



## Electrodeposition of functionalized pyrrole (*N*-[3-(dimethylpyridyl-2-yl)aminopropyl], *N*-(3-aminopropyl), *N*-(3-acetamidopropyl) and *N*-(2-cyanoethyl)) on stainless steel gauze for membrane preparation

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### Abstract

The preparation of dense membranes for ion separation by the electropolymerization of functionalized pyrrole has been carried out using pyrrole monomers with complexing groups such as amino and bis pyridine. The synthesis conditions of polymer films depend mainly on the applied potential and electrolyte composition; for polymer films derived from pyrrole monomers bearing amino groups, the film synthesis has been achieved only in acid solution. The main results obtained for the electropolymerization of *N*-(2-cyanoethyl)pyrrole, *N*-(3-aminopropyl)pyrrole, *N*-(3-acetamidopropyl)pyrrole and *N*-[3-(dimethylpyridyl-2-yl)aminopropyl]pyrrole are compared and the experimental conditions for membrane preparation discussed. The thickness and the morphology of the supported conducting polymer membrane prepared at a constant potential depend on the precursor monomer used. The duration of electrolysis should be sufficient to cover the metallic support, particularly for the *N*-[3-(dimethylpyridyl-2-yl)aminopropyl]pyrrole polymer membrane.

### 1. Introduction

The preparation of polymer films derived from pyrrole [1, 2], thiophene [3], aniline [4] by the electropolymerization of the corresponding monomer for the preparation of modified electrodes which find application as selective sensors has been widely reported in the literature. The electrochemical synthesis of the polymer requires the control of experimental conditions and the final result depends on both the solvent and the supporting electrolyte used. Several studies have been carried out in order to understand the polymer formation mechanism and the anion exchange phenomenon which occurs when the polymer changes from the oxidized to the reduced state. It has been shown that the oxidized form of the polymer behaves as an anion exchanger [5, 6] if the electrolyte anions used are sufficiently 'mobile' in the polymer matrix. Polymer reduction generally leads to an expulsion of the anion from the polymer chain. In a situation where the anion is not able to move along the chain, the reduced form is obtained by the fixation of a cation, resulting in the polymer behaving as a cation exchanger [5, 6]. By controlling the applied potential and the nature of the supporting electrolyte, it is possible to prepare a conducting anion or cation exchanger polymer. We have used polypyrrole as a

membrane for the separation of organic mixtures by pervaporation [7]; however, despite the achievement of good selectivity, the solute fluxes through the membrane were generally low.

Other kinds of conducting polymer films have also been tested using modified monomers bearing specific groups, for example a sulfonate cation exchanger; in this case, the oxidized form of the polymer can be obtained without the addition of a specific supporting electrolyte since the sulfonate groups are able to provide the necessary anion required to neutralize the positively charged oxidized form [5]. Due to the presence of the sulfonate groups, the oxidized form of the polymer behaves as a cation exchanger. In the same way the preparation of copolymers between pyrrole and 3-(pyrrol-1-yl)propane sulfonate should be mentioned [5]. Considering that it would be interesting to develop membrane applications of polypyrrole derived films for transport of chemical species, we tried to use modified polypyrroles prepared by the electropolymerization of pyrrole substituted with specific complexing groups such as pyridine ( $L_1$ ), since it is known that they form stable complexes with metallic cations [8]. The anodic electropolymerization of monomers containing complexing groups presents a certain interest [9, 10] and mainly concerns the synthesis of polymers with N or S heteroatoms. Unfortunately, the experimental conditions for the electropolymerization of

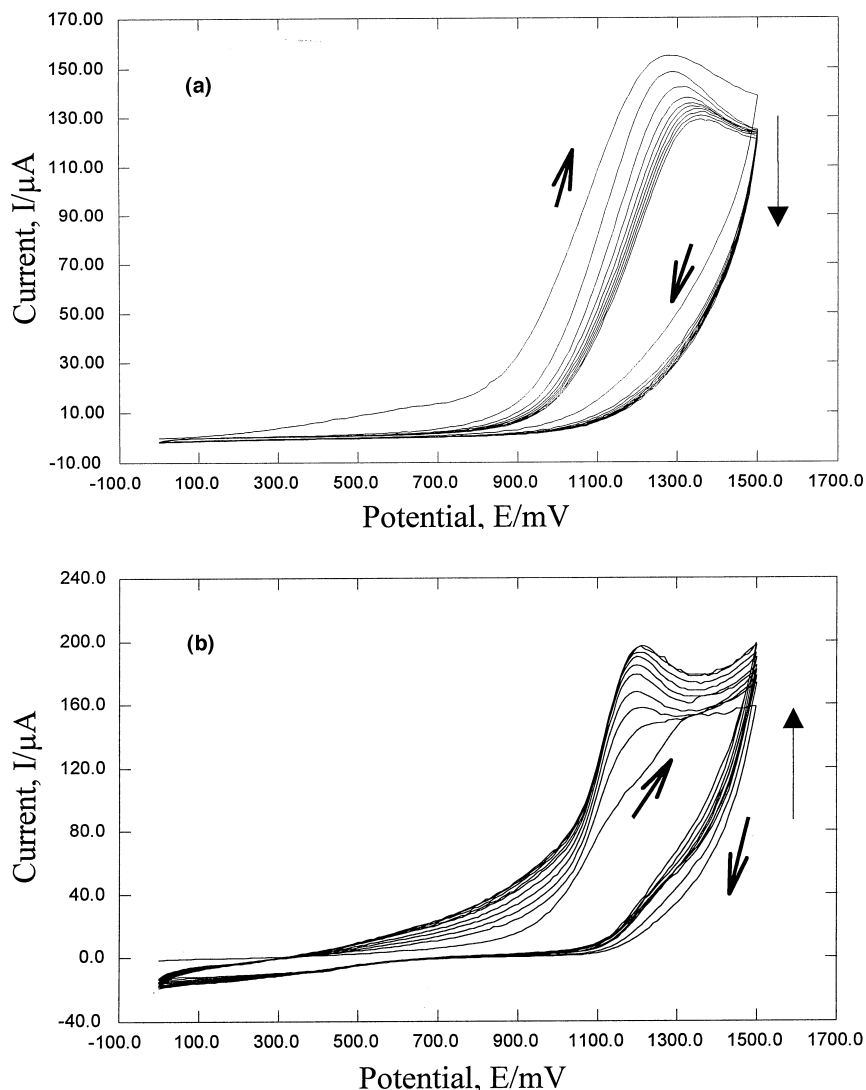


Fig. 1. Polymerization by potential cycling of  $L_1$  ( $100 \text{ mV s}^{-1}$ ). (a)  $L_1 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile (1:1)}$ ,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ . (b)  $L_1 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile (1:1)}$ ,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$ .

the bis pyridine aminopropyl pyrrole monomer ( $L_1$ ) are not easy to control [8]. This can be explained by the presence of the amino group, a known electrochemical inhibitor [11–13]. Since this kind of monomer shows interesting complexing properties, the preparation of polymer films with the monomers  $L_1$  for membrane transport applications is presented. The electrochemical behaviour of pyrrole derivatives with a structure close to  $L_1$  will also be discussed in order to clarify the electropolymerization mechanism for this class of compounds. The polymer films obtained will be characterized by the classical cyclic voltammetry and by the EQCM technique for studying the charge–discharge phenomenon.

## 2. Experimental details

### 2.1. Monomer preparation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AC 250 spectrometer. Chemical shifts are given in ppm downfield from the internal TMS standard.

Mass spectra were obtained on a Platform II Micro-mass spectrometer using positive electrospray ionization in a mixture acetonitrile:water:formic acid (49:49:2 percentage by volume). The source temperature was  $50 \text{ }^\circ\text{C}$ , the eluant flow  $10 \mu\text{L min}^{-1}$  and cone voltage  $30 \text{ V}$ .

#### 2.1.1. *N*-(3-aminopropyl)pyrrole $L_2$

A solution of 1-cyanoethylpyrrole (0.041 mol) in anhydrous ether (30 ml) was added to a suspension of  $\text{LiAlH}_4$  (0.1 mol) in anhydrous ether (300 mL) and the mixture was refluxed for 20 h. After cooling, the excess hydride was destroyed by the successive addition of water (3.4 mL), a solution of 15% NaOH (3.4 mL) and water (10.2 mL). The solution was heated to  $40 \text{ }^\circ\text{C}$  for 2 h and filtered on celite before evaporating to dryness. A yellow oil was obtained.

Yield = 92%. ES-MS  $m/z = 125$ .  $^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 1.90 (m, 2H,  $\text{CH}_2\text{-2}$ ); 2.70 (t, 2H,  $\text{CH}_2\text{-3}$ ); 3.95 (t, 2H,  $\text{CH}_2\text{-1}$ ); 6.14 (d, 2H,  $\text{CH-}\beta$ ); 6.65 (d, 2H,  $\text{CH-}\alpha$ ).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 35.5 ( $\text{CH}_2\text{-2}$ ); 39.7 ( $\text{CH}_2\text{-3}$ ); 47.7 ( $\text{CH}_2\text{-1}$ ); 108.4 ( $\text{C-}\beta$ ); 120.9 ( $\text{C-}\alpha$ ).

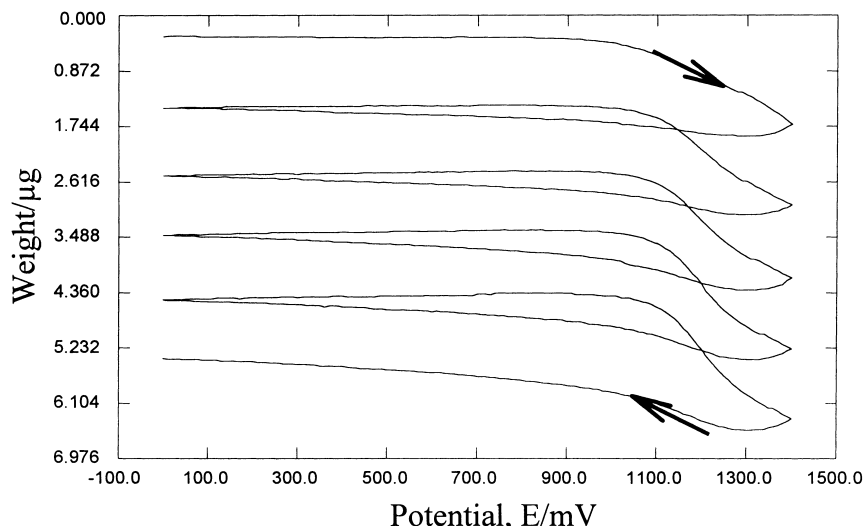


Fig. 2. EQCM measurement of the mass growth of  $L_1$  polymer.  $L_1 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile} (7:3)$ ,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$ .

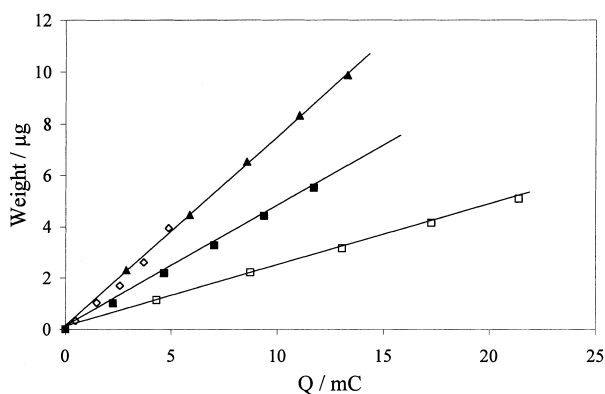


Fig. 3. Mass growth vs electricity amount for  $L_1$  to  $L_4$  polymers. Key: ( $\square$ )  $L_1 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile} (7:3)$ ,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$ . ( $\blacktriangle$ )  $L_2 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile} (7:3)$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$ . ( $\blacksquare$ )  $L_3 = 0.02 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ . ( $\diamond$ )  $L_4 = 0.01 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ .

### 2.1.2. *N*-[3-(dimethylpyridyl-2-yl)aminopropyl]pyrrole $L_1$

2-Chloromethylpyridine (24.4 mmol), amine  $L_2$  (12.2 mmol) were added to a suspension of sodium carbonate (0.146 mmol) in anhydrous acetonitrile (300 mL) in the presence of catalytic amounts of potassium iodide. The mixture was heated to  $80^\circ\text{C}$  for 7 h, filtered on celite and evaporated to dryness. The residue was purified by chromatography on alumina (eluant =  $\text{CH}_2\text{Cl}_2:\text{AcOEt}$ , 80:20). Brown oil was obtained.

Yield = 60%. ES-MS  $m/z = 307$ .  $^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 1.95 (m, 2H,  $\text{CH}_2-2$ ); 2.56 (t, 2H,  $\text{CH}_2-3$ ); 3.79 (s, 4H,  $\text{CH}_2\text{-py}$ ); 3.83 (t, 2H,  $\text{CH}_2-1$ ); 6.04 (d, 2H,  $\text{CH-}\beta$ ); 6.50 (d, 2H,  $\text{CH-}\alpha$ ); 7.11 (t, 2H,  $\text{H-}\beta'$ ); 7.42 (d, 2H,  $\text{H-}\delta'$ ); 7.60 (t, 2H,  $\text{H-}\gamma'$ ); 8.52 (d, 2H,  $\text{H-}\alpha'$ ).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 29.6 ( $\text{CH}_2-2$ ); 47.8 ( $\text{CH}_2-1$ ); 51.8 ( $\text{CH}_2-3$ ); 60.9 ( $\text{N-CH}_2\text{-Py}$ ); 108.2 ( $\text{C-}\beta$ ); 120.8 ( $\text{C-}\beta'$ );

122.4 ( $\text{C-}\alpha$ ); 123.4 ( $\text{C-}\delta'$ ); 136.8 ( $\text{C-}\gamma'$ ); 149.5 ( $\text{C-}\alpha'$ ); 159.9 ( $\text{C-}\lambda'$ ).

### 2.1.3. *N*-(3-acetamidopropyl)pyrrole $L_3$

The same procedure used for ligand  $L_1$  was also used to prepare  $L_3$ . [Amine  $L_2$  (8.06 mmol) and acetyl chloride (8.06 mmol)]. Yellow oil was obtained.

Yield = 73%. ES-MS  $m/z = 167$ .  $^1\text{H-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 1.90 (s, 3H,  $\text{CH}_3$ ); 1.95 (m, 2H,  $\text{CH}_2-2$ ); 3.25 (t, 2H,  $\text{CH}_2-3$ ); 3.95 (t, 2H,  $\text{CH}_2-1$ ); 5.05 (broad, 1H, NH); 6.15 (d, 2H,  $\text{CH-}\beta$ ); 6.65 (d, 2H,  $\text{CH-}\alpha$ ).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{CDCl}_3$ ): 23.5 ( $\text{CH}_3$ ); 31.6 ( $\text{CH}_2-2$ ); 37.8 ( $\text{CH}_2-3$ ); 48.2 ( $\text{CH}_2-1$ ); 108.9 ( $\text{C-}\beta$ ); 120.8 ( $\text{C-}\alpha$ ); 170.7 (CO).

### 2.1.4. *N*-(2-cyano ethyl)pyrrole $L_4$

The monomer (Aldrich, 99%) was used as received.

## 2.2. Instrumentation

All electrochemical studies were performed using a three-electrode potentiostatic system EG&G type M273, using a classical calomel electrode as the reference electrode.

The Seiko mark electrochemical quartz crystal microbalance (EQCM) was used for mass change measurements. This device is used with a counter platinum electrode wire and a Ag/AgCl reference electrode. The frequency variations measured by an oscillator are converted to a mass difference by means of the Sauerbrey equation [14]. The oscillator is able to detect a mass difference of  $1.18 \times 10^{-9} \text{ g}$ .

## 2.3. Solution preparation

The monomer solutions were prepared with the synthesized monomer at a concentration of  $10^{-2} \text{ mol L}^{-1}$  in pure acetonitrile, water:acetonitrile mixture or pure water depending on the experimental conditions.

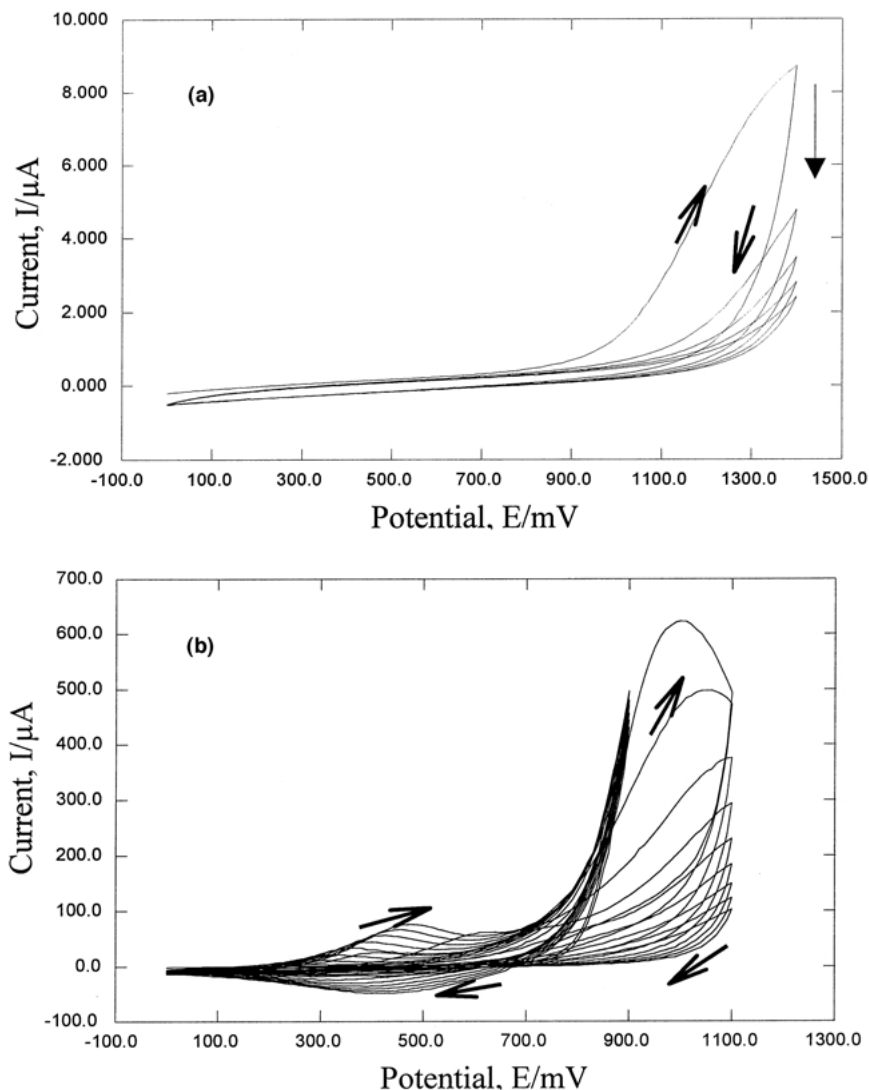


Fig. 4. Polymerization by potential cycling of  $L_2$  ( $100 \text{ mV s}^{-1}$ ). (a)  $L_2 = 0.5 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ . (b)  $L_2 = 0.1 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile}$  (7:3),  $\text{NaPTS} = 0.1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$ .

pa grade (Fluka) tetrabutylammonium hexafluorophosphate or sodium paratoluene sulfonate (PTS) salts were used as supporting electrolytes ( $C = 10^{-1} \text{ mol L}^{-1}$ ).

Perchloric acid was prepared from a commercial pa concentrated solution.

### 3. Results and discussion

#### 3.1. Electropolymerization of *N*-[3-(dimethylpyridyl)-2-yl]aminopropyl]pyrrole $L_1$

With the aim of synthesizing new membranes, electropolymerization of monomer  $L_1$  has been considered because it may coordinate to transition metal cations. Unfortunately, the electropolymerization of  $L_1$  in a solution of a classical supporting electrolyte does not occur and no polymer deposition is observed at the electrode surface.

The cyclic voltammograms of  $L_1$  obtained for these conditions (Figure 1(a)) are very different from those observed for the classical pyrrole monomer. The first oxidation scan presents a broad oxidation current peak at 1.3 V, whereas no reduction current occurs for the return scan. Subsequently for increasing scans, similar behaviour is observed, but the oxidation current decreases with increasing scan number. This kind of curve is observed for both the  $\text{Bu}_4\text{NPF}_6$  and the NaPTS electrolytes dissolved in a water:acetonitrile 50:50 mixture. The absence of polymer deposition at the electrode surface suggests that the nucleophilic amino group prevents radical cation formation which would allow the polymerization to progress. The same behaviour has been previously observed for other pyrrole monomers where an amino group has been attached to the pyrrole [12, 13]. After the addition of low concentrations of perchloric acid to the  $L_1$  monomer solution, the electropolymerization of  $L_1$  is still not observed, but increasing the concentration of acid ( $1 \text{ mol L}^{-1}$ ), results

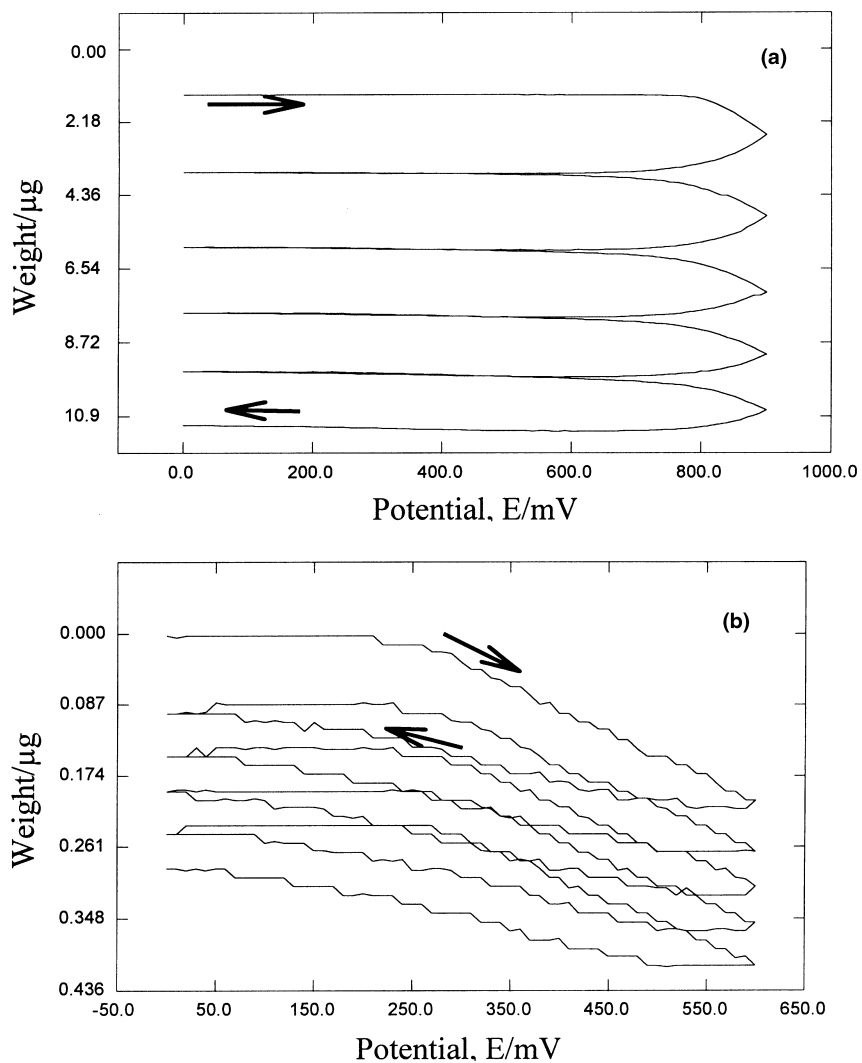


Fig. 5. EQCM measurement of the mass growth of L<sub>2</sub> polymer. (a) L<sub>2</sub> = 0.02 mol L<sup>-1</sup>, H<sub>2</sub>O:acetonitrile (7:3), HClO<sub>4</sub> = 1 mol L<sup>-1</sup>. (b) polymer L<sub>2</sub>, H<sub>2</sub>O:acetonitrile (7:3), HClO<sub>4</sub> = 1 mol L<sup>-1</sup>.

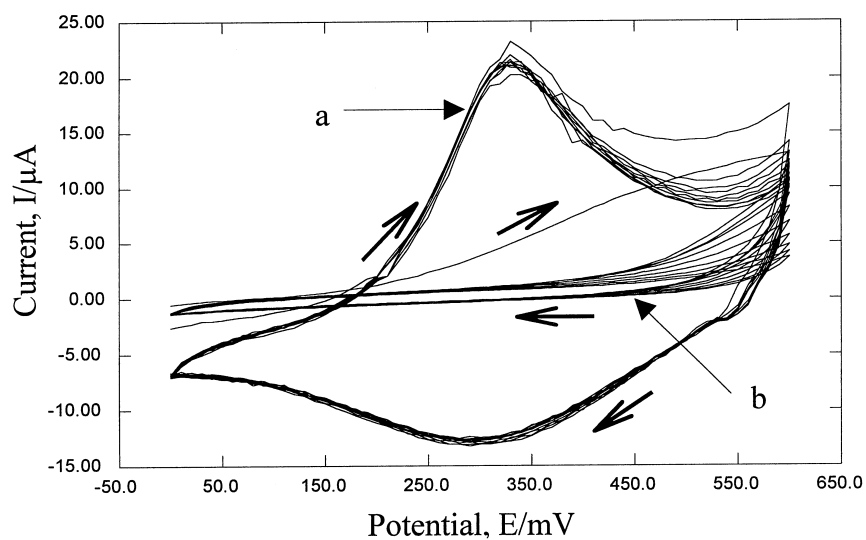


Fig. 6. Voltammogram of L<sub>2</sub> (100 mV s<sup>-1</sup>). (a) polymer L<sub>2</sub>, H<sub>2</sub>O:acetonitrile (7:3), LiClO<sub>4</sub> = 0.1 mol L<sup>-1</sup>, HClO<sub>4</sub> = 1 mol L<sup>-1</sup>. (b) polymer L<sub>2</sub>, H<sub>2</sub>O:acetonitrile (7:3), LiClO<sub>4</sub> = 0.1 mol L<sup>-1</sup>.

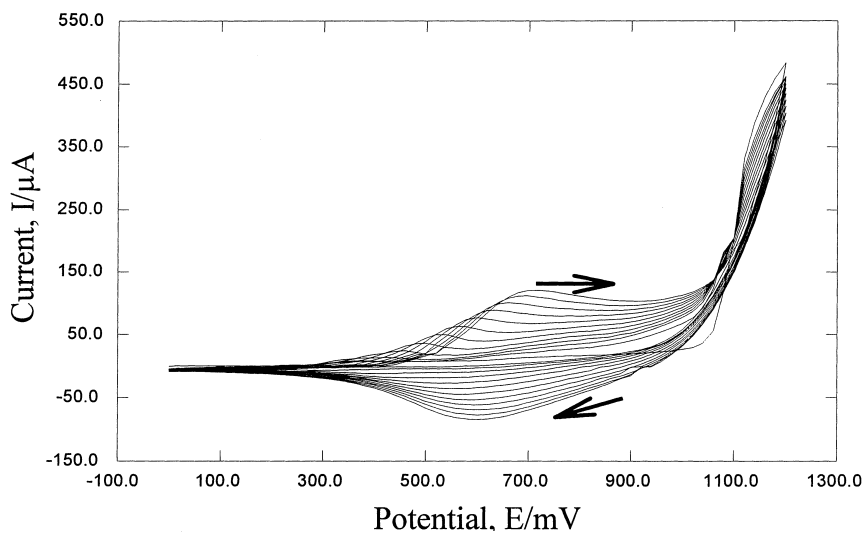


Fig. 7. Polymerization by potential cycling of  $L_3$  ( $100 \text{ mV s}^{-1}$ ).  $L_3 = 0.02 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ .

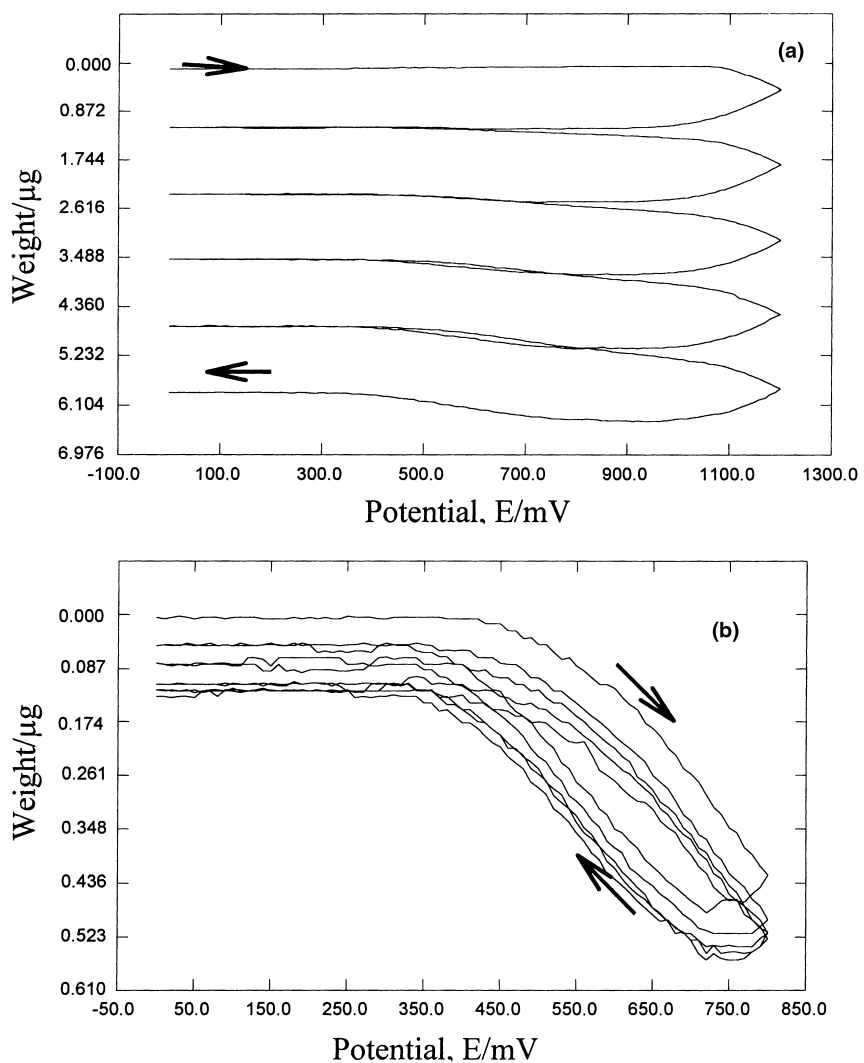


Fig. 8. EQCM measurement of the mass growth of  $L_3$  polymer. (a)  $L_3 = 0.02 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ . (b) polymer  $L_3$ , acetonitrile,  $\text{Bu}_4\text{PF}_6 = 0.1 \text{ mol L}^{-1}$ .

Table 1. Electropolymerization potential for the different monomers

| Monomer     | L <sub>1</sub> | L <sub>2</sub> | L <sub>3</sub> | L <sub>4</sub> |
|-------------|----------------|----------------|----------------|----------------|
| Potential/V | 1.3            | 0.9            | 1.2            | 1.3            |

in film growth at the electrode surface (Figure 1(b)). An increase in the oxidation current at each scan occurs for both electrolytes at 1 V, although no reduction current is observed on the return scan. Under these conditions, the oxidation of the monomer requires a relatively high potential with oxidation beginning at 0.6 V. Figure 2 shows that the mass of the deposited polymer measured by means of the EQCM increases for potentials higher than 1 V. During the voltammetric scans, the deposited mass is proportional to the charge (Figure 3), which confirms that the polymer is linked to the electrode surface [15]. Nevertheless, this deposited mass is low compared to those obtained with other pyrrole monomers studied (Figure 3). On the other hand, no mass variation has been observed with EQCM during the

charge discharge of the film after transfer in a free monomer solution, suggesting that anion exchange between the polymer and the solution is either inhibited or impossible. To understand the influence of the nature of the substituted group with *N* functions, we studied the electropolymerization of simple *N* substituted monomers derived from pyrrole with successively attached cyano-ethyl, amino-propyl and acetamido-propyl groups.

### 3.2. Electropolymerization 1-(3-aminopropyl)pyrrole L<sub>2</sub>

As for the previous experiments performed with the L<sub>1</sub> monomer, the direct aminopropylpyrrole electropolymerization failed under the same experimental conditions. The cyclic voltammograms present an oxidation wave at 0.9 V for the first scan (Figure 4(a)), which strongly shifts towards more positive potentials during the following four scans. Moreover, it was impossible to obtain polymer deposition at the electrode and no

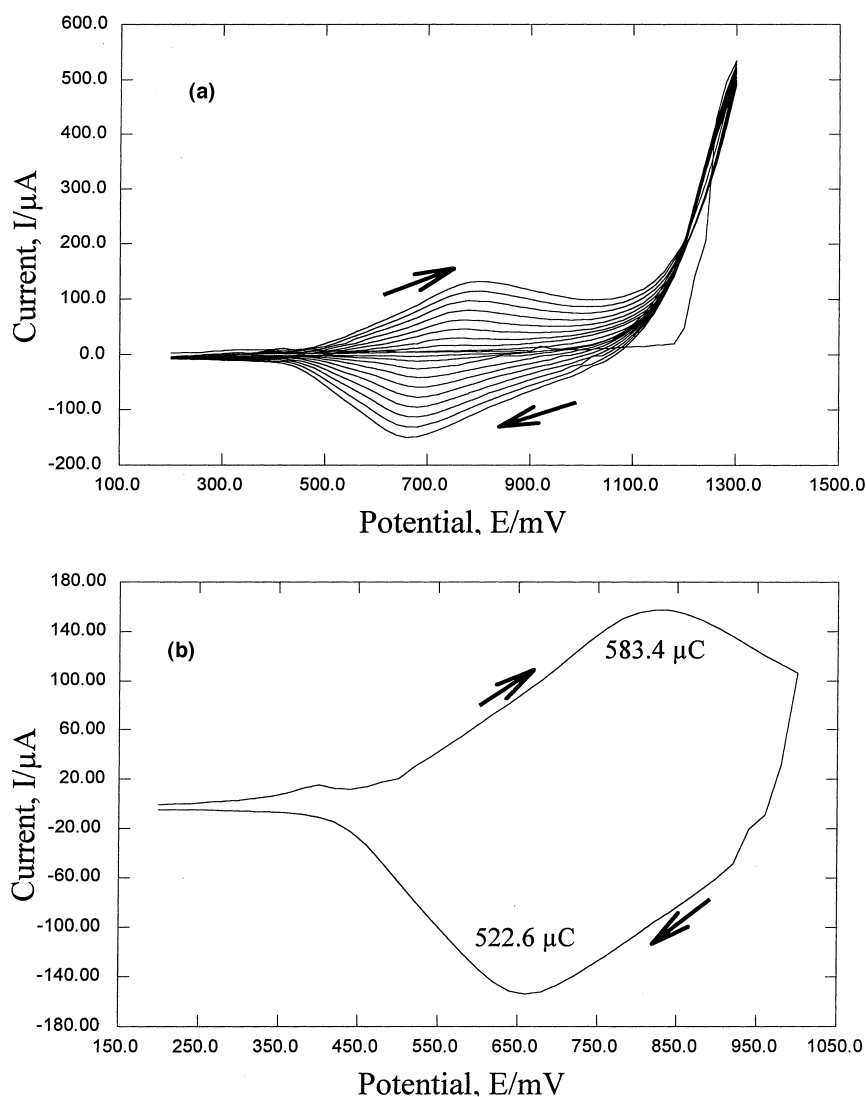


Fig. 9. Polymerization by potential cycling of L<sub>4</sub>. (a) L<sub>4</sub> = 0.01 mol L<sup>-1</sup>, acetonitrile, Bu<sub>4</sub>NPF<sub>6</sub> = 0.1 mol L<sup>-1</sup>. (b) polymer L<sub>4</sub>, acetonitrile, Bu<sub>4</sub>NPF<sub>6</sub> = 0.1 mol L<sup>-1</sup>.

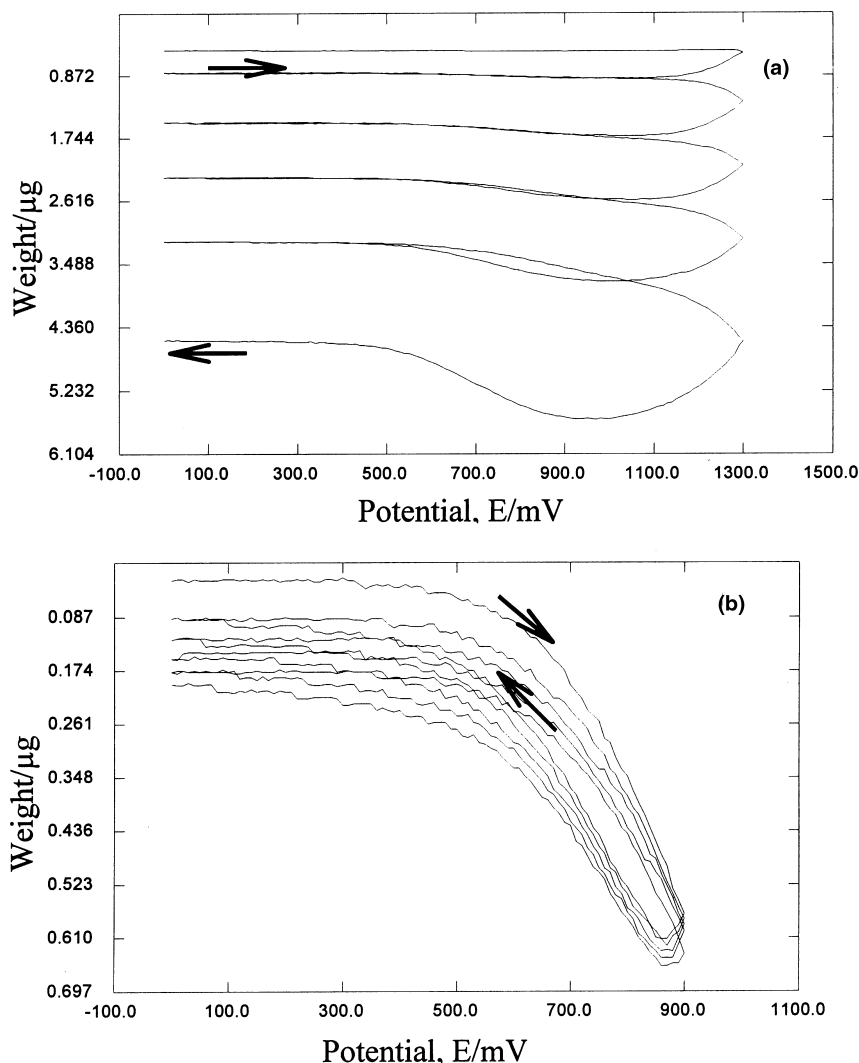


Fig. 10. EQCM measurement of the mass growth of  $L_4$  polymer. (a)  $L_4 = 0.01 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ . (b) polymer  $L_4$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ .

reduction current was observed while the maximum oxidation current decreased with increasing scan number. These observations confirm that the addition of a nucleophilic amino group to the pyrrole prevents radical cation formation and thus polymer formation [11]. In strong acid medium, the electropolymerization of the aminopropylpyrrole occurs (Figure 4(b)), nevertheless, the scanning range potential must be well controlled; particularly the film quality strongly depends on the final oxidation potential applied for the radical cation production. Furthermore, the polymer solubility depends on the amount of water in the electrolyte solution; in pure acetonitrile the solution becomes dark. Several authors attribute this phenomenon to the competitive formation of oligomers by a chemical route during electropolymerization [16]. To limit this drawback, we performed the electropolymerization experiments in pure water or in a water:acetonitrile mixture. The different cyclic voltammograms show that the best conditions for electropolymerization are obtained if the oxidation potential is fixed no

higher than 0.9 V. For higher potential values, the oxidation and reduction currents do not increase with increasing scan number; probably due to the formation of a nonconducting overoxidized form of the polymer, which is generated irrespective of the supporting electrolyte [17, 18]. At a fixed potential limit of 0.9 V (Figure 5(a)), the growth of the film can be followed by means of EQCM, it occurs between 0.7 and 0.9 V and the amount of electricity remains proportional to the scan numbers. Moreover, the amount of electricity depends on the limit potential applied. When the limit potential reaches 1 V, the deposited mass is higher for the first scan but decreases for subsequent scans. For a limit potential fixed at 0.6 V, the charge discharge of the polymer in a free monomer solution can be observed in acid solution but disappears in a non acidic electrolyte solution (Figure 6). Such behaviour has previously been reported in the literature for *N,N*-bis-(2-pyrrole-1-yl ethyl) *N* ethylamine [13]. Figure 5(b) shows that the mass increases from 0.2 to 0.6 V by fixing anions



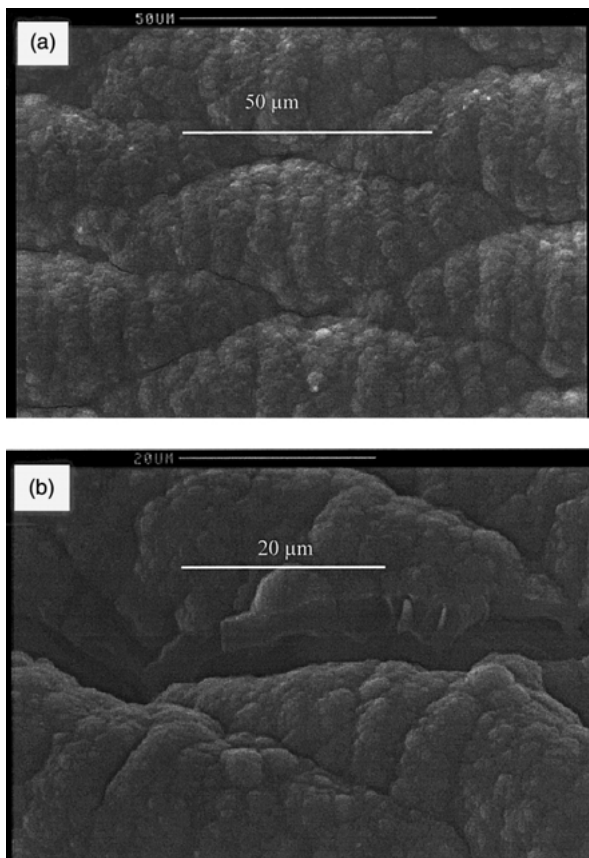


Fig. 11. SEM view of polymer  $L_4$  membrane prepared by controlled potential electrolysis  $L_4 = 0.01 \text{ mol L}^{-1}$ , acetonitrile,  $\text{Bu}_4\text{NPF}_6 = 0.1 \text{ mol L}^{-1}$ , ( $E = 1.4 \text{ V}$ ,  $t = 30 \text{ min}$ ) Key: (a) surface view and (b) cross section view.

whereas it decreases for potential below 0.57 V. The mass variation observed for the charge discharge phenomenon is lower for the amino propyl pyrrole than for the cyano ethyl pyrrole polymer (Figure 10(b)), and this is presumed to be due to the amino propyl pyrrole polymer expelling protons fixed by acid protonation either from the pyrrole or from the amino group rather than fixing anions during the oxidation step [19].

### 3.3. Electropolymerization of the 1-(3-acetamidopropyl) pyrrole $L_3$

The results of the experiments performed with the  $L_3$  monomer show that the polymer growth can be obtained in neutral medium. This confirms that the substitution of the acetamido group by the nucleophilic amino group is sufficient to prevent electropolymerization. The oxidation limit potential for electropolymerization of the acetamido functionalized monomer  $L_3$  is located at 1.2 V, with that of cyano-ethyl-pyrrole requiring 1.3 V, whereas 0.9 V is sufficient for amino-propyl-pyrrole in an acidic medium (Table 1). The oxidation potential difference observed between the amino and amido groups may be explained by the attractive effect of the acetyl function. The position

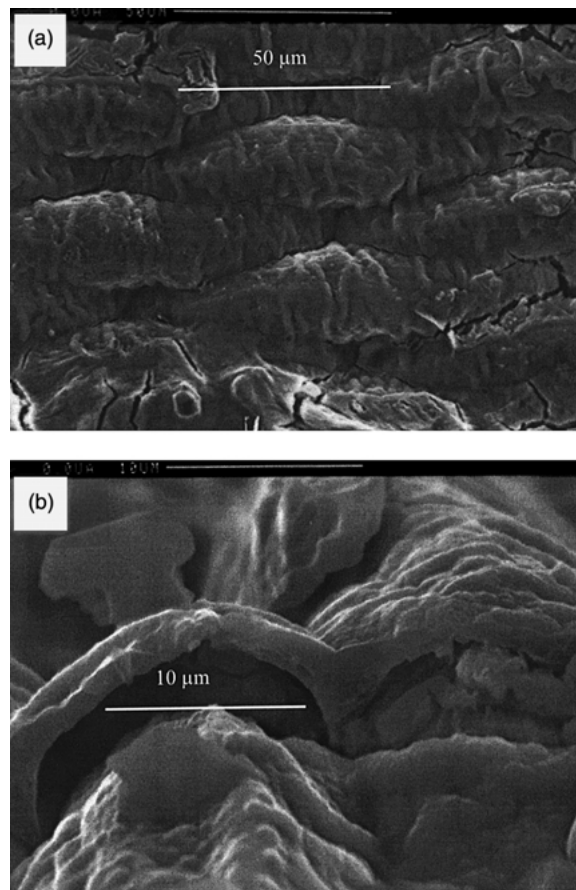


Fig. 12. SEM view of polymer  $L_2$  membrane prepared by controlled potential electrolysis  $L_2 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}$ :acetonitrile (7:3),  $\text{NaPTS} = 0.1 \text{ mol L}^{-1}$ ,  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$  ( $E = 1 \text{ V}$ ,  $t = 30 \text{ min}$ ). Key: (a) surface view and (b) cross section view.

of oxidation and reduction steps of the polymer  $L_3$  on the voltammetric curves are shown in Figure 7. As for the other pyrrole monomers, the EQCM results confirm the linear relationship between the amount of electricity and the deposited mass which increases for applied potentials greater than 0.9 V (Figures 3 and 8(a)). As previously described, the mass decrease observed when a lower potential is applied, also corresponds to the ejection of anions out of the polymer chain. In a monomer free solution, the charge-discharge of the polymer  $L_3$  occurs between 0.3 and 0.8 V (Figure 8(b)), and the symmetrical amount of electricity exchanged suggests that the expulsion of the anion is complete during the scanning potential.

### 3.4. Electropolymerization of 1-(2-cyanoethyl)pyrrole $L_4$

For the electropolymerization experiments, the cyano ethyl pyrrole monomer behaves as the acetamido  $L_3$  monomer and the polymer film can be obtained without difficulties. In Figure 9(a), the oxidation potential of the monomer is located at 1.3 V in good agreement with other  $N$  substituted pyrroles [12]. On the return scan, the resulting polymer is reduced whereas the following scan

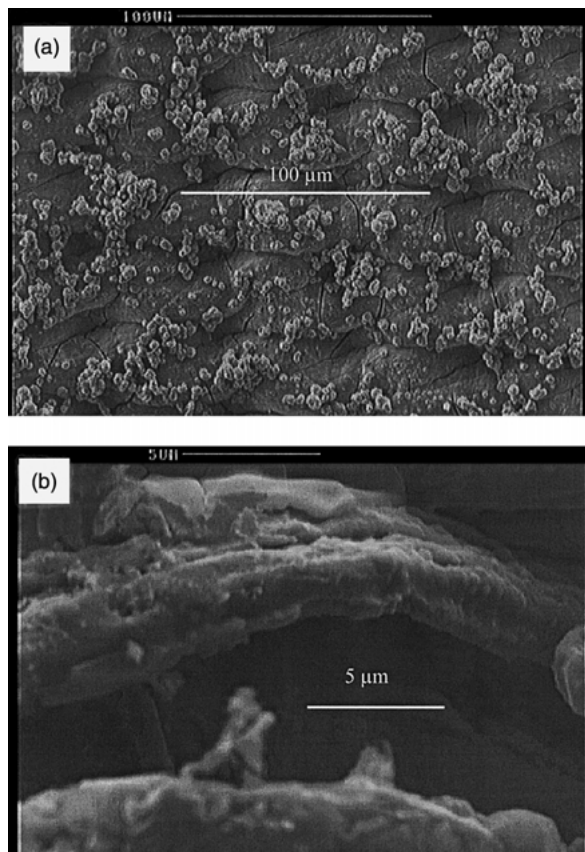


Fig. 13. SEM view of polymer  $L_1$  membrane prepared by controlled potential electrolysis  $L_1 = 0.02 \text{ mol L}^{-1}$ ,  $\text{H}_2\text{O}:\text{acetonitrile}$  (7:3),  $\text{HClO}_4 = 1 \text{ mol L}^{-1}$  ( $E = 1.15 \text{ V}$ ,  $t = 90 \text{ min}$ ). Key: (a) surface view and (b) cross section view.

shows the oxidation of the formed polymer at  $0.65 \text{ V}$  before the monomer oxidation potential. A linear relationship still exists between the deposited mass measured using EQCM and the charge (Figure 3). Moreover, the charge and therefore the deposited mass also depend on the monomer concentration. The comparison of the curves  $i/E$  (Figure 9(a)) and  $\Delta m/E$  (Figure 10(a)) illustrates the different steps for growth of the polymer. Between  $0$  and  $1 \text{ V}$ , the mass increases due to the oxidation of the monomer and this is followed by the nucleation of the cation radical formed. At the return scan, the mass marginally decreases from  $0.9$  to  $0.6 \text{ V}$  due to the expulsion of the fixed anion during the oxidation step. We also observed that the mass increase is not exactly proportional to the scan number at the beginning, but becomes proportional with increasing scan number. After transferring the film in a free monomer solution, the electroactivity of the film corresponds to the charge discharge phenomenon (Figure 9(b)). The integration area clearly shows that the amount of electricity consumed either for oxidation or reduction are not exactly the same, and this is probably due to a partial ejection of the fixed anions during the reduction step (Figure 9(b)). The mass loss vs potential plot (Figure 10(b)) for the charge-discharge phenomenon registered using EQCM shows that the mass increases between  $0.6$  and  $0.9 \text{ V}$  due to the insertion of

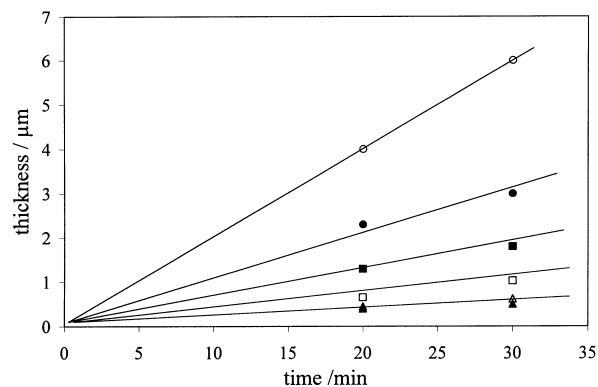


Fig. 14. Comparison of the thickness of the polymer films obtained with the different monomers against time electrolysis. Key:  $L_1$  ( $\Delta$ ,  $1.1 \text{ V}$ ) and ( $\blacksquare$ ,  $1.3 \text{ V}$ );  $L_2$  ( $\blacktriangle$ ,  $0.9 \text{ V}$ ) and ( $\square$ ,  $1 \text{ V}$ );  $L_4$  ( $\bullet$ ,  $1.3 \text{ V}$ ) and ( $\circ$ ,  $1.4 \text{ V}$ ).

the counter ion which is necessary to neutralize the positive charge of the oxidized polymer, and thus decreases during the return scan between  $0.9$  and  $0.6 \text{ V}$  due to the ejection of the anion.

### 3.5. Membrane preparation

Plane circular membranes ( $47 \text{ mm}$  dia.) of conducting polymer deposited at the surface of a stainless steel mesh have been prepared using a laboratory cell previously described [20]. The electrolysis have been performed at a constant fixed potential value. The morphologic structure of the prepared electropolymerized film depends on the monomer used. For the cyano-ethyl-pyrrole monomer (Figure 11), the surface of the film is smooth, just like the pyrrole films previously prepared [7, 20]; the holes in the stainless steel support are perfectly covered, but the thickness of the deposited films depends both on the applied potential value and also on the duration of electrolysis. For the amino-propyl-pyrrole polymer, the thickness of the film is not as great as those obtained for the cyano-ethyl-pyrrole film; this is a drawback preventing the formation of a regular dense surface film on the stainless steel mesh. Moreover, the film presents surface cracks that may be due to the drying operation (Figure 12). Compared to the  $L_1$  bis-pyridine polypyrrole film, we observed that the film thickness growth occurs only in the presence of an acid which is added to the paratoluene sulfonate sodium solution prepared in an acetonitrile:water solution (3:7) in order to limit oligomer formation. The film surface also has cracks and blisters at the surface of the wires, resulting in a lack of flexibility of the formed polymer which is necessary for adherence to the wires (Figure 13). For membrane use, the electropolymerization duration should be sufficient to cover the blisters and also to clog the hole at the stainless steel wire intersections. Figure 14 shows that a linear relationship exists between the duration of electrolysis and the thickness of the film deduced from SEM, irrespective of the polymer prepared. Nevertheless, the final thickness of the film also depends on the

applied potential which should be at least equal to the potential necessary for the induction of polymerization. At higher potentials there is a risk of producing an overoxidized polymer with poor electrical conductivity.

#### 4. Conclusion

Synthesis of conducting polymer membranes based on the electropolymerization of *N*-[3-(dimethylpyridyl-2-yl)aminopropyl]pyrrole ( $L_1$ ) has been achieved. The electropolymerization conditions were compared with those for other *N* substituted pyrroles containing a nitrogen heteroatom. The behaviour depends on the nature of the attached functions. *N*-(3-acetamidopropyl) pyrrole ( $L_3$ ) and *N*-(2-cyanoethyl) pyrrole ( $L_4$ ) are easier to polymerize than the pyrrole itself. For monomers which contain an amino group ( $L_1$  and  $L_2$ ), the electropolymerization occurs only in acidic solutions and the experimental conditions need to be strictly controlled to obtain sufficient reproducibility. Despite the difficulties encountered in obtaining large surface membranes of conducting pyrrole prepared with *N* substituted pyrrole monomers, and particularly with the *N*-[3-(dimethylpyridyl-2-yl) aminopropyl] pyrrole monomer  $L_1$ , the electropolymerized films prepared will be tested for the transport of ionic species. Such studies are now in progress.

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