Formation and modification of polypyrrole films on platinum electrodes by cyclic voltammetry and anodic polarization

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The influence of different electrochemical and chemical variables on polypyrrole film formation, and on the charge transfer occurring on the electrode was studied. The potentiodynamic behaviour of some of the polymer films formed were studied in the absence of the monomer. The film conductivity and electrochromic characteristics were compared. A mechanism is proposed to explain the polymerization of nucleated oligomers. The potential region involved in charge-transfer polymer–perchlorate complex formation is identified. A mechanism of monomer oxidation and reduction and another to explain the polymer conductivity lost at anodic potentials in aqueous solution is proposed. The charge efficiency of polymer formation was studied by anodic polarization polymerization.

(Keywords: polypyrrole film; platinum electrode; cyclic voltammetry; anodic polymerization)

INTRODUCTION

Different electrochemical methods have been used with the aim of obtaining semiconducting polypyrrole layers on an electrode[1-11]. Constant polarization potentials, potential steps or a potential sweep have been the most commonly used methods. Pletcher *et al.* studied the influence of the anodic potential limit, for potential sweeps, on the voltammograms from an electrode subjected to two consecutive potential sweeps in aqueous solution of monomer in KNO_3[5]. We propose here a systematic study of the different electrochemical and chemical variables in polypyrrole film formation, from an aqueous solution of monomer in ClO_4^-, by cyclic voltammetry and anodic polarization (achieved by a potential ramp). Some of the polymer film formed was studied by cyclic voltammetry in the electrolyte solution with the aim of comparing its conductivity and electrochemical characteristics.

EXPERIMENTAL

Reagents

The monomer used (pyrrole (Merck, G.A)) was distilled at 60–70 mm Hg at 64°C–68°C to eliminate the inhibitor. The central fraction of the distillate was gathered and was stored in darkness at low temperature.

The electrolyte (Merck, G.A.) was used without further purification. The solution was prepared with ultrapure water.

Instrumentation

A one-compartment cell (Metrohm) was used, hermetically sealed with a five-hole cap used as an electrode support and for nitrogen bubbling. A platinum sheet was used as the working electrode.

A saturated calomel electrode was used as reference (Crison Instruments).

For the cyclic voltammetry experiments FHI-6050-15 equipment (Heka Electronic) was used, connected to a J. J. Lloyd Instruments PL 4 recorder.

The voltammetric measurements at constant polarization were made with a Wenking ST 72 potentiostat and a Wenking VSG 72 sweep generator. Potentials were controlled by a digital multimeter (Circuitmate DM 40). The corresponding curves were obtained with a chart recorder (J. J. Lloyd Instruments PL 4).

Platinum electrode preparation

To obtain maximum result reproducibility, the electrode was always treated in the same way before each experiment. Initially the electrode was mechanically cleaned of the polymer with filter paper (when this was possible), and then it was immersed in a hot sulphochromic mixture for ten minutes. After that it was rinsed with doubly distilled water.

Film formation

As mentioned earlier, the formation of polypyrrole films on the platinum electrode was achieved by both cyclic voltammetry, and a potential ramp followed by anodic polarization.

RESULTS

When a platinum electrode was subjected to consecutive potential sweeps in 0.1 M $NaClO_4$ and 0.02 M (aq.) pyrrole solution, the consecutive voltammogram evolution was dependent on the potential limit for the sweeps.

The influence of the anodic limit was followed by keeping the cathode potential constant at −80 mV. *Figure 1* shows the evolution of consecutive voltammograms when anodic limits were 800, 1000, 1100, 1400 and 1800 mV (S.C.E.).

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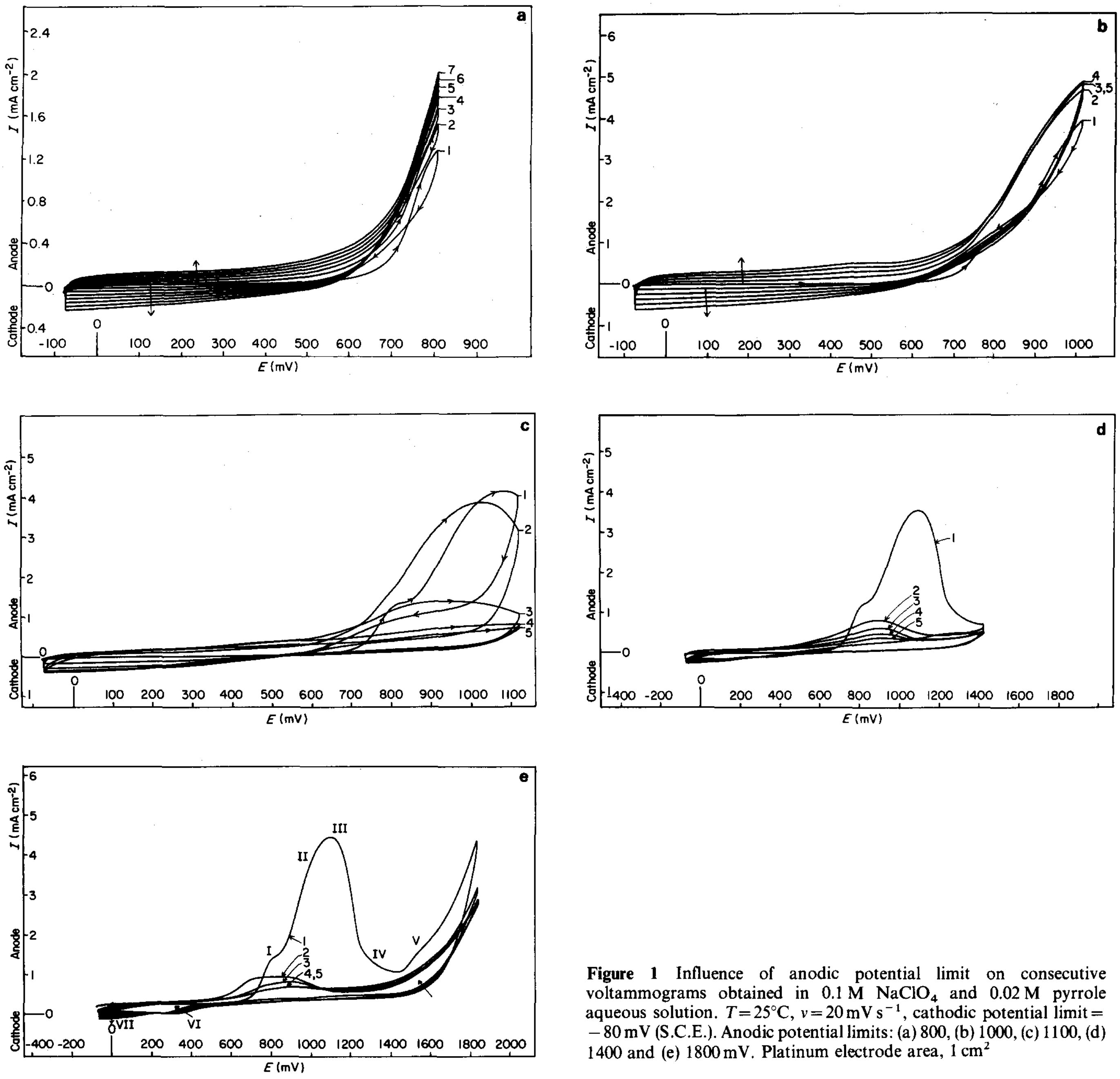


Figure 1 Influence of anodic potential limit on consecutive voltammograms obtained in 0.1 M $NaClO_4$ and 0.02 M pyrrole aqueous solution. $T=25°C$, $v=20\,mV\,s^{-1}$, cathodic potential limit = -80 mV (S.C.E.). Anodic potential limits: (a) 800, (b) 1000, (c) 1100, (d) 1400 and (e) 1800 mV. Platinum electrode area, 1 cm^2

Figures 1a–c allows us to observe, clearly, a characteristic of the nucleation-controlled processes: between 600 and 700 mV the first voltammogram shows greater anodic current on the cathodic sweep than on the anodic one. This fact was reinforced by the overpotential decrease for the initiation of monomeric oxidation, as the oxidation current density increases on consecutive sweeps (*Figure 1a*).

Between -80 and $+500$ mV a constant increase of oxidation and reduction current densities (on the anodic and cathodic branches, respectively, of the consecutive sweeps) was observed. A blue polymeric film, darker at each sweep, at anode potentials above 500 mV, and transparent and yellow below that potential, was formed. For anodic limits below 500 mV there was no film formation.

These results indicate a polymerization process in solution, initiated by a pyrrole molecular oxidation on the metal, followed by a polymer nucleation process on the electrode. The monomeric oxidation takes place more easily on the polymer than on the metal, as has been described by Pletcher *et al.*, and by Díaz *et al.*$^{1-3}$. This explains the loop seen on the first voltammogram and the increase in the anodic current density at potentials above 550 mV on consecutive sweeps.

Polymeric film formation and growth favours new oxidation and reduction processes occurring at anodic potentials lower than 500 mV. The relation between the current densities of these processes and the polymer layer thickness points towards oxidation and reduction processes into the polymer layer.

When the anodic limit reaches 1000 mV, the evolution for consecutive sweeps described takes place more quickly (*Figure 1b*). A monomer shoulder appears at 800 mV on the first voltammogram, followed by a more intense oxidation. This fact shows the existence of at least two oxidation processes at anodic potentials lower than 1000 mV; in addition to the oxidation–reduction process that accompanies polymeric film growth at anodic potentials lower than 500 mV.

For an anodic limit of 1100 mV (*Figure 1c*) a new surface process appears. The first voltammogram shows the oxidation shoulder at 800 mV. At greater anodic potentials a large maximum and, on the cathodic sweep, a loop related to a hard oxidation is present, and the current densities surpass those for an anodic sweep between 550 and 750 mV. The monomeric oxidation overpotential decreases on the second and third voltammograms, which promotes a well defined oxidation maximum, accompanied by progressive electrode inactivity.

The inactivity maximum appeared well defined when more anodic limits for the potential sweeps were reached (*Figure 1d,e*). The electrode shows very inactive behaviour on the second voltammogram, becoming increasingly passive on the following voltammograms. This behaviour includes all the potential zones of the voltammograms; electrode activity below 500 mV was much lower than for the previous anodic limits.

On the first voltammogram of *Figure 1e* the different electron transfer process, occurring on the electrode during the sweep, can be seen. Transfer processes I and III have been described previously and will be justified later. Process II appears to be completely hindered here, but it appears when the electrolyte concentration is increased. Two shoulders, which we have called IV and V, appear before the polymeric film break potential is reached, with O_2 evolution (by H_2O discharge at 1600 mV). Processes VI and VII correspond, respectively, to the oxidation and reduction processes taking place between -80 and 500 mV.

The electrochromic behaviour of the electrode disappears as the electrochemical behaviour becomes less active. In fact, when the anodic limit for the potential sweeps pass 1100 mV the electrode shows a dark violet colour during all the potential sweeps. For lower limits, the colour change becomes more difficult to observe when the polymer film thickness increases. The film was obtained by consecutive sweeps until the lower anodic potential limit provided a uniform surface which demonstrated a strong adherence to the metal, and could not be removed from the electrode by scraping with paper. For greater anodic potential limits, the film developed a rougher appearance. For anodic limits higher than 1400 mV adherence was very poor, and the film was easily removed from the electrode.

Figure 2 shows the potentiodynamic behaviour of the polypyrrole electrodes (with the films obtained from conditions shown in *Figure 1a, c, e*) in 0.1 M $NaClO_4$. The voltammograms show reversible behaviour. The charges related to the oxidation and reduction process were higher when the anodic potential limit shifted higher (always keeping lower than 1100 mV). When the anodic limit for the formation potential shifted up, the potentiodynamic behaviour of the films in 0.1 M $NaClO_4$ became less reversible and the charges related to the oxidation and reduction processes were lower. When the more reversible layers were cycled in the electrolyte a slow evolution was observed, between consecutive voltammograms, toward a less reversible and passive result. These facts point to a transformation of polymer layer conductivity by modification of the polymer chain structure.

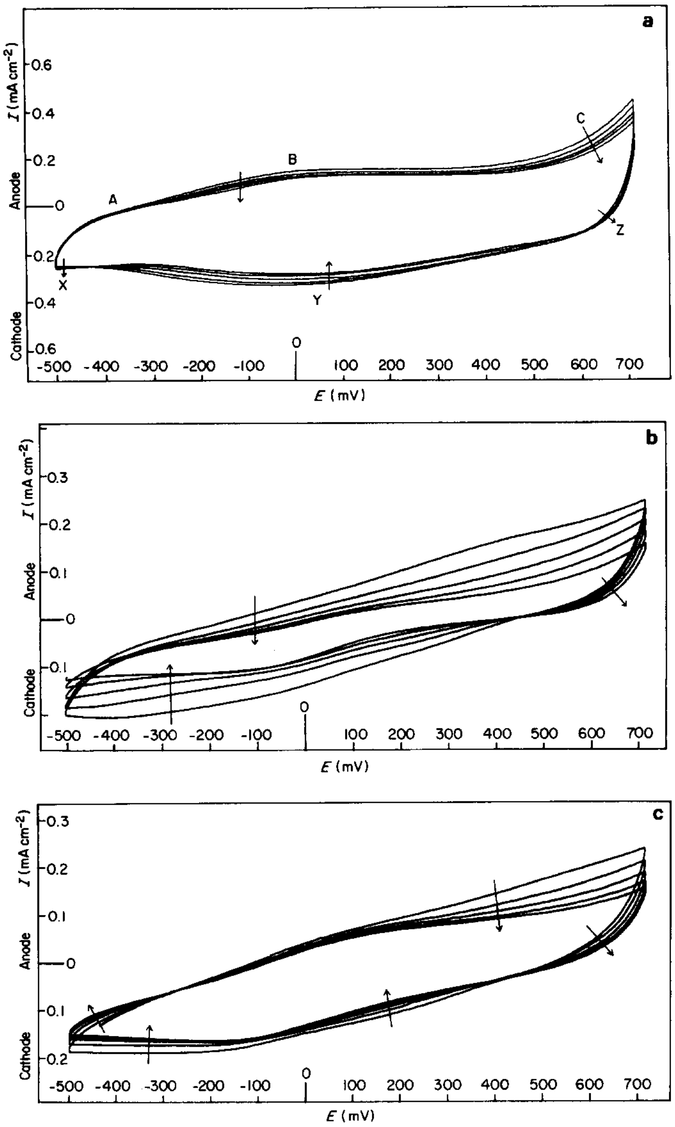


Figure 2 Consecutive voltammograms obtained with the conditions indicated in *Figure 1a, c* and *e*, in 0.1 M $NaClO_4$: $v = 20\,mV\,s^{-1}$; $T = 25°C$; potential sweep limits $-500/+700$ mV

When the influence of temperature on the polymerization process was studied, a decrease in the monomer oxidation overpotential was observed, with a current density increase on the different maxima. This does not favour the formation of a thicker and more adherent layer, because all the other processes taking place on the electrode, undergo the same overpotential shift (*Figure 3*). The occurrence of a mixed process on the electrode surface with competition between monomer and water discharge may be postulated. The temperature increase activates both processes in a similar way: it favours monomer oxidation, but this fact was not capable of promoting an increase of oxygen evolution overpotential on the electrode. From a $\log j_{\max. III}$ *versus* $1/T$ plot an apparent activation energy of $6.12\,kJ\,mol^{-1}$ was obtained.

The influence of temperature was also studied by the evolution of consecutive voltammograms obtained by potential sweeps between -80 and $+1000$ mV (*versus* S.C.E.) (*Figure 4*). At 10°C slow film growth was observed resulting in a more conductive film (see current densities at cathodic potentials greater than 500 mV). The temperature increase favours polymer growth (see

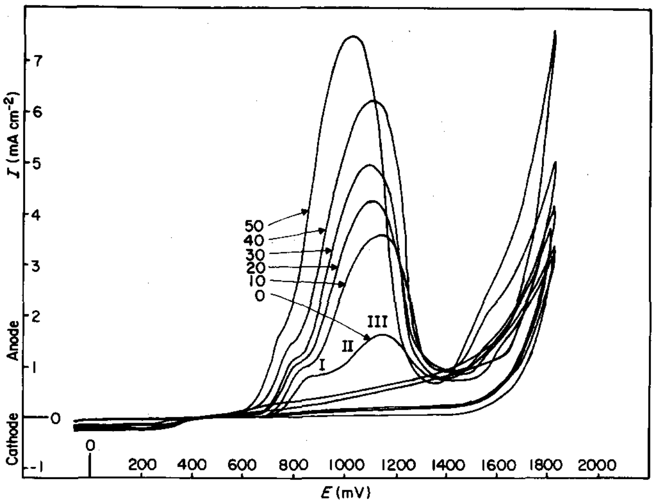


Figure 3 Temperature influence on the first voltammogram obtained in 0.02 M pyrrole and 0.1 M $NaClO_4$ aqueous solution: $v=20\,mV\,s^{-1}$

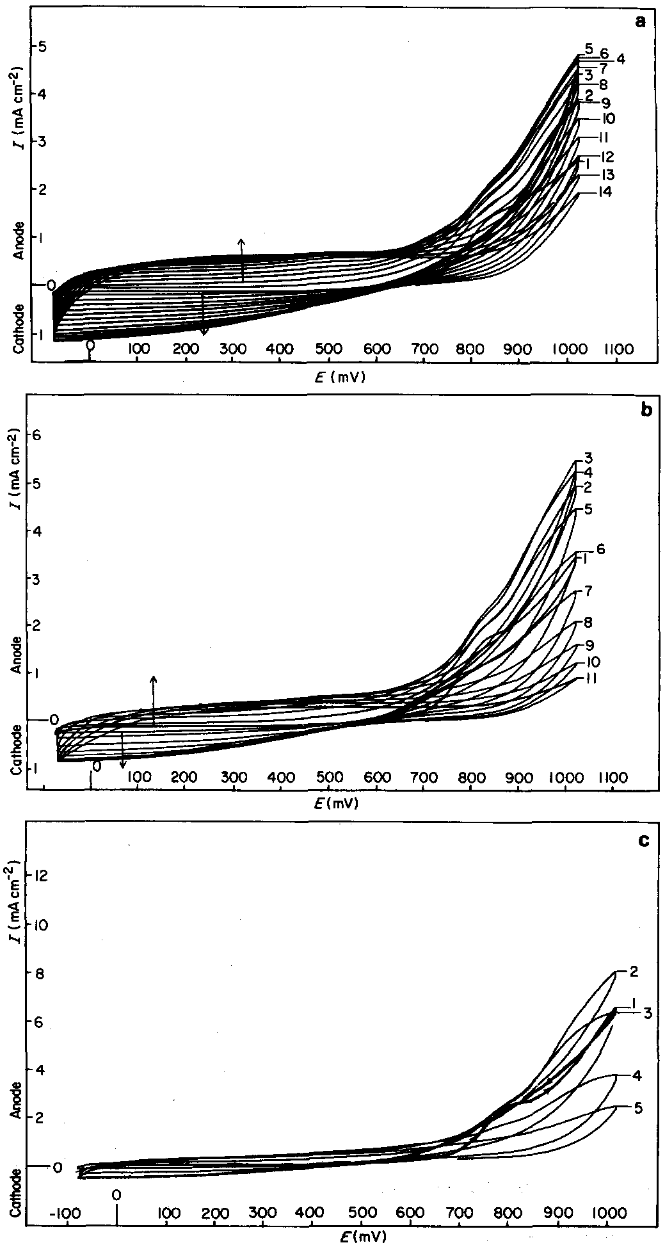


Figure 4 Temperature influence on consecutive voltammogram evolution obtained by electrode potential cycling (−80/+1010 mV, $20\,mV\,s^{-1}$) in 0.02 M pyrrole and 0.1 M $NaClO_4$ aqueous solution: (a) 0°C, (b) 20°C, (c) 40°C

current densities on consecutive voltammograms at anodic potentials above 500 mV); but the films formed had lower conductivity (see the current densities in the cathodic region).

These facts are related to the overpotential decrease when the temperature increases, which promote an increase of monomer and water oxidation. Under these conditions the water was oxidized on the polymer, promoting a nucleophilic attack and a ring opening mechanism producing a break in conductivity (along the polymer chain). In this way the effect of the temperature increase is different from the anodic shift of the anodic limit of potential in the region 600–1100 mV. There the kinetics of the water discharge on the polymer was constant and did not influence the polymer layer conductivity.

By studying the influence of monomer concentration achieved by potential cycling up to the potential required for oxygen evolution) a decrease of monomer oxidation overpotential, with monomer concentration increase, was observed (*Table 2*). Nevertheless, the overpotential of the process, related to process III, increases with the rise in monomer concentration; accordingly the oxygen evolution overpotential increases and the conductivity of the polymer layer formed during the first voltammogram decreases (*Figure 5*). This agrees with the previous hypothesis of a mixed process on the electrode. Water discharge in the polymer, with consequential nucleophilic attack on the polymer chain, becomes increasingly difficult with rising monomer concentration. Faster monomer oxidation and polymer nucleation processes expel water molecules more quickly, hindering water discharge and the deactivation process. From a $j_{max.III}$ *versus* monomer concentration plot, an apparent reaction order of one was obtained.

Electrolyte concentration plays as an important role in polymer film growth as in its conductivity. The first voltammograms obtained in solutions with constant monomer concentration and variable electrolyte concentration are shown in *Figure 6*. The most significant effect appears over region II, where current density rises quickly with increasing perchlorate concentration; at the same time its overpotential decreases. This overpotential decrease influences all the other charge-transfer processes: initiation of monomer oxidation, electrode deactivation and oxygen evolution, all of which take place at a greater cathodic potential with increasing electrolyte concentration.

The results presented agree with an increase of solution conductivity with rising electrolyte concentration. The strong influence of the electrolyte on all the oxidation processes points to a difficult electrolyte interaction at the electrode surface. The electrolyte influence on charge transfer in region II is related to polymer–perclorate

Table 1 Influence of monomer concentration on monomer oxidation overpotential

Monomer oxidation overpotential (mV)	[Pyrrole] (M)
700	0.010
650	0.025
600	0.050
570	0.075
540	0.100

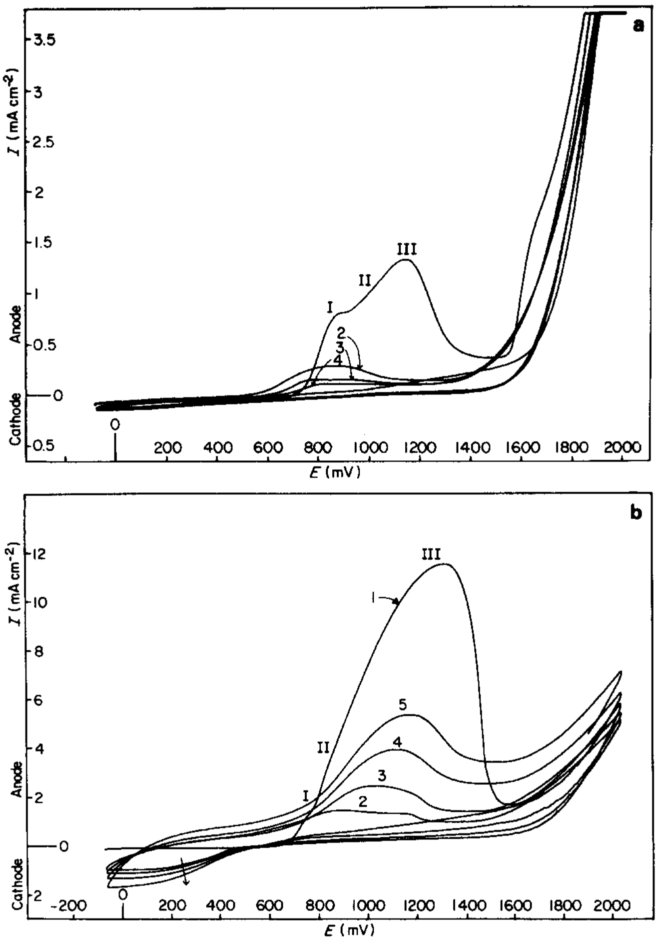


Figure 5 Monomer concentration influence on consecutive voltammogram evolution, obtained by potential cycling (-80/$+2000$ mV, 20 mV s^{-1}) at 25°C in 0.1 M NaClO$_4$ and (a) 0.01 M, (b) 0.05 M pyrrole solutions

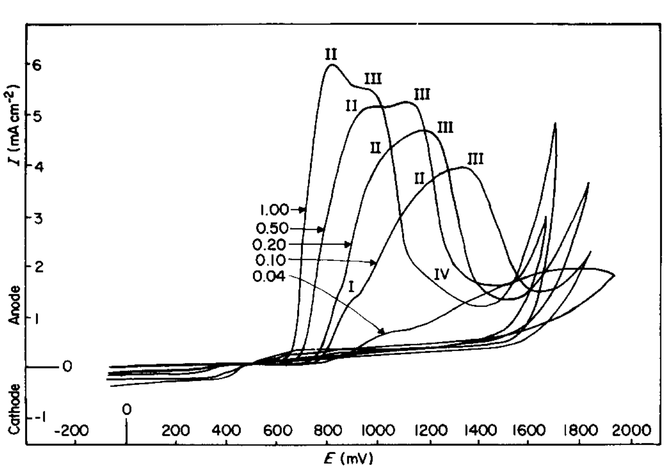


Figure 6 Electrolyte concentration influence on the first voltammogram obtained in 0.02 M pyrrole aqueous solution ($T = 25$°C, $v = 20$ mV s^{-1})

charge-transfer formation immediately after the surface polymer nucleation. However, electrolyte arrival at the electrode surface enhances water mobility in the polymer and water discharge on the polymer, with consequent inactivity and oxygen evolution at lower overpotentials.

From the effect of sweep rate on the first potential sweep made in the monomer solution for the sweep rates: 5, 10, 20, 50, 100, 200 and 500 mV s^{-1}, a region I charge-transfer diffusion control and a mixed nucleation–diffusion control of the region III charge-transfer process were obtained (*Figure 7*).

Polymer layer growth was also studied at constant potential, attained by a potential ramp. The electrode process was followed by 'throwing' the current density at the electrode (*Figure 8*). This variation was similar to that obtained by Pletcher *et al.*[5] with potential steps. *Table 2* gives the charge flow through the electrode at different polarization potential and polarization times (obtained by integration), the mass of the polymer film, and the charge/mass relation. The current efficiency generally increases with increasing polarization time. This is related to the monomer-radical lost by transfer into solution of part of the oligomers formed near the electrode before polymer nucleation on the metal. The blue colour of the polymer layer darkens with polarization time as quickly as for increasing the anodic polarization potential.

The polymer films obtained by polarization were studied in the electrolyte solution, without monomer, by consecutive potential sweeps. *Figure 9* shows the voltammograms obtained when the films were obtained at 600 mV after 5, 15, and 30 min of polarization. *Figure 10* depicts the voltammograms obtained with polymer films obtained by polarizations at 550, 650, 700 and 750 mV after 15 min. The effect of increasing the polarization time, at lower polarization potentials, on the potentiodynamic behaviour of the electrode attained was similar to increasing the polarization potential, with conductivity increasing at regions B and Y, which become larger, shifting regions C and X. At the same time the electrochromic result becomes less clear. Nevertheless, in this way it is essential to study the influence of potential sweep limits together with all other chemical variables. In any case, when region C was significant, the evolution between consecutive voltammograms in 0.1 M NaClO$_4$ was important, owing to water discharge (region C) on, and into, the polymer layer.

All the experimental results agree with the presence of monomeric oxidation initiated around 600 mV (the temperature, monomer and electrolyte concentration influence this overpotential). The formation of ion radicals in the solution promotes the formation of dimers and oligomers, as have been explained by Diaz, Pletcher *et al.* Two electrons are transferred by monomeric-unit transfer at the polymer. The values obtained from published literature and from our experimental results are closer to three. This fact can be explained by the presence of polymerization on the nucleated polymer and charge-transfer complex formation. Polymerization on the

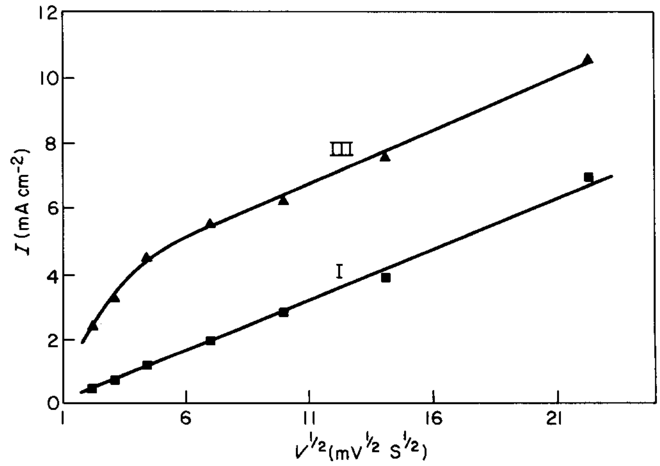


Figure 7 Influence of sweep rate on current density maxima I and III obtained in 0.1 M NaClO$_4$ and 0.02 M pyrrole aqueous solution at 25°C

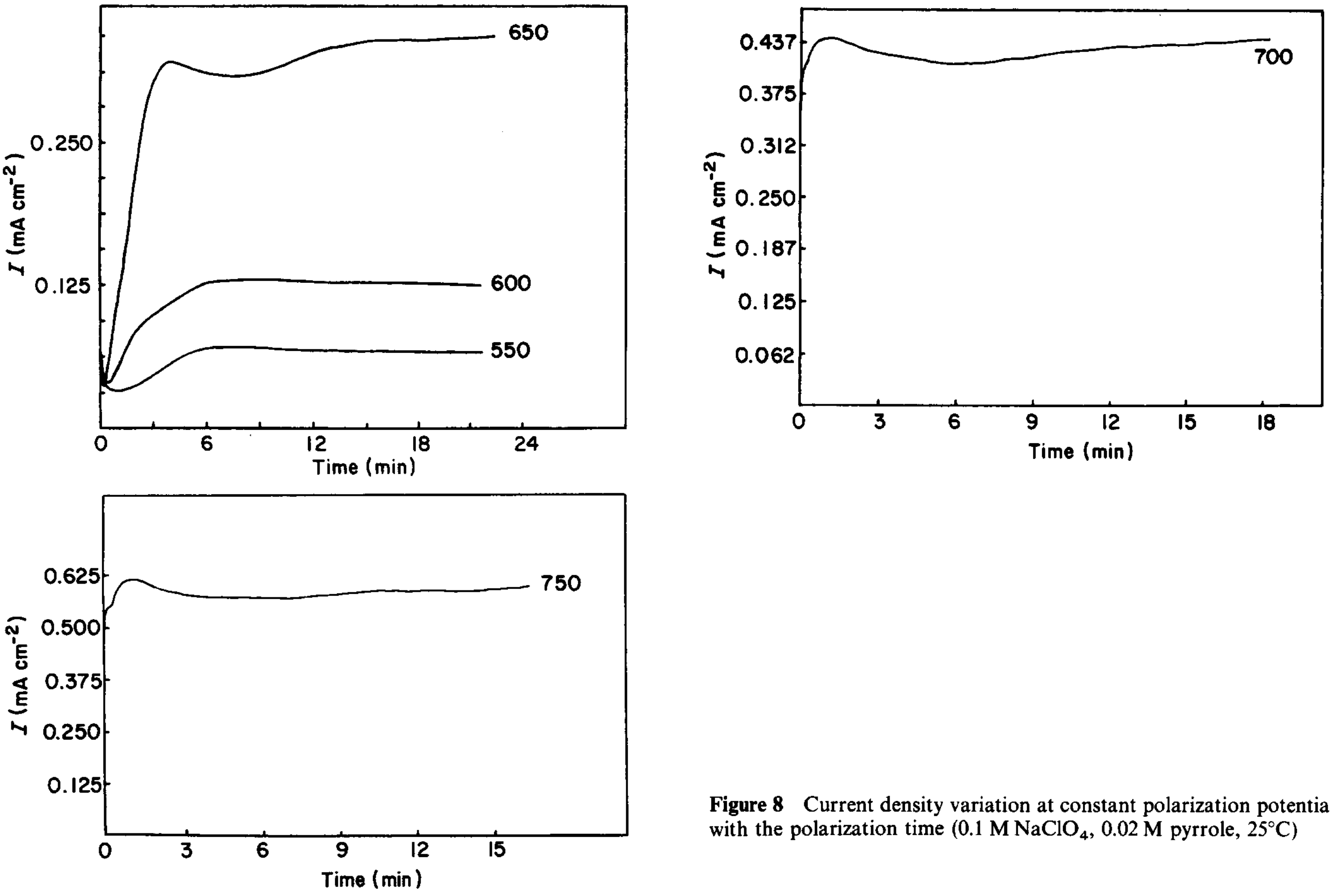


Figure 8 Current density variation at constant polarization potential with the polarization time (0.1 M $NaClO_4$, 0.02 M pyrrole, 25°C)

nucleated oligomers brings three electrons into the metal by monomer-unit addition:

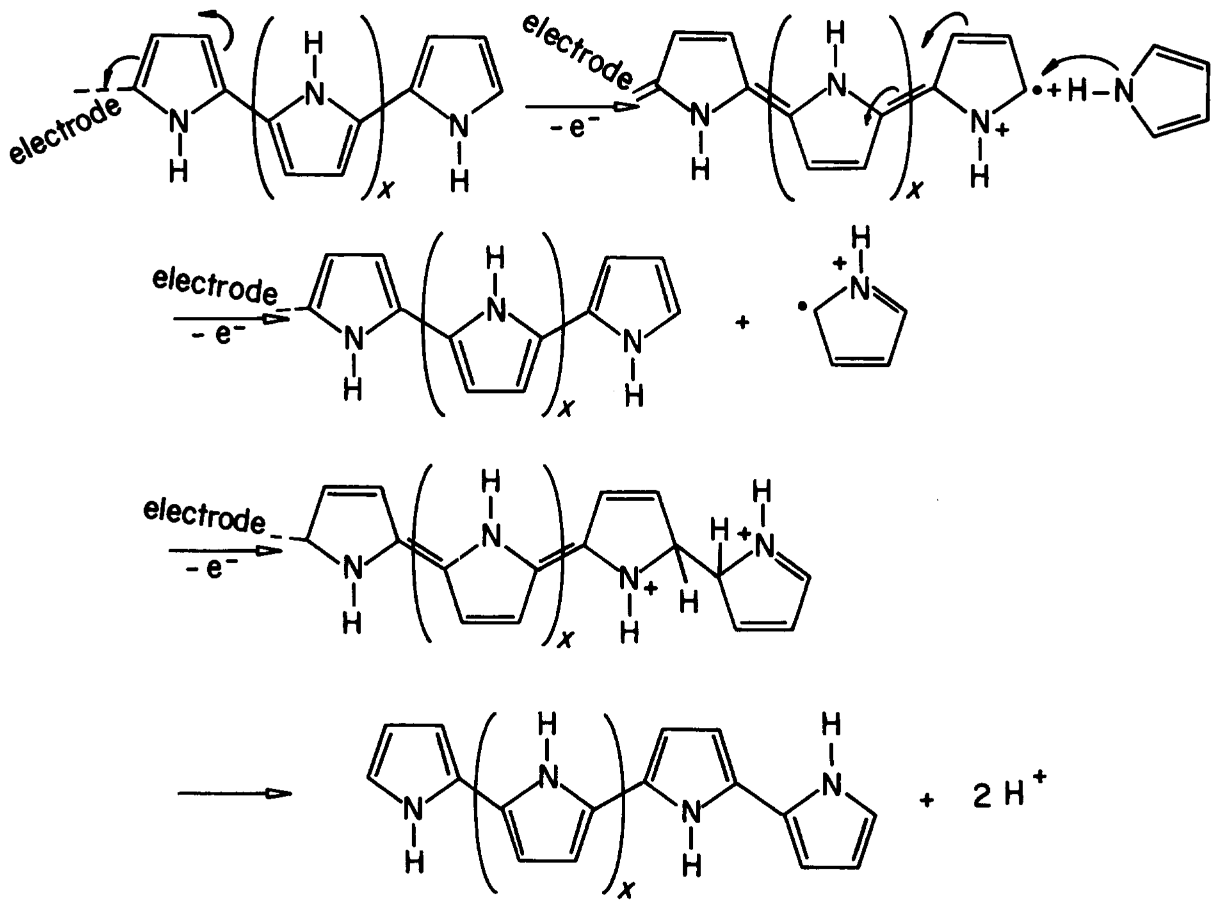


Table 2 Influence of polarization time and potential on polymer production and current efficiency

E (mV)	t (min)	Q (mC)	Mass (g) $\times 10^4$	Q(M) (C g^{-1})
550	30	277.1	1.0	2771
550	15	87.4	0.6	1456
600	30	499.6	2.7	1850
600	15	300.1	1.2	2501
600	5	23.5	0.6	392
650	30	1888.0	6.9	2736
650	15	804.2	3.4	2365
650	5	197.2	1.4	1408
700	30	3290.6	8.8	3739
700	15	1967.2	6.4	3073
700	5	502.2	2.4	2092
750	30	4280.0	11.5	3722
750	15	1996.8	7.6	2626
750	5	809.8	2.4	3374

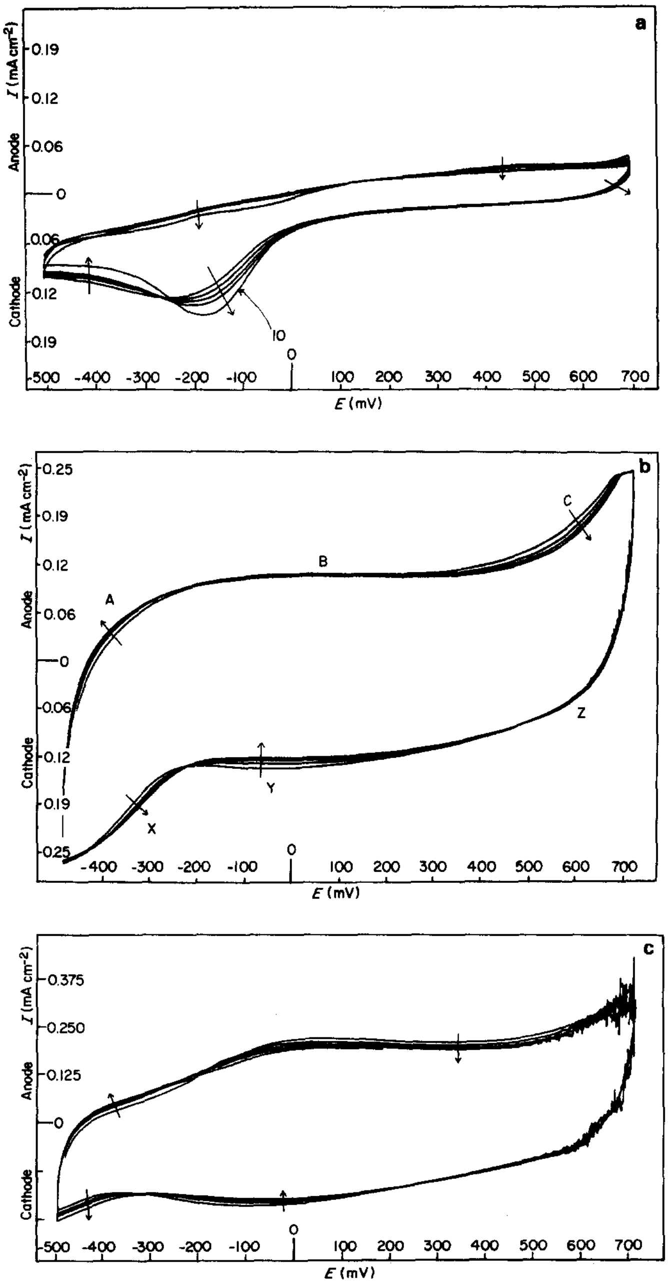


Figure 9 Consecutive voltammograms in 0.1 M $NaClO_4$ with a polypyrrole coated electrode by anodic polarization at 600 mV ($T = 25°C$, $v = 20\,mV\,s^{-1}$) and different polarization times: (a) 5 min, (b) 15 min and (c) 30 min (in 0.1 M $NaClO_4$, 0.02 M pyrrole, 25°C)

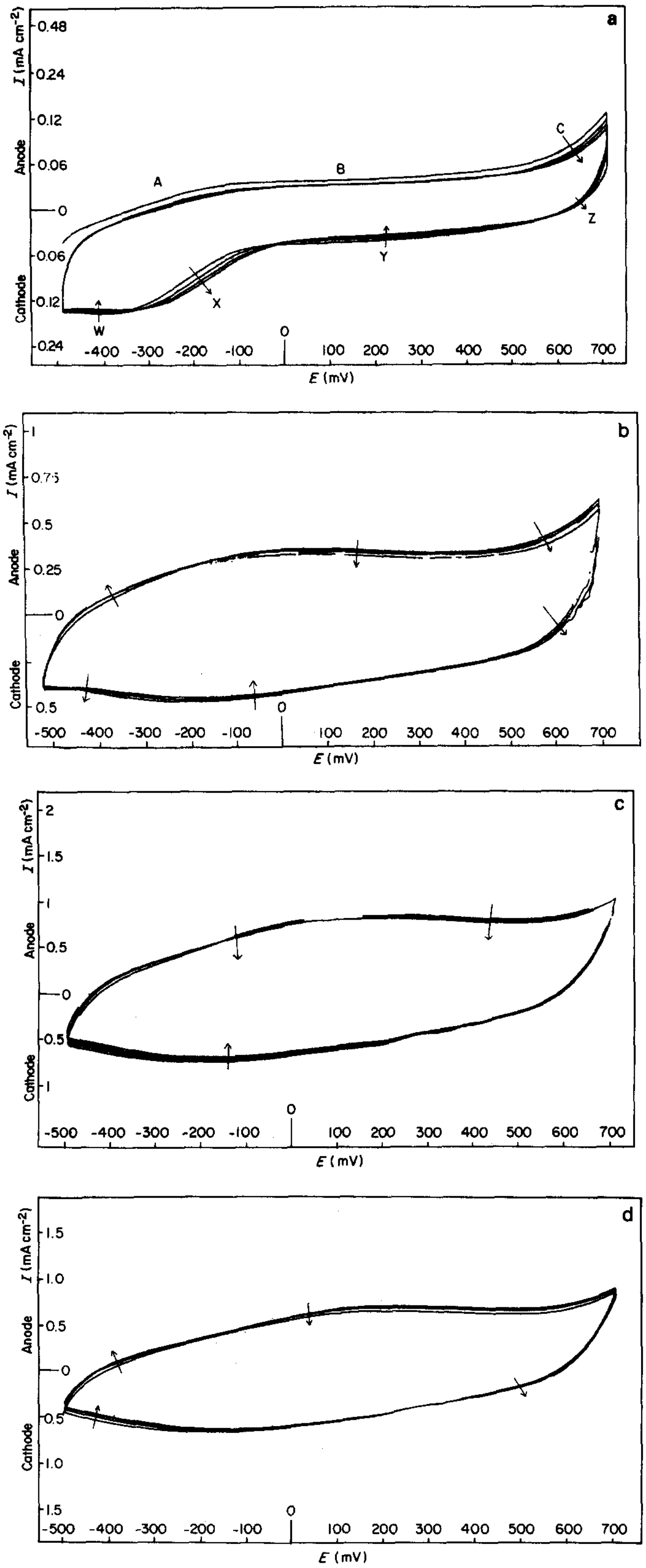
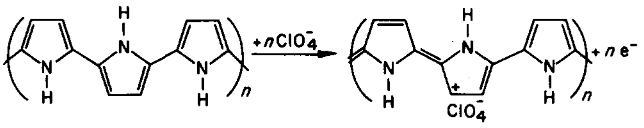
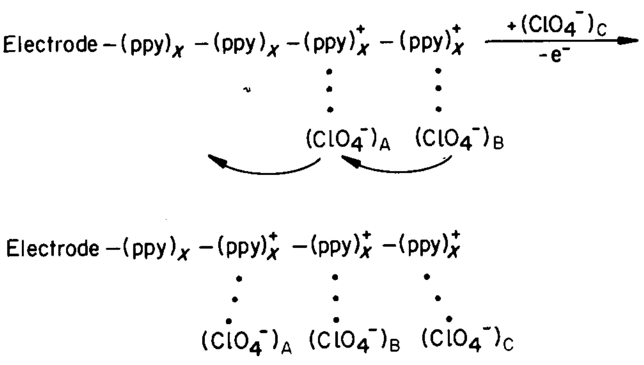


Figure 10 Consecutive voltammograms obtained in 0.1 M $NaClO_4$ by using a Pt electrode coated with a polypyrrole film obtained by 15 min of polarization in monomer solution at (a) 500 mV, (b) 650 mV, (c) 700 mV and (d) 750 mV

This process begins immediately after the beginning of oligomer nucleation, which takes place some time after the beginning of monomer oxidation. At the same time, the anodic polarization of the polymer promotes polymer oxidation with formation of a charge-transfer complex. Every two, three or four monomeric units into the polymer (depending on polymerization conditions; principally on the electrolyte concentration), a positive charge is stored, compensated by the migration of a perchlorate anion into the polymer film. The increase of stored charge with increasing electrolyte concentration promotes a maximum region II relative rise with respect to the other significant voltammogram regions

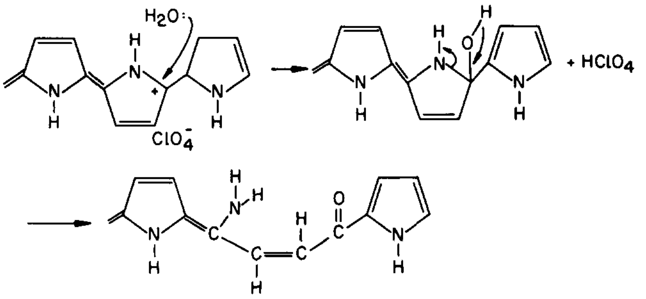


Once the polymer layer had formed the charge-transfer complex was oxidized and reduced into a large region (depending on the polymer film thickness) around 0 mV. This influence of the polymer film thickness is related to ClO_4^- diffusion into the film during the anodic sweep and toward the electrolyte during the cathodic sweep. The charge-transfer complex was built from the exterior of the polymer layer towards the metal during the anodic potential sweep; polymer reduction occurs inversely. This is in accord with the unidimensionality of the conductivity along the polymer chain, forcing oxidation and reduction in the directions described. The reversibility of both processes suggests the translation of ClO_4^- ions between consecutive oxidized units



The reverse process occurs during the cathodic sweep.

On the first voltammogram, after the formation process of the charge-transfer complex, we see the maximization and deactivation process, with a strong influence of electrolyte concentration (favouring the deactivation and monomer concentration keeping a high polymer-film conductivity and increasing the oxygen-evolution overpotential. These facts suggest a nucleophilic attack with irreversible opening of a ring.



The aim of our present work is to try to obtain analytical evidence for this reaction so as to optimize the electrochromic coefficient of the films formed by consecutive sweeps under different experimental conditions.

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