

Electrochemical generation of polythiophene films on platinum electrodes

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The formation and growth of polythiophene films on platinum electrodes has been undertaken using cyclic voltammetry, a square-wave potential and polarization at constant potential. A nucleation process promotes the formation of a polymer layer. The growth of the polymer layer initially causes an increase in the total conductivity of the polymer in spite of the continuous decrease in ionic conductivity necessary to retain film electroneutrality. At high polymer thickness, the lower ionic conductivity and the chemical activity loss of the film cause a drop in conductivity.

(Keywords: electropolymerization; polythiophene; cyclic voltammetry; square waves; constant potential)

INTRODUCTION

Great effort is being devoted to the electrochemical synthesis and study of conducting polymer films such as polypyrrole, polyanilines, polythiophene, polyfuran, etc.¹⁻²¹. Such heterocyclic polymers can, among other things, be electrochemically oxidized and reduced. This process needs counterion diffusion from the electrolyte (the film has electronic and ionic conductivity) to retain electroneutrality. Oxidation and reduction processes are accompanied by changes in properties: for example, change the conductivity and the colour shown by the polymer film also changes, which is interesting from the viewpoints of electronic and display device applications as well as electrical energy storage²²⁻²⁵.

We present here a study of polythiophene generation using different electrochemical methods.

EXPERIMENTAL

Polythiophene films were electrogenerated on platinum electrodes from 0.1 M thiophene (Merck, G.A.) and 0.1 M LiClO₄ (Janssen) acetonitrile solution. The monomer and the solvent were purified prior to use by distillation under vacuum. The electrolyte was dehydrated in an oven at 60°C. A platinum sheet (several square centimetres surface area) was employed as counterelectrode. All the potentials are referred to the saturated calomel electrode (SCE) (Crison Instruments).

A one-compartment cell (Metromm) was employed. Electrical contact between the working and reference electrodes was guaranteed by a bridge of 0.1 M LiClO₄ acetonitrile solution in a Luggin capillary. In this way, the second vessel, containing the calomel electrode, hinders the Cl⁻ and water contamination of the electrochemical cell.

The solution was deaerated by bubbling nitrogen for 10 min; after this an inert atmosphere was assured by nitrogen flowing over the solution. All the experiments were made at ambient temperature.

The electrochemical methods employed were as follows: polarization at constant potential, cyclic

voltammetry and consecutive potential steps (square waves). These were obtained from three experimental set-ups:

(a) FHI-6050-15 Potentio-Galvanoscan (Heka-Electronic) with a PL4 JJ Lloyd Inst. recorder.

(b) Electrochemical interface 1286 (Solartron), connected to an HP 7470A plotter.

(c) Wenking ST-72 potentiostat connected to a Tacussel signals generator with a PL4 JJ Lloyd Inst. recorder.

RESULTS

A platinum electrode (1 cm²) was subjected to consecutive potential sweeps (-500 + 1700 mV vs. SCE) in 0.1 M thiophene plus 0.1 M LiClO₄ acetonitrile medium at a sweep rate of 50 mV s⁻¹ at ambient temperature. The consecutive voltammograms obtained are shown in *Figure 1*. On the first anodic excursion, no significant differences exist between the current density potential obtained in the presence of monomer and in the background electrolyte (in the absence of monomer) (*Figure 2*). At 1400 mV a rapid increase of the current density takes place when the voltammograms were obtained from the monomer solution (*Figure 1*) as well as from the background electrolyte (*Figure 2*).

Cathodic excursion of the potential gives a voltammogram with more anodic current densities (in the +1700 to +1350 mV region) than that obtained for anodic excursion. The formation of this loop is a characteristic of nucleation processes, and only appears on the first voltammogram. At the same time, a blue compound is formed on the platinum electrode, which is related to the formation of a thin layer of polythiophene¹¹.

In the region between 1200 and 0 mV during the cathodic potential sweep, reduction of the conducting polymer layer takes place. Related to this reduction process, a colour change occurs, showing a red colour on the electrode surface. Polymer oxidation takes place in the same potential region in the second anodic excursion,

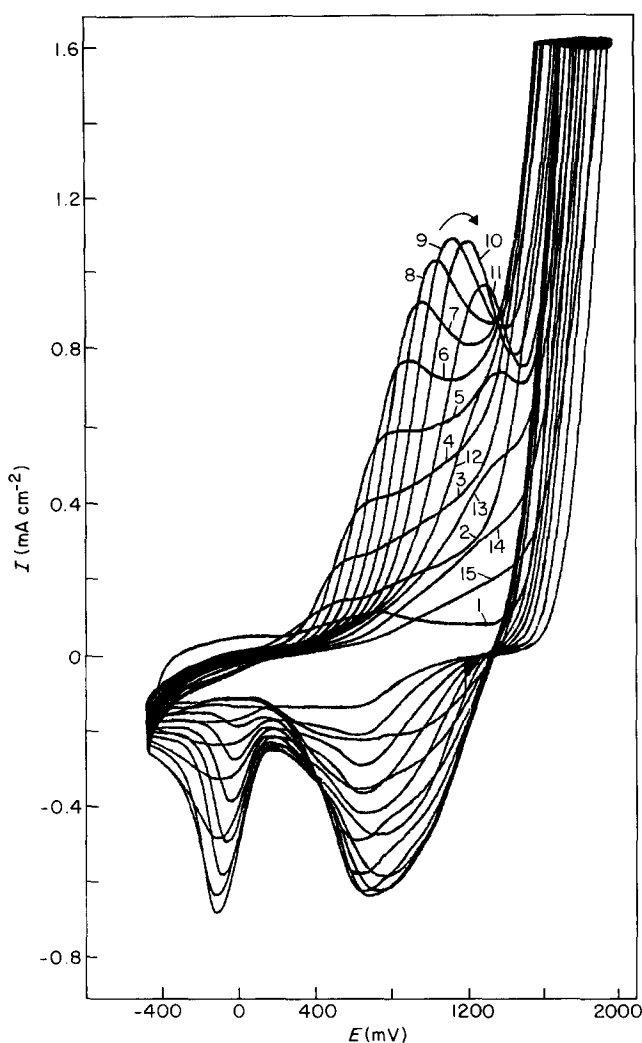


Figure 1 Consecutive voltammograms of the platinum scanned between -500 and $+1700$ mV at 50 mV s $^{-1}$ in 0.1 M thiophene and 0.1 M LiClO $_4$ in acetonitrile solution

before the beginning of monomer oxidation, which happens at a lower overpotential than for the first voltammogram. Steric reasons favour monomer oxidation on a conducting polymer surface in relation to a metal surface.

Polymer growth occurs on every new anodic sweep of the potential. This fact promotes the growth of the polymer layer, and, therefore, the increase in the anodic and cathodic current densities in the polymer oxidation and reduction region. This is observed on the first nine anodic branches of the voltammograms and on the first eight cathodic branches.

At the same time, an overpotential increase is observed at the beginning of polymer oxidation, which is related to an increase in the resistivity of the polymer layer. In spite of this, once oxidized, the polymer layer is a better conductor the greater the polymer thickness, as can be deduced from the decrease of the monomer oxidation overvoltage on the first eight voltammograms.

When the polymer thickness was greater than that in voltammogram 9, the conductivity and redox reversibility of the conducting polymer layer decrease, promoting a decrease in the anodic and cathodic maxima of the current density and an increase in the monomer oxidation overvoltage. The overvoltage changes are more important on the anodic branches than on the cathodic

ones, which means it is more difficult to oxidize the polymer layer. Nevertheless, once oxidized (totally or partially), the final conductivity of the polymer layer at 1700 mV decreases slowly with increase in film thickness, as is shown by the potential of the cathodic maxima shift.

At more cathodic potentials than 0 mV, a current density maximum appears on the cathodic branches of the voltammograms. The variation of the current density for this maximum is similar to that for the anodic maximum of polymer oxidation. The overvoltage variation is smaller. When a coated electrode was transferred into the background solution and there subjected to consecutive potential sweeps, this maximum disappears (Figure 3). It disappears, too, if once attained the situation showed by a middle polymer growth (say sweep 9), the anodic limit of potential is shifted, to the next sweep, until a potential prior to the monomer oxidation. These facts point to a direct relation between monomer oxidation and the formation of the cathodic maximum.

A similar effect was observed when an activated iridium electrode was subjected to consecutive potential sweeps in NaNO $_3$ aqueous solution, and was proved to be related to local acidification during the anodic potential excursion²⁶. If a potential sweep such as number 9 (on Figure 1) is stopped on 600 mV (cathodic branch) and N $_2$ is bubbled through, the related maximum does not appear on voltammogram continuation. If we put the coated electrode in the background solution with a drop

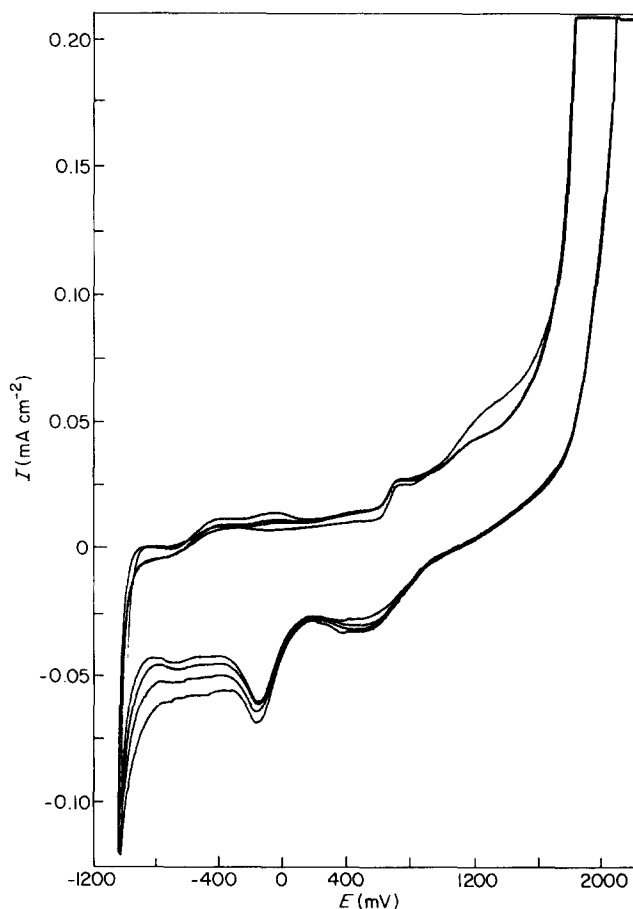


Figure 2 Consecutive voltammograms of the platinum scanned between -1000 and $+2200$ mV at 50 mV s $^{-1}$ in 0.1 M LiClO $_4$ in acetonitrile solution

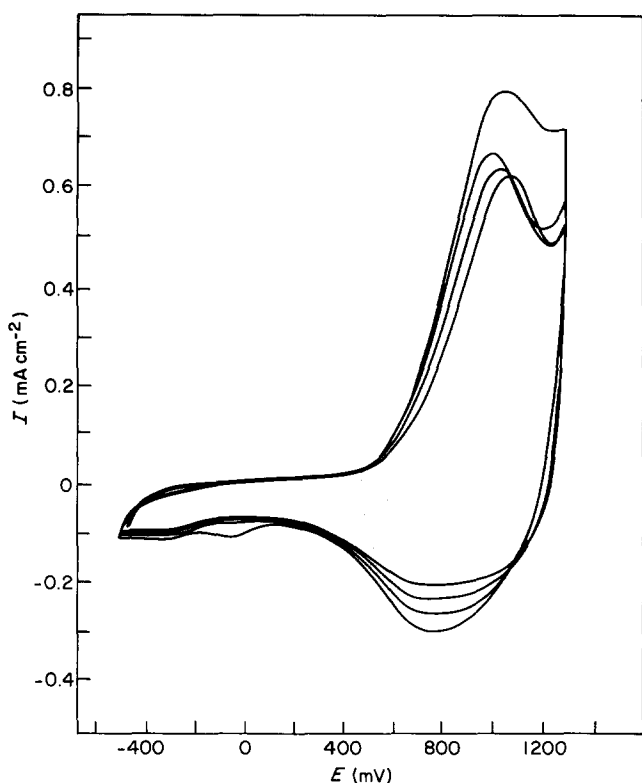


Figure 3 Consecutive voltammograms obtained by cyclic voltammetry (-500 to $+1300$ mV) at 50 mV s^{-1} in a 0.1 M LiClO_4 in acetonitrile solution, on a polythiophene film grown on a platinum electrode

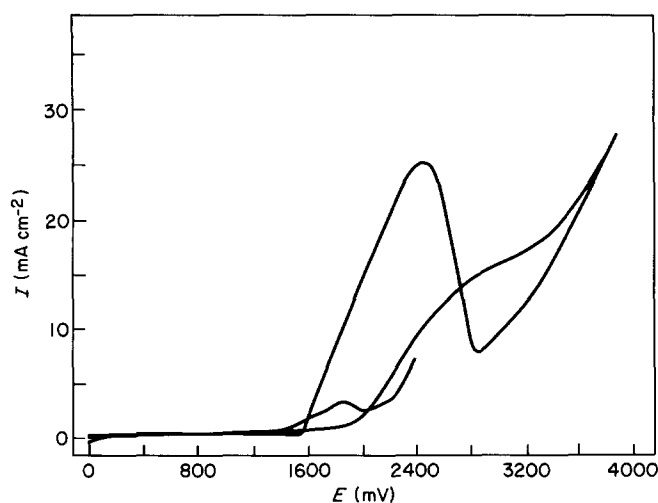


Figure 4 Consecutive voltammograms for the electropolymerization of a polythiophene film on a Pt surface from a 0.1 M thiophene and 0.1 M LiClO_4 in acetonitrile solution between 0 and 3800 mV at 20 mV s^{-1}

of 1 M HCl , a great current density response appears on the voltammogram at more cathodic potentials than $+50$ mV. All this points to a local acidification process taking place in the polymer layer, related to monomer oxidation. This hypothesis is supported, too, by the figure: voltammogram 9 shows a monomer oxidation overpotential greater than that of voltammogram 8 and the subsequent monomer oxidation is lower, similar to the maximum formed on 0 mV, and this trend continues on subsequent voltammograms.

The evolution of the current density and potential

between consecutive voltammograms depends, among other variables, on the anodic limit of consecutive potential sweeps. At sufficiently anodic potential limits, thiophene oxidation gives an irreversible maximum (2400 mV), as depicted by *Figure 4*. When the anodic potential excursion attains the anodic maximum, a black polymer film coats the platinum electrode. This polymer film can be released from the metal, and shows a smooth grey aspect on the metal side and a black and wrinkled one on the electrolyte side.

When the anodic maximum is surpassed, the polymer layer does not show any redox behaviour on the second voltammogram. On the other hand, at more anodic potentials than 2400 mV a violet-blue dust is released from the black electrode surface. The potentiodynamic characteristics (current density and potential) of the anodic maximum are influenced by the electrochemical and chemical variables. *Table 1* shows the influence of monomer concentration on those characteristics and on monomer oxidation potentials.

An electrolyte concentration increase promotes a slow shift of monomer oxidation at lower overpotentials (*Table 2*). The current density of the irreversible maximum increases, and the overpotential decreases when the electrolyte concentration increases (*Figure 5*). At higher electrolyte concentration, the maximum becomes narrower and the subsequent current density of the passivation minimum drops.

The powerful influence of electrolyte concentration on the potential of the irreversible maximum is related to the conductivity increase of the system, principally in the polymer film, when the ionic concentration rises. Nevertheless, the subsequent minimum indicates a greater resistivity at higher potentials, which increases, too, when the electrolyte concentration rises. These facts point to a conductivity loss related to polymer reaction with an oxidation product of the monomer or of the solvent, probably similar to the nucleophilic attack of polypyrrole films proposed in aqueous solution⁴.

Formation and growth of polythiophene films by electrode polarization at constant potentials gives the chronoamperometric curves shown in *Figures 6* and *7*.

Table 1 Influence of monomer concentration on the irreversible oxidation-polymerization maximum (peak)

Monomer concentration	E_{ox} (mV)	E_{p} (mV)	I_{p} (mA)
0.020	1660	1840	1.9
0.050	1640	2000	6.8
0.075	1590	2400	15.3
0.100	1550	2600	20.5
0.125	1540	3320	27.2
0.150	1520	3340	33.2

Table 2 Effect of electrolyte concentration increase on the potential of thiophene oxidation

Electrolyte concentration	E_{ox} (mV)
0.025	1570
0.050	1560
0.100	1550
0.250	1520

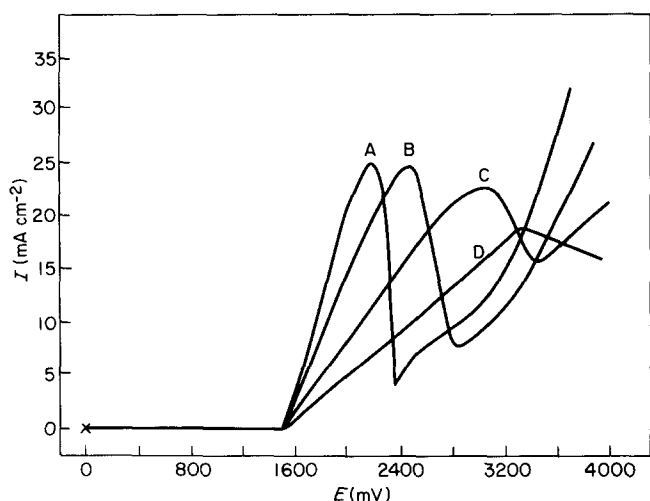


Figure 5 Superposition of the first scan of the electropolymerization of polythiophene on a Pt surface by cyclic voltammetry between 0 and +3800 mV at 20 mV s^{-1} from a 0.1 M thiophene solution and different concentrations of the electrolyte solution: A, 0.25 M; B, 0.10 M; C, 0.05 M; and D, 0.025 M

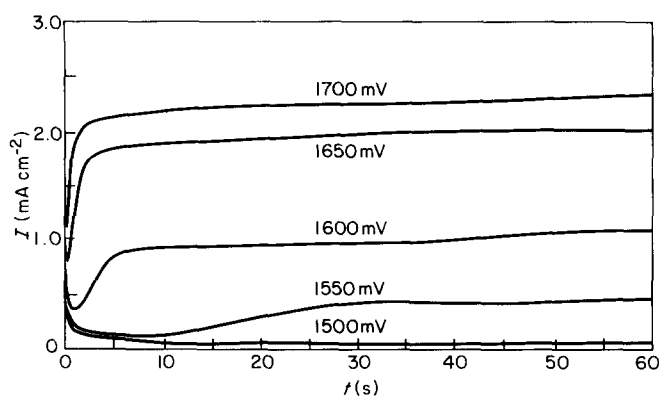


Figure 6 Chronoamperometric curves of potential steps for the growth of a polythiophene film on a Pt electrode from a 0.1 M thiophene and 0.1 M LiClO_4 in acetonitrile solution for different anodic potentials

nucleation minimum was not observed and no polymer appears on the electrode surface.

Finally the electropolymerization process was studied using square waves. The platinum electrode was submitted to consecutive square potential steps from a sufficiently cathodic potential to reduce the polymer layer (if it is present) up to a more anodic potential than the monomer oxidation potential. The chronoamperometric curve obtained is depicted in Figure 8. On the first anodic step, monomer oxidation takes place, promoting polymer nucleation. On the subsequent anodic steps, we have polymer oxidation plus monomer oxidation-polymerization. The consecutive cathodic steps promote the electric charge flow necessary to reduce the polymer layer. These facts explain the experimental curve obtained: the anodic current density maxima for the consecutive steps increases initially due to the presence of a thicker polymer layer at each new step. Nevertheless, this process attains a limit and the consecutive maxima of the chronoamperometric curve shows a maximum. The subsequent slow decrease of the current density on the

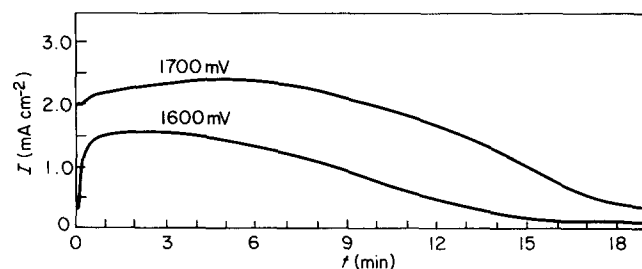


Figure 7 Chronoamperometric curves of potential steps for the growth of a polythiophene film on a Pt electrode from a 0.1 M thiophene and 0.1 M LiClO_4 in acetonitrile solution at different anodic potentials

Table 3 Influence of anodic potential step on the nucleation

E_{ox} (mV)	1500	1550	1600	1650	1700
Time (s)	—	6.0	1.8	0.8	0.2

When the electrode is polarized to a more anodic potential than that needed for monomer oxidation, by a potential step from a cathodic potential (-60 mV), a high anodic current density flows in the cell, decreasing quickly (it is used up in changing the double-layer capacity, oxidizing monomer present on the electrode and trying to generate the diffusion layer). The current density reaches a minimum and rises again at longer times. This is characteristic of nucleation processes. The time necessary to attain the minimum from the beginning of the polarization step is the nucleation time, and depends on the potential of polarization (Table 3).

When the timescale was enlarged at higher polarization times, a new current density maximum is attained. Beyond this maximum, the current density decreases slowly (Figure 7).

The presence of a minimum in current density on the chronoamperometric curve is related to nucleation processes and easier monomer oxidation on the polymer film than on the platinum metal (for steric reasons). This is similar to the decrease of overpotential for monomer oxidation on the consecutive voltammograms of Figure 1.

At lower anodic potentials than 1550 mV, the

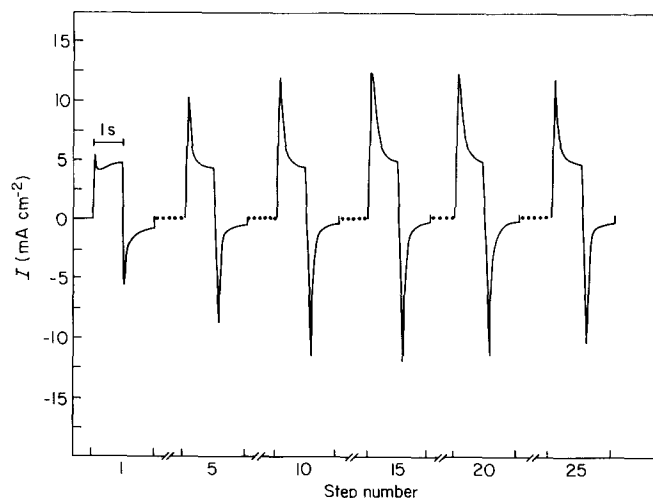


Figure 8 Chronoamperometric curves of Pt electrode subjected to consecutive potentials steps (-500 to $+1700 \text{ mV}$) in 0.1 M LiClO_4 and 0.1 M thiophene in acetonitrile solution

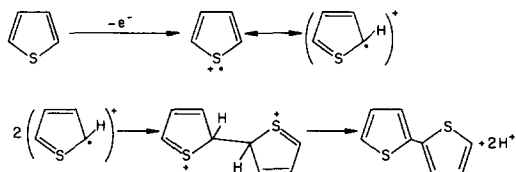
Table 4 Ration between the number of the step (-500 to +1700 mV) and its anodic charge obtained by integration of the area under the anodic curve

Step	1	2	3	4	5	7	9
Q_{ox} (mC)	4.00	4.80	5.00	5.25	5.50	6.40	6.90

maxima can be due, as on the consecutive voltammograms, to a resistivity increase of the polymer layer, probably due to a polymer degradation process. In any case, the electric charge related to anodic and cathodic steps remains greater on the anodic step due to the presence of monomer oxidation (Table 4).

All these experimental facts point to the electrogeneration of a polythiophene film on the platinum electrode initiated by monomer oxidation. It is not clear if the oxidation process is direct from the monomer (as was thought until now) or indirect from acetonitrile charge transfer. Comparing the first voltammogram of Figure 1 and the voltammograms of Figure 2, we can see that the oxidation processes coincide. If we try to electrogenerate a polythiophene film from tetrahydrofuran (THF) solutions, no polymer was obtained in the same potential region.

In any case direct or indirect monomer discharge generates monomer radical cations, which form dimers, trimers and oligomers, as was proposed by Garnier *et al.*⁶:



When the oligomers attain a high enough concentration, they precipitate on the electrode, forming a polymer nucleus, and direct electropolymerization on the nucleus begins. Each new monomer unit incorporated into the polymer structure promotes the loss of two protons, which are responsible for the cathodic maxima of the current density formed on the cathodic voltammogram branches at more cathodic potentials than 50 mV (Figure 1).

The nucleation process is much faster the greater the concentration of radical cations, which is related to the current density flowing in the system. All the electrochemical and chemical variables that influence the current flow will modify the electrogeneration of the polymer film. So, an increase in electrolyte concentration favours the conductivity increase of the system and therefore oxidation-polymerization, such as was observed by voltammetry (Figure 5). On the other hand, polarizations at anodic potentials are capable of generating more radical cations the more anodic the potential, and the nucleation time decreases (Figure 6). Furthermore, steric reasons justify easier monomer oxidation on the polymer nucleus than on the metal electrode, which explains the loop in the current density on the first voltammogram (Figure 1) and the presence of a nucleation time on the chronoamperometric curves.

The continuous increase of the current density after the minimum in the nucleation (Figure 6) and the cathodic

shift of the monomer oxidation potential on the first voltammogram (Figure 1) point to an increase in conductivity when the thickness of the polymer layer increases (both with reference to the oxidized state of the polymer layer). Nevertheless, polymer layer oxidation becomes more difficult when the polymer thickness increases, which is due to the greater resistance to ionic conductivity into the polymer (the ions are necessary to retain electroneutrality) to produce the doped state²⁷. This is deduced from the anodic shift of the polymer oxidation maxima (Figure 1).

At greater polymer thickness, the ionic quantity needed to oxidize the polymer layer is so high that the electronic conductivity is affected: the monomer oxidation overpotential increases on consecutive voltammograms (Figure 1, voltammogram 9 and following); or the current density decreases on the polarization curve (Figure 6) so that the maximum of current density is on the square steps (Figure 8). Certainly the conductivity loss is an inherent property of the polymer reactivity and instability, which can be observed by evolution of the consecutive control voltammograms obtained in the background solution (Figure 3). A similar effect was observed when polymer films obtained by polarization at constant potential or square waves were studied. Nevertheless, changing the electrochemical and chemical parameters of polymer nucleation rate and growth of the film allows one to control the polymer structure and adherence to the electrode surface, as will be shown in a following paper.

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