Δ and Ψ nor of the curve $I = f(V)$ at the following cathodic sweep). Modifications appear only at a higher potential and for a much more important charge, indicating that a species arrived at and stuck to the electrode (*Figure 1*, curve C).

In the case of a potential step, the electric current first increases suddenly, then decreases, following a $t^{-1/2}$ law which corresponds to the diffusion-limited oxidation of the monomer. It has to be pointed out that optical signals appear only after the electric current reincreases (*Figure 2c*), showing the presence of species on the electrode.

Finally, the study of the oxidation current as a function of the sweep rate before any modification of the electrode (*Figure 3*) shows that the process is not

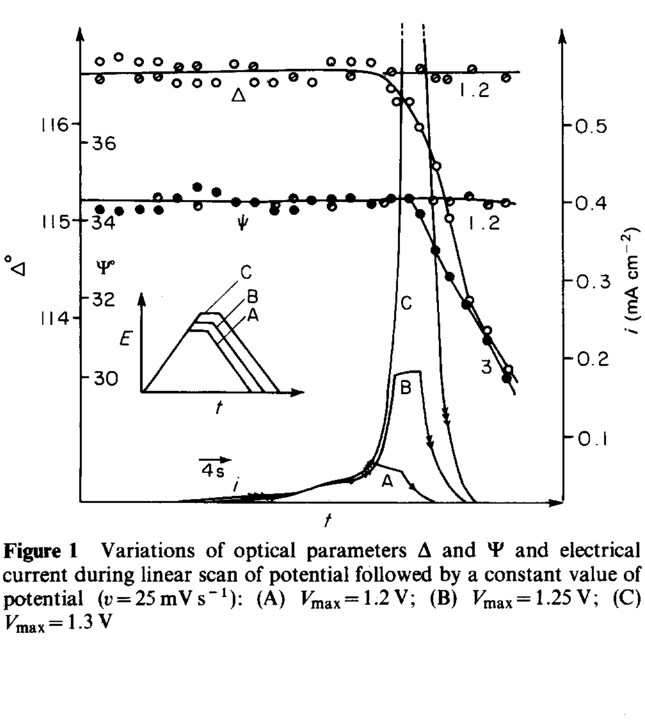


Figure 1 Variations of optical parameters Δ and Ψ and electrical current during linear scan of potential followed by a constant value of potential ($v = 25\,\mathrm{mV\,s^{-1}}$): (A) $V_{max} = 1.2$ V; (B) $V_{max} = 1.25$ V; (C) $V_{max} = 1.3$ V

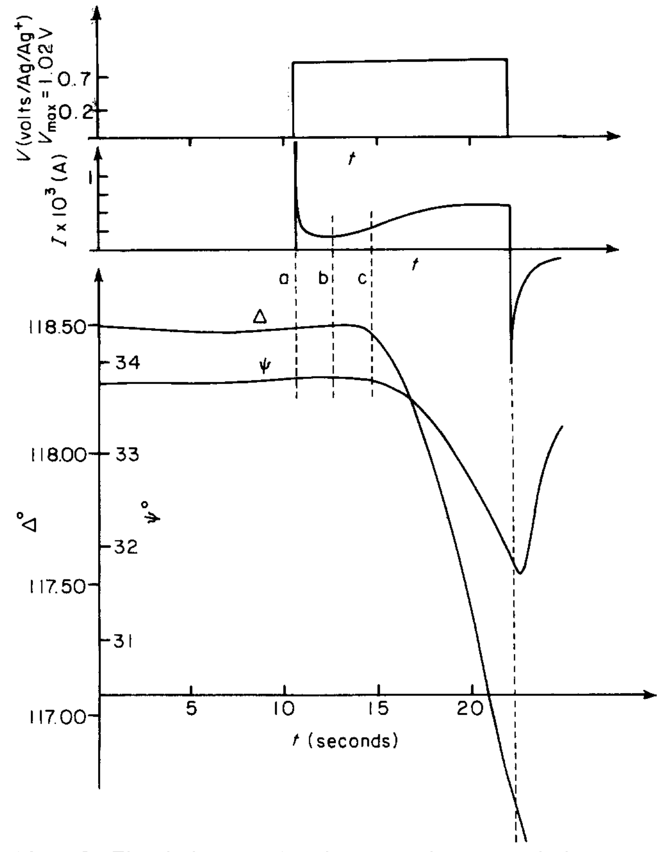


Figure 2 Electrical current Δ and Ψ *versus* time curves during a step potential with a maximum value sufficiently low, $V_{max} = 1.08$ V/Ag/Ag$^+$

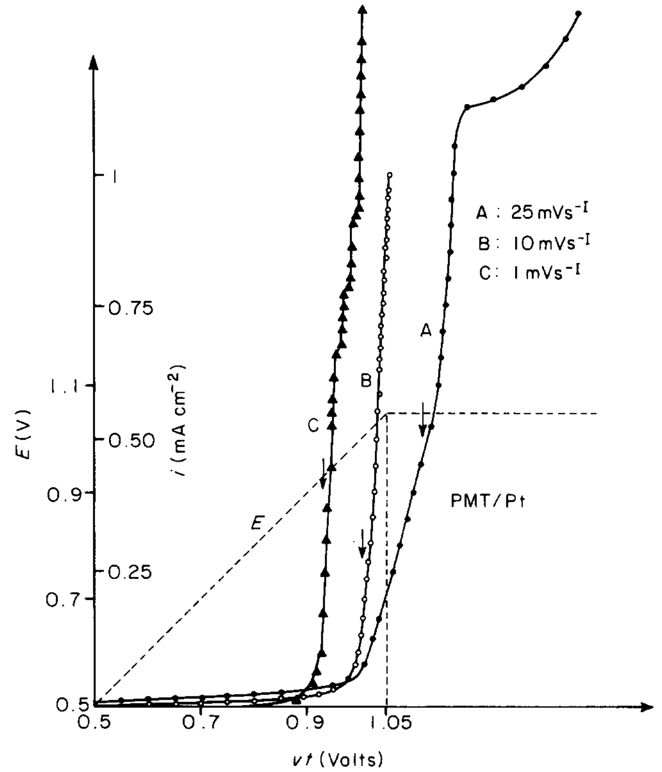


Figure 3 Rôle of scan rate on the current during grafting by linear scan of potential (arrows indicate the start of optical signals i.e. the adhering of species at the electrode)

thermodynamically controlled: the intensity increases as the rate decreases for a given potential.

These observations clearly show that a preliminary step takes place in solution prior to the grafting. In fact, the coupling of monomeric radical cations generates oligomers in solution, which possess a lower oxidation potential than the monomer and bring a limit to the overall process kinetically. From the number of coulombs used before the onset of the optical signals, the minimum length of the oligomers can be estimated[12] to be 3 or 4 methylthiophene rings.

Furthermore, it has been observed that during a very slow rate potential scan (*Figure 4*), the differences between the onset of the optical density of the solution and the grafting of species onto the electrode (indicated by the sudden increase of the signals Δ and Ψ; see arrow A in *Figure 4*) could be large. The mean absorption coefficient per exchanged electron just before the grafting was evaluated to $\alpha/n_e = 6.3\ 10^5\ \mathrm{cm^2\ mole^{-1}}$. Consequently the massive absorption coefficient of the species should be $\alpha_s = 0.65 \times 10^5\ \mathrm{cm^{-1}}$, assuming an identical density to the polymer. This value has to be compared with that of the film itself ($\alpha_s = 10^5\ \mathrm{cm^{-1}}$)[21]. The optical density of the solution increases after the grafting which indicates that the growth proceeds through oligomer fixation as previously suggested in ref. 22.

Study of grafting using rotating disc electrode

In order to confirm the proposed mechanism and to characterize the oligomers present in the solution, we have used a rotating disc electrode (RDE) in a 0.2 M monomer solution. The electrode is a platinum disc which can rotate at various controlled angular rates. The convection induced by electrode rotation provides a stationary distribution of electroactive species[23]. For rotation rates decreasing from 8100 rpm to 260 rpm, the electrode was submitted to a cycle of linear potential sweep, the positive potential limit being 1.1 V vs. Ag/Ag$^+$. After each cycle at a given sweep rate, a voltammogram between 0.7 V and −0.40 V at 50 mV s^{-1} was recorded to analyse the presence of grafted species on the surface electrode. The grafting only begins at rotation rates of 2900 rpm. In this case the grafted film does not coat the whole electrode surface but preferentially its centre. Moreover, the spiral shape of this coating shows that it follows the lines of the hydrodynamic field of the fluid (*Figure 5*). The centre of the electrode is indeed known to be the less perturbated zone. On the other hand, if we assume that the first step concerns the absorption of the radical cation, the film would then uniformly cover the electrode since the radical cation concentration does not depend on the distance to the centre (steady state). Thus the results confirm the existence of kinetically limiting chemical reactions in the solution preliminary to the grafting itself.

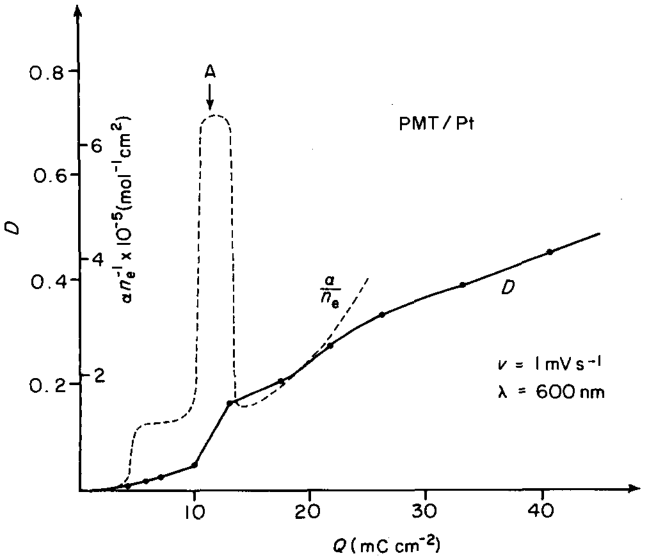
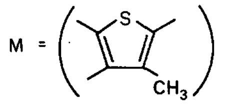


Figure 4 Variation of optical density and mean absorption coefficient per electron exchanged $\bar{\alpha}/n_e$ of oligomers in the solution *versus* electrical charge (linear scan of potential at 1 mV s^{-1})

Figure 5 Micrograph showing spiral shaped coating of grafted film onto rotating disc electrode at 7500 rpm

The proposed mechanism would then involve, as a first step in solution, a succession of electrochemical and chemical reactions $E(\mathrm{CE})_n$ (or $E(\mathrm{EC})_n$):



Initiation

$$\mathrm{MH_2} \xrightarrow{E_1} \mathrm{MH_2^{\cdot+}} \rightleftarrows \mathrm{MH^{\cdot}}$$

Propagation

$$\mathrm{MH_2} + \mathrm{MH^{\cdot}} \rightarrow \mathrm{M_2H_3^{\cdot+}}$$

$$\mathrm{M_2H_3^{\cdot+}} \xrightarrow{E_2} \mathrm{M_2H_3^{+}} \rightleftarrows \mathrm{M_2H_2} + \mathrm{H^+}$$

$$\mathrm{M_pH_2} + \mathrm{MH^{\cdot}} \rightarrow \mathrm{M_{p+1}H_3^{\cdot+}}$$

$$\mathrm{M_{p+1}H_3^{\cdot+}} \xrightarrow{E_P} \mathrm{M_{p+1}H_3^{+}} \rightleftarrows \mathrm{M_{p+1}H_2} + \mathrm{H^+}$$

with $E_1 > E_2 > E_P > E_n$.

At a critical chain length (⩾3–4 methylthiophene rings), insoluble oligomers are formed, which precipitate on the electrode surface, being held either by a physical or a chemical interaction. In order to reach a better understanding of this electrode surface/polymer interface, we have analysed the role of the electrode state.

ROLE OF THE ELECTRODE STATE

As previously indicated, no surface reaction was detected before the oligomers become attached to the electrode. In fact, the addition of monomer does not modify the optical spectrum[12,20] of the electrode; in the same way, the solvated monomer is not chemisorbed on platinum[19]. Finally the chemical state of the electrode just before grafting is not well defined, owing to the already known reactivity of platinum. This is one of the main reasons why the electrodeposition of the polymer at a low potential initiates from preferential sites of the electrode (due to some different crystallographic orientations or chemical states), leading to non-uniformly coated electrodes. Some authors have described the process as 'nucleation growth'[8–10]. Thus, in order to better understand the real influence of the chemical state of the electrode on the grafting and on the film properties, we have carried out various electrochemical and chemical pretreatments. We then tried to graft films, using a fast linear scan potential ($v = 200\,\mathrm{mV\,s^{-1}}$) followed by constant low potential (1.038 V/Ag/Ag^+). These conditions allow better observation of the differences in the electrochemical behaviour of the pretreated electrodes. Through optical observations, it was possible to study directly the processes in solution and at the electrode.

In order to measure the influence of the pretreatments, the surface state of thermally treated platinum (see experimental) was chosen as a reference (*Figure 7a*). The coverage was evaluated visually by the covered area of the electrode and also by the intensity of the reduction in current of H_2O at −1.44 V/Ag/Ag^+. The influence of crystalline orientation has already been discussed[12b,20]: the coverage with adsorbed oxygen, varying with the crystallographic planes could influence the kinetics.

Electrochemical pretreatments

The surface reactions induced by cyclic voltammetry with increasing potential ranges, with or without monomer in the solution, were followed electrochemically and optically (*Figures 6* and *7*). A reduction in oxygen thermally adsorbed at −1 V/Ag/Ag^+ slightly modifies the grafting curves (*Figure 7*). During a cycle between 0.7 V and −1 V (pretreatment 1) with or without monomer in the solution, no reaction is observed either electrochemically or optically. The adsorption–desorption reaction of oxygen (or OH^-) does not occur, although it could have been expected in this potential range. The grafting conditions (*Figure 7c*) are nearly the same as with the two previously mentioned pretreatments (*Figure 7a, b*). However the film is less uniform (*Table 1*).

After a more cathodic potential (−1.44 V/Ag/Ag^+) is applied (*Figure 7d*) the anodic current increases indicating the vicinity of the grafting onset (see previous section on 'Optical study of grafting' and *Figure 2*). The films only then covers about 10% of the electrode in the region of the solution–inert gas interface (*Table 1*).

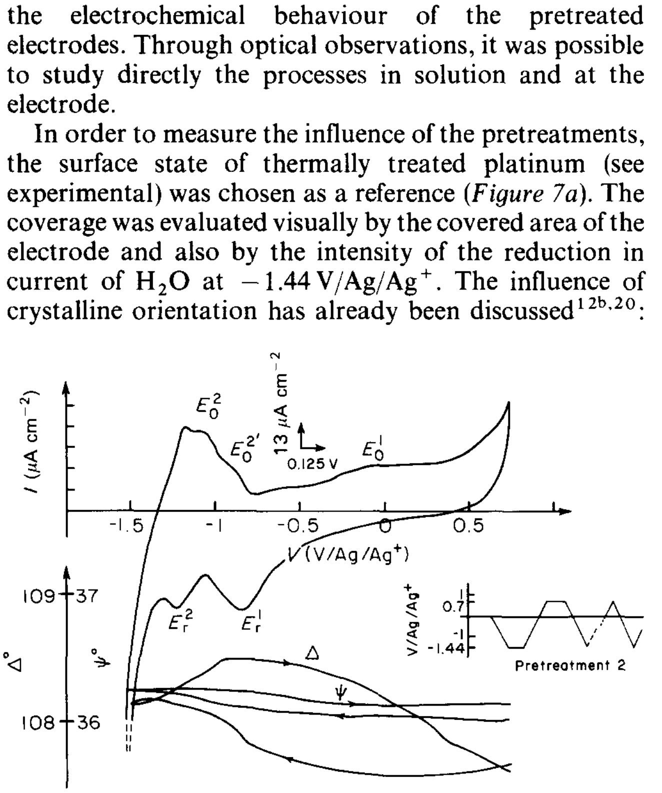


Figure 6 Electrochemical current and optical parameters Δ and Ψ *versus* potential of a platinum electrode in CH_3CN, $LiClO_4$ 0.2 M after pretreatment 2 ($v = 20\,\mathrm{mV\,s^{-1}}$)

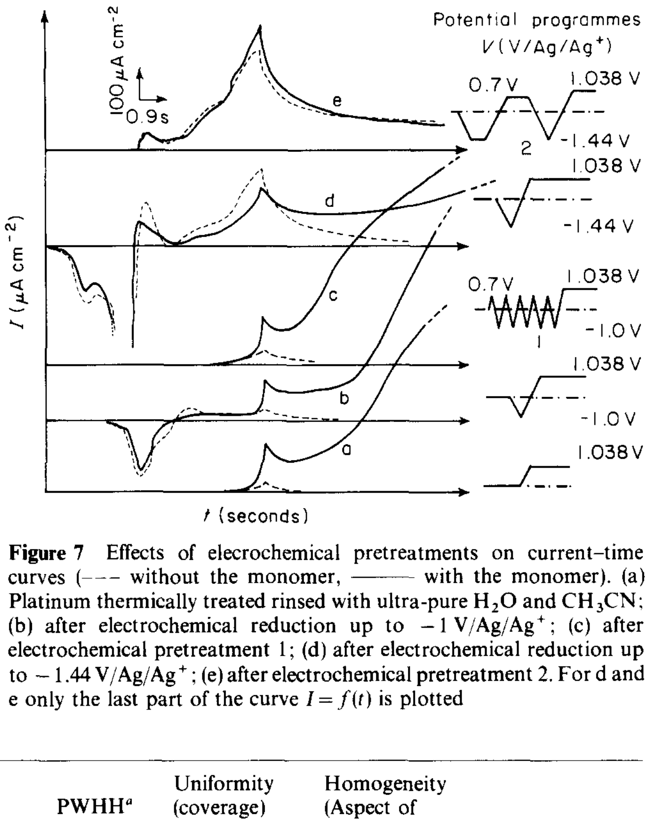


Figure 7 Effects of elecrochemical pretreatments on current–time curves (--- without the monomer, ——— with the monomer). (a) Platinum thermically treated rinsed with ultra-pure H_2O and CH_3CN; (b) after electrochemical reduction up to −1 V/Ag/Ag^+; (c) after electrochemical pretreatment 1; (d) after electrochemical reduction up to −1.44 V/Ag/Ag^+; (e) after electrochemical pretreatment 2. For d and e only the last part of the curve $I = f(t)$ is plotted

Table 1

$v = 20\,\mathrm{mV\,s^{-1}}$; $d \approx 100$ Å Treatments and figures $V_{\mathrm{grafting}} = 1.038$ V/Ag/Ag^+	$E_{pa}{}^a$ (mV/Ag/Ag^+)	$E_{pc}{}^a$ (mV/Ag/Ag^+)	$E_{pa} - E_{pc}{}^a$	PWHH^a (mV)	Uniformity (coverage) (%)	Homogeneity (Aspect of the film)	Reproducibility
PtO thermal *Figure 7a*	235	295	−60	230	70	Good	Medium
Reduction of PtO thermal *Figure 7b*	235	285	−50	234	70	Good	Good
After cycling 0.7 V to −1 V *Figure 7c*	245	295	−50	230	50	Good	Excellent
After reduction to −1.44 V *Figure 7d*	260	290	−30	270	10	Medium	Good
After pretreatment 2 *Figure 7e*			no film grafted				Good

[a] 2nd cycle after waiting one minute at −0.4 V/Ag/Ag^+

At a constant cathodic potential of -1.44 V (1 to 2 min), followed by an anodic holding at $+0.7$ V (*Figure 2a*), the optical and electrochemical characteristics (*Figure 6*) show that surface reactions occur between these limits: oxygen adsorption ($E_O^1 = -0.15$ V) and desorption ($E_R^1 = -0.9$ V) (*Figure 6*).

The second adsorption–desorption process ($E_R^2 = -1.25$ V, $E_O^2 = -1.05$ V, $E_O^{2\prime} = -0.9$ V) could be caused by a species derived from water (PtH or an aqueous complex with lithium or with the solvent) but which does not give any significant optical signal at 600 nm. Moreover, the reduction of water at -1.44 V (cyclic voltammetry), causes a kinetically important delayed surface process, as observed near -1 V during the anodic sweep. When holding the potential at -1.44 V, this process occurs after about 30 s. The addition of monomer does not modify the stationary curves I, Δ, $\Psi = f(V)$. Neither in this case is the solvated methylthiophene adsorbed. A small amount of monomer is oxidized during the sweep at 1.038 V and the intensity decreases continuously when the potential reaches this constant value. No polymer film is detected electrochemically by a voltammogram between -0.4 V and $+0.7$ V, but the formation of an oxide can be observed in the negative sweep near -0.9 V.

It may be concluded that in all cases, the addition of the monomer weakly modifies the voltammogram inferring that the monomer is not chemisorbed in the platinum surface. On the other hand, between 0.7 V and -1 V, no oxygen (or OH^-) adsorption is observed on the platinum electrode. The solvent (or maybe impurities) prevents water from reaching the metal surface. In a larger range of potential (potential programme 2 in *Figure 7*), the surface state is chemically modified allowing adsorption and desorption of oxygen (or OH^-) to be observed. The presence of electrochemically adsorbed oxygen makes the grafting more difficult, if not impossible; when films are produced, they are inhomogeneous, non-uniform and poorly adhesive.

Chemical pretreatments

Numerous electrochemical[24] and gas phase[25,26] experiments have shown that sulphur and its derivatives can be strongly adsorbed on platinum, hindering for example catalytic reactions[27]. In the same way, methylthiophene adsorbed on platinum in the vapour phase reduces thermally adsorbed oxygen, hinders hydrogen adsorption and partially hinders oxygen adsorption[19].

Therefore we tried, by reproducing such treatments with CH_3T and H_2S, to graft PMT under the same electrochemical conditions as discussed in the previous section. For CH_3T, after thermal treatment, the electrode is placed, either immediately or after having been covered with ultra-pure water, in methylthiophene vapour ($P =$ 1 atm, $20°C \leq T \leq 150°C$). The electrode is then rinsed with acetonitrile and is then placed into the solution. As in the aqueous medium, the electrode is inactive for the reduction of water near -1.44 V or its oxidation near 0.9 V. After addition of the monomer, the grafting occurs at a lower potential (*Figures 8* and *9*) and the film homogeneously covers the whole electrode (*Table 2*). In the same way, after thermal treatment, the electrode remains in an saturated aqueous H_2S solution for a few seconds, is then rinsed with water and CH_3CN and immersed in the solution. In this case, the electrode is less blocked for the water reactions than with methylthiophene and with the monomer in the solution, the grafting is also appreciably enhanced (*Figures 8* and *9*). As with CH_3T, the electrochemical properties of the films are improved (*Table 2*) as are their uniformity and homogeneity. For a comparison, *Figure 8* presents the grafting characteristics on a platinum electrode cleaned in boiling H_2SO_4 50%, then rinsed with boiling ultra-pure water and air dried. From the optical curves $I_u = f(V)$ (*Figure 9*), we first observe that when the electrodes are pretreated with H_2S or CH_3T, the solution absorbs long

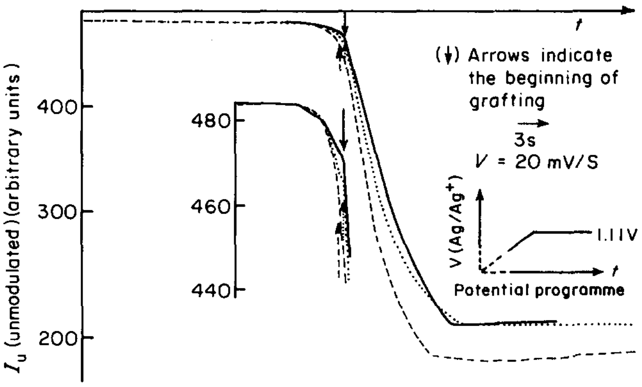


Figure 8 Variations of optical unmodulated signal during linear scan of potential following by a plateau with different chemical pretreatments: (——) thermal adsorbed oxygen; (---) H_2S pretreatment; (····) CH_3T pretreatment

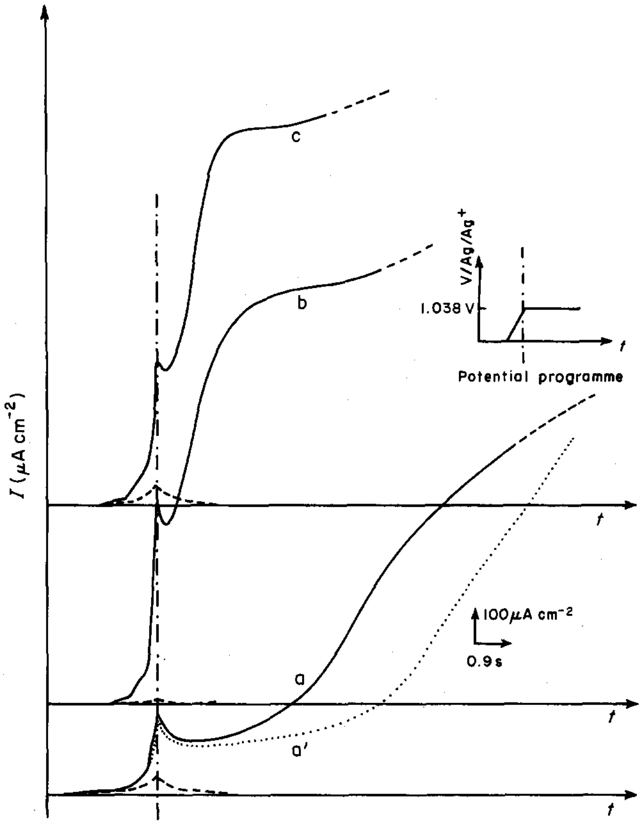


Figure 9 Growth of film (current–time curves) of PMT on pretreated electrodes: (---) without monomer; (——) with monomer. (a) Platinum recovered with thermal adsorbed oxygen (rinsed with H_2O ultra-pure and CH_3CN); (a') 'Usual' platinum boiled in concentrated sulphuric acid, rinsed with UP H_2O, and air dried; (b) platinum treated with methylthiophene vapour ($t = 30°C$; $p = 1$ atmosphere); (c) platinum treated with H_2S (aqueous saturated solution)

Table 2

$v=20\,ms^{-1}$; $d\approx 100$ Å Treatments and figures $V_{grafting}=1.038/Ag/Ag^+$	$E_{pci}{}^a$ (mV/Ag/Ag$^+$)	$E_{pv}{}^a$ (mV/Ag/Ag$^+$)	$E_{pa}-E_{pc}{}^a$ (mV)	PWHH^a (mV)	Uniformity (coverage) (%)	Homogeneity (Aspects of the film)	Reproducibility
PtO thermal *Figure 9a*	235	295	−60	230	70	Medium	Medium
Figure 9a′ Pt partially contamined	245	295	−40	235	15	Bad	Bad
Figure 9b CH_3T treatment	225	310	−85	226	100	Excellent	Good
Figure 9c H_2S treatment	215	310	−95	216	100	Excellent	Good

[a] 2nd cycle after waiting one minute at −0.40 V/Ag/Ag$^+$

before the beginning of the variations of the optical signals Δ and Ψ, and also that the growth of the films occurs earlier.

The optical density (*Figure 10*) of the solution, calculated from I_u, first increases, then becomes steady in the zone where the first species adheres and then finally increases again.

We can conclude that chemical treatments with sulphurated species make the grafting easier and markedly improve the uniformity and homogeneity of the films. In the gaseous phase, methylthiophene in contact with platinum is certainly at least partially decomposed where sulphur is bound to some carbons $[S(C)_nH_P, n\leq 5]$ or where monoatomic sulphur and carbonated residues are present[28]. With H_2S pretreatment, monoatomic sulphur certainly covers the whole electrode. Thus the fundamental role of the surface chemical homogeneity on the quality of the grafted film is demonstrated: in these conditions, the nucleation growth model is not valid. For all treatments, the shape of the *I versus t* curve for a potential step can be assigned to the synthesis of oligomers near the electrode surface.

In conclusion, we have shown that, with or without chemical treatment, the first step of this electropolymerization reaction starts with prepolymerization in solution leading to oligomers. These oligomers then precipitate or chemically interact with the electrode surface. Finally the growth of the polymer film proceeds by the subsequent grafting of radical ions. Whereas electrochemical treatments hinder the grafting process, chemical treatments with H_2S or methylthiophene catalyse the electrodeposition and improve the electrochemical characteristics, and homogeneity of the polymer film.

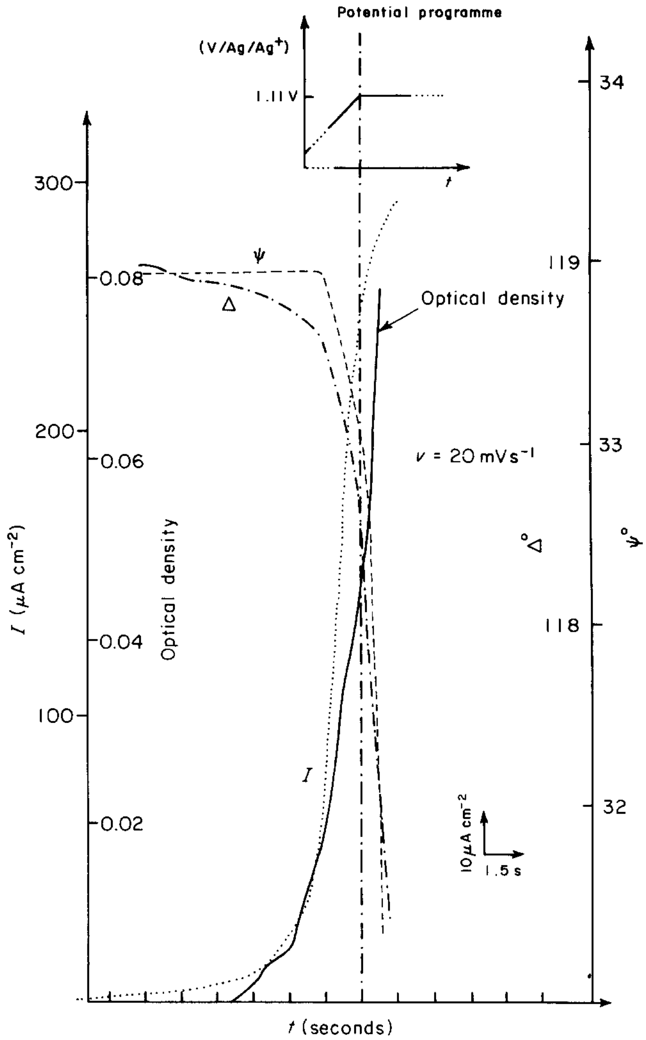


Figure 10 Optial density (———) of the solution, optical parameters Ψ (- - - - -) and Δ (— · —), and electrical current (· · · · ·) *versus* time with a H_2S pretreated electrode

REFERENCES

1 Diaz, A. F., Kanazawa, K. K. and Gordini, G. P. *J. Chem. Soc. Chem. Comm.* 1979, 645

2 Tourillon, G. and Garnier, F. *J. Electroanal. Chem.* 1982, **135**, 173

3 Diaz, A. F. and Baryon, J. 'Handbook of Conducting Polymers', (Ed. T. Skotheim), Marcel Dekker, 1986, pp. 81–116

4 Noufi, R., Frank, A. S. and Nozik, A. J. *JACS* 1981, **103**, 1849; Skotheim, T., Frank, A. S. and Piezza, J. *J. Electrochem. Soc.* 1981, **128**, 1625

5 Tourillon, G. 'Handbook of Conducting Polymers', (Ed. T. Skotheim), Marcel Dekker, 1986, p. 293

6 Roncali, J. and Garnier, F. submitted

7 Kaneto, K., Kohno, Y., Yoshino, K. and Inuishi, Y. *J. Chem. Soc. Chem. Comm.* 1983, 382

8 Asavapiriyanont, L. S., Chandler, G. K., Gunawardena, G. A. and Pletcher, D. *J. Electroanal. Chem.* 1984, **177**, 229

9 Genies, E. M., Bidan, G. and Diaz, A. F. *J. Electroanal. Chem.* 1983, **149**, 101

10 Chandler, G. R. and Pletcher, D. 'Special Reports Electrochemistry', *Roy. Soc. Chem.* 1985, **10**, 117; Downard, A. S. and Pletcher, D. *J. Electronal. Chem.* 1986, **206**, 139 and 147

11 Prejza, J., Lundstrom, I. and Skotheim, T. *J. Electrochem. Soc.* 1982, **129**, 1685

12 (a) Chao, F., Costa, M., Lang, P., Lheritier, E., Garnier, F. and Tourillon, G. *Ann. Phys., Colloque Suppl.* 1986, **11**, 21; (b) Chao, F., Costa, M., Lang, P., Lheritier, E. and Garnier, F. Communication at the 'Journées d'Electrochimie 1985', Florence, Italy, 18–31 May, 1985

13 Chao, F., Costa, M. and Lang, P. Proceedings of the International Conference 'Electrodynamics and Avantum Phenomena at Interfaces', Telavi, USSR, 1984

14 Chao, F., Costa, M. and Lang, P. ISE 35th Meeting, Berkeley, USA, 1984

15 Clavilier, J., Faure, R., Guinet, G. and Durand, R. *J. Electroanal. Chem.* 1980, **107**, 205

16 Chao, F. and Costa, M. *J. Chem. Phys.* 1981, **78**, 411

17 Chao, F. and Costa, M. *Surf. Sci.* 1983, **135**, 497

18 Wegner, G. *Angew. Chem. Int. Ed. Eng.* 1981, **20**, 361

19 Lang, P., Clavilier, J. and Garnier, F. to be published

20 Lang, P., Chao, F., Costa, M., Lheritier, E. and Garnier, F. *Nouv. J. Phys.* to be published

21 Tourillon, G. and Garnier, F. *J. Electrochem. Soc.* 1983, **130**, 2043

22 Roncali, J., Lemaire, M., Garreau, R. and Garnier, F. submitted

23 Bard, A. J. and Faulkner, L. R. 'Electrochemical Methods. Fundamentals and Applications', John Wiley & Sons, Inc. Publishers, 1980

24 Protopopoff, E., Marcus, P. and Oudar, J. *C.R. Acad. Sci. Paris* 1984, t.298, Sèrie II, n°5

25 Berthier, Y., Oudar, J. and Huber, M. *Surf. Sci.* 1977, **65**, 361

26 Biley, J. and Abon, M. *Surf. Sci.* 1984, **146**, 525

27 Grillith and Marsh, 'Contact Catalysis', 3rd Edn, Oxford University Press, p. 199

28 Stohr, J., Gland, J. L., Kollin, E. B., Koestner, R. J., Allen, J., Johnson, Muetterties, E. L. and Sette, F. *Phys. Rev. Lett.* 1984, **53**, 2161