

Comparative kinetic studies of polypyrrole electrogeneration from acetonitrile solutions

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The formation and growth of polypyrrole films on platinum electrodes from acetonitrile media has been followed by microgravimetric *ex situ* determination of the polymer grafted on the electrode. Kinetic parameters were also obtained from the charge consumed during polymerization. The electrogenerated polymer films were checked in the background electrolyte by voltammetry and chronoamperometry. Assuming a constant oxidation or reduction charge per unit of polymer weight, these charges were used to obtain the reaction order during the polymerization processes. The kinetics were found to be dependent on $[\text{pyrrole}]^{0.5} [\text{LiClO}_4]^{0.5}$ from gravimetric determination; $[\text{pyrrole}]^{0.4} [\text{LiClO}_4]^{0.5}$ from the polymerization charge; $[\text{pyrrole}]^{0.4} [\text{LiClO}_4]^{0.5}$ from the anodic charge of the control voltammograms and $[\text{pyrrole}]^{0.4} [\text{LiClO}_4]^{0.4}$ from the anodic and cathodic charge of the control chronoamperograms. Good agreement was found between the different methods. The good agreement between order dependence was due to the low water content.

1. Introduction

The electrochemical polymerization of monomers such as pyrrole and thiophene is presently the focus of interest from a mechanistic point of view. A useful and simple mechanism was proposed by Díaz *et al.* [1] which explains electropolymerization by means of an alternative monomer or polymer discharge followed by a radical-cation combination process. This model has been used as a starting point for more elaborate variants, including parallel reactions such as water [2–4] and electrolyte discharges [3], salt attack [5], etc.

Most kinetic studies on conducting polymers were carried out by purely electrochemical methods [6–9]. Only a small portion of the papers published in this field were dedicated to the application of gravimetric techniques in which a quartz crystal microbalance was employed. The polymer generation and the redox activity were followed [10–14].

The influence of the monomer and electrolyte concentration on the processes in which they take part has been studied in order to optimize the film conductivity [15, 16]. In the present work, the monomer and electrolyte, as well as the temperature influence are quantified in the electropolymerization of pyrrole, attempting to obtain gravimetric reaction orders. At the same time the validity of the electrical parameters (electrical charge consumed during polymerization, or electrical charges stored in the polymer during redox processes in the background electrolyte) to obtain kinetic parameters will be evaluated.

2. Experimental details

The present work was carried out in pyrrole and

lithium perchlorate acetonitrile solutions. The pyrrole (Janssen) was distilled in vacuum (64–68°C, 60–70 mm Hg) before use. Anhydrous lithium perchlorate (Janssen) was kept in an oven at 80°C and used without previous purification. Acetonitrile (Panreac synthetic grade) was distilled in presence of P₂O₅, warranting a water content of less than 0.04% in weight, measured by the Karl-Fischer method. A 0.1 M LiClO₄ and 0.1 M pyrrole acetonitrile solution give a water content lower than 0.06 wt %.

Polypyrrole films were synthesized at constant potential. Polarizations were accomplished with the aid of a M273 PAR potentiostat connected to a PS-55 IBM microcomputer. Working and auxiliary electrodes were two platinum sheets of surface area 1 and 4 cm², respectively.

All experiments were performed in a one compartment cell. The reference electrode (saturated calomel, Crison Instruments) was connected to the cell by means of a salt bridge filled up with the background solution (LiClO₄ 0.1 M/acetonitrile). The solution level in the calomel compartment was lower than the level in the working cell so that contamination by chloride ions was prevented.

The generation procedure was as follows. The platinum electrode was first polarized at –100 mV (SCE) for 5 s. The potential was then stepped up to 800 mV (generation potential) and was maintained for varying periods of time (10 s to 100 s).

The weight of the generated films were obtained by weight difference between the uncoated working electrode and the coated electrode, using a 4504 MP8 Sartorius ultramicrobalance (10^{–7} g precision). The temperature of the electrochemical cell was fixed by means of a Huber Ministat cryostat.

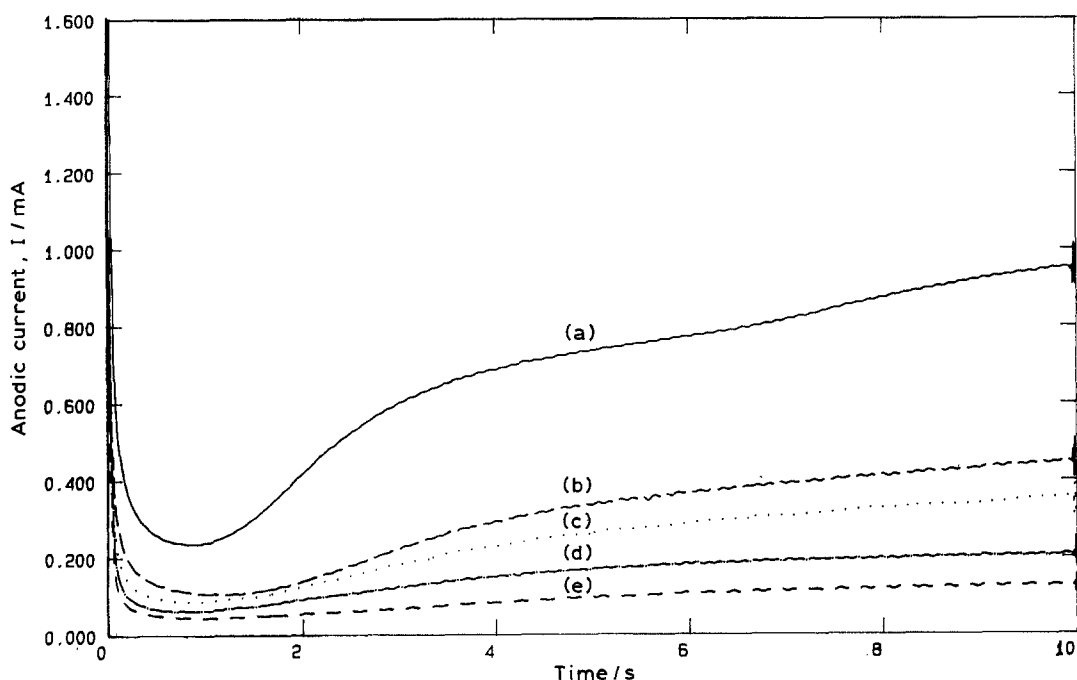


Fig. 1. Chronoamperograms obtained during polypyrrole film generation on platinum at 800 mV. The polymerization solutions were 0.1 M LiClO_4 and different pyrrole concentrations: (a) 1, (b) 0.4, (c) 0.2, (d) 0.1, and (e) 0.05 M in acetonitrile.

After generation the electrode was rinsed with acetonitrile and dried in the air until constant weight. Electrochemical controls of the polymer films were carried out later in the background solution (0.1 M LiClO_4 /acetonitrile). The coated electrode was submitted to a potential sweep between -500 and 1000 mV/SCE at 50 mV s^{-1} , and a square wave of potential between -500 mV and 1000 mV. The platinum electrodes were later burned in a reducer flame and the process was initiated again using a new solution.

3. Results and discussion

3.1. Pyrrole concentration influence

All the polymerizations were carried out by a potential step from -100 mV/SCE to 800 mV. The initial potential was chosen due to the inactivity of the platinum electrode in this potential region. The polymerization solutions were 0.1 M LiClO_4 with different monomer concentrations, in the 0.05 to 1 M range, in acetonitrile.

The chronoamperograms obtained in 1, 0.4, 0.2, 0.1 and 0.05 M pyrrole solutions at 25°C are shown in Fig. 1. The general shape of chronoamperograms has been previously described [17–20]. The first maximum is related to the charge of the double layer after the jump of the electric potential, the oxidation of the metal (if water impurities are present [21, 22]), and the monomer oxidation on the platinum electrode [17–20]. The minimum of the current density is related to the new phase (polymer) nucleation on the electrode. The new maximum of current density present at higher times of polarization can be related to a diffusion control of the monomer molecules, or with the presence of parallel reactions promoting a polymeric passivation [23–29].

After the maxima, currents stabilize at increasing values for greater concentrations of monomer. The electrical charge flowing through the electrode increases with time promoting a linear increase of the polymer weight (Fig. 2). The flow of increasing current densities at greater concentrations of monomer and constant polarization times promotes steeper slopes on the correlative straights. When a polymer film obtained after a short polarization time was dried, weighed and polarized again in the working solution to obtain a new film corresponding to a longer polarization time, gravimetric results were not reproducible. Thus, each of the experimental points on Fig. 2 were obtained from independent separate experiments (clean electrodes, and cells and a new working solution).

The physical meaning of the slopes is the rate of

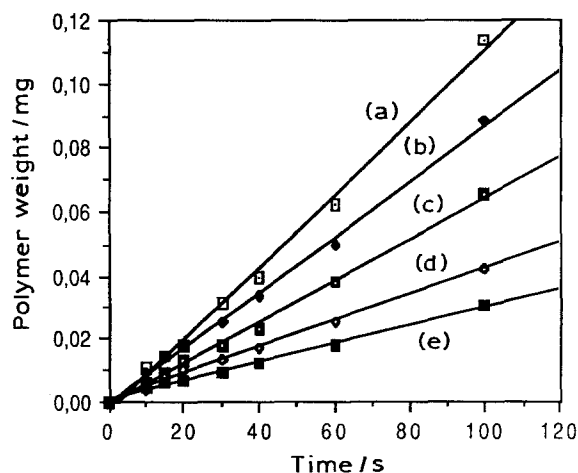


Fig. 2. Evolution of polypyrrole film weight with polymerization time for different pyrrole concentrations employed in synthesis at 800 mV: [Py]: (a) 1, (b) 0.4, (c) 0.2, (d) 0.1 and (e) 0.05 M. $[\text{LiClO}_4] = 0.1$ M, $T = 25^\circ\text{C}$.

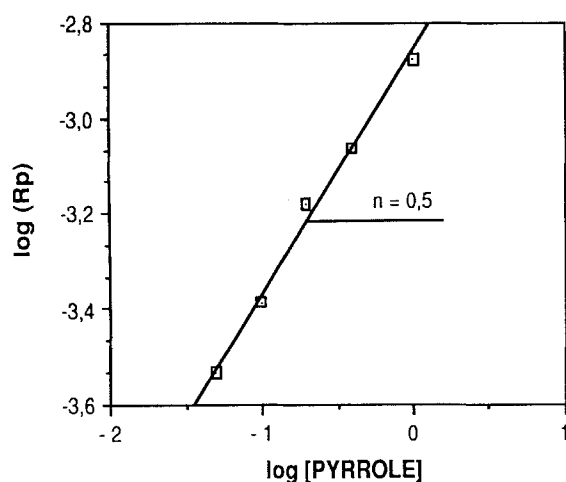


Fig. 3. Determination of the reaction order relative to pyrrole concentration from gravimetric results (R_p values were obtained from the slopes of the weight-time lines for different pyrrole concentrations).

polymerization: *i.e.* polymer weight produced by unit of time under the defined experimental parameters. Figure 2 shows an increase in polymerization rate (R_p) at increasing monomer concentrations. In this way an order dependence on the monomer may be obtained:

$$R_p = k[\text{monomer}]^a$$

A double logarithmic representation of the R_p against monomer concentration gives a straight line whose slope is the order dependence. Figure 3 shows such a linear variation; in this case the empirical reaction order is 0.5:

$$R_p = k[\text{pyrrole}]^{0.5}$$

3.2. Electrolyte influence

Polypyrrole films were electrogenerated at 800 mV in 0.1 M pyrrole, and different LiClO_4 concentrations in acetonitrile solutions. Four different LiClO_4 concentrations were studied: 0.1, 0.25, 0.3 and 0.4 M. The upper limit of concentration is limited by the solubility of the electrolyte in acetonitrile.

The experimental results shown in Fig. 4 were obtained. An increase in the polymer production is observed at increasing electrolyte concentrations. As above, the slope of each line is the polymerization rate: polymer weight produced per unit of time. The existence of an order dependence of the polymer production relative to the LiClO_4 concentration can be observed according to:

$$R_p \propto [\text{LiClO}_4]^b$$

A representation of $\log R_p$ against $\log [\text{LiClO}_4]$ implies a straight line, as was obtained experimentally (Fig. 5). The order dependence for LiClO_4 , determined from the slope, is 0.5.

The experimental results allow us to write the empirical kinetics for the process, followed by gravimetric determination of the polymer generated on the electrode. Thus,

$$R_p = k[\text{pyrrole}]^{0.5} [\text{ClO}_4^-]^{0.5}$$

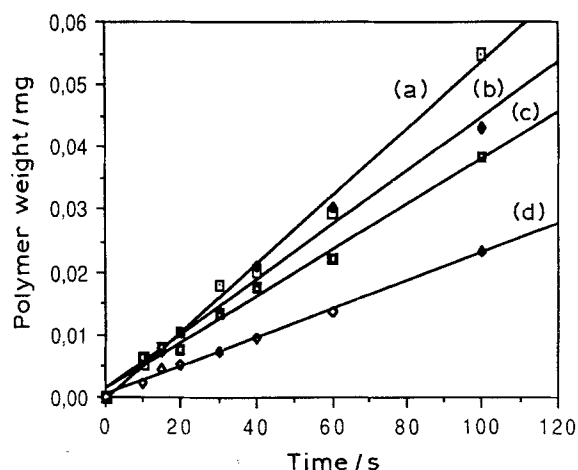


Fig. 4. Evolution of polypyrrole film weight with polymerization time for different LiClO_4 concentrations employed in synthesis at 800 mV. $[\text{LiClO}_4]$: (a) 0.6, (b) 0.3, (c) 0.25 and (d) 0.1 M. $[\text{pyrrole}] = 0.1 \text{ M}$, $T = 25^\circ \text{C}$.

Such a high reaction order relative to the electrolyte is difficult to explain by the influence of the electrolyte on the polymer oxidation exclusively. Other, even more complex, explanations take into account the parallel transfer processes occurring on the electrode. The direct influence of the ClO_4^- anions on the polymerization process has also been suggested, by the absence of polymerization in other supporting electrolytes [30, 31].

3.3 Temperature influence

Working with 0.2 M pyrrole and 0.1 M LiClO_4 acetonitrile solutions, *ex situ* microgravimetric kinetics were followed at different temperatures: -10 , 0 , 20 , 30 and 40°C . The experimental kinetics shown in Fig. 6 were obtained. As is usual in this work each experimental point was obtained through a separate experiment.

Linear variations of the polymer weight against polarization time were observed. Increasing polymer weights were obtained at increasing temperatures: the

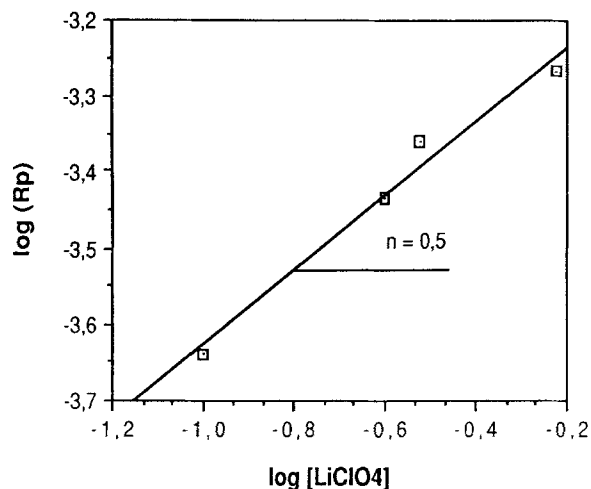


Fig. 5. Determination of the reaction order relative to lithium perchlorate concentration from gravimetric results (R_p values were obtained from the slopes of the weight-time curves for different LiClO_4 concentrations).

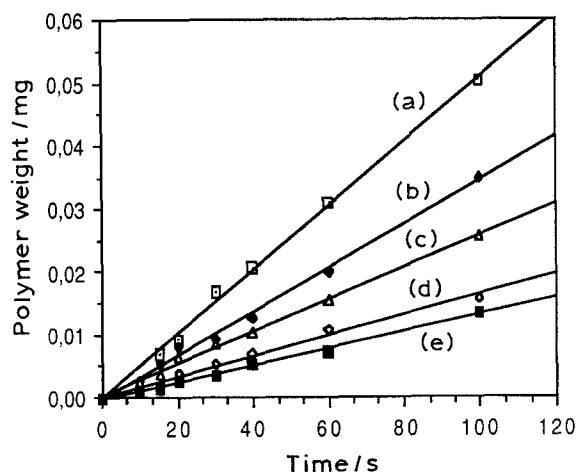


Fig. 6. Evolution of polypyrrole film weight with polymerization time for different temperatures employed in synthesis at 800 mV. T : (a) 40, (b) 30, (c) 20, (d) 0 and (e) -10°C . $[\text{pyrrole}] = 0.2\text{ M}$, $[\text{LiClO}_4] = 0.1\text{ M}$.

polymerization process is favoured by the increase of the experimental temperature. From the representation of the $\ln R_p$ against $1/T$ function an apparent activation energy of 17.4 kJ mol^{-1} was obtained (Fig. 7).

3.4. Polymerization charges: monitoring of kinetics

When single charge transfer processes occur at the electrode, kinetic parameters can be obtained from the electrochemical data. One of the more direct electrochemical magnitudes related to an electropolymerization process is the electrical charge consumed during polymerization. Quantitative correlations have already been proposed between electrical charge and the thickness of the polymer layer [32, 33].

For some electrochemically initiated polymerizations taking place at high overpotential, parallel reactions occur during the polymerization process giving changes in the current efficiency when experimental parameters change [23–26]. In this study, the polarization potential was distant from the electrolyte discharge. Only the generation of oxides from residual

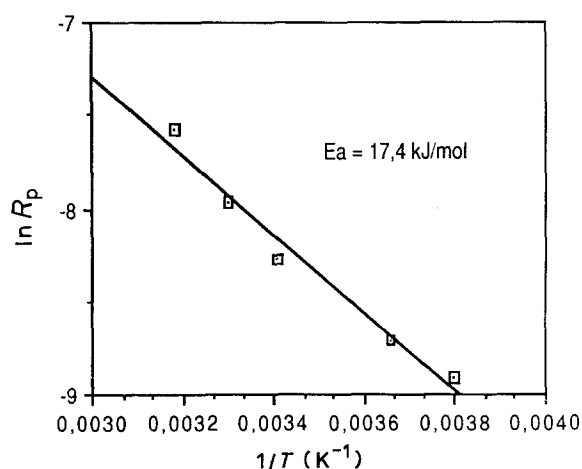


Fig. 7. Determination of the activation energy from gravimetric results (R_p values were obtained from the slopes of the weight-time lines for different temperatures).

water can occur on the platinum and a possible slow water discharge can take place on polypyrrole [27–29]. Under these conditions electrical parameters are suitable for obtaining kinetic parameters.

In this way, electrical charge consumed during polymerization may be obtained by integration of the relative chronamperograms. The results for different monomer concentrations and polarization times are shown on Fig. 8a. The electrical charge spent to generate polymer films at increasing polarization times, starting with a clean electrode for each experiment, grows linearly. For the same polarization times increasing constant current densities were obtained at increasing concentrations of monomer for polarization times exceeding 10 s (Fig. 1 shows the tendency to this stabilization).

If we assume a linear relation between consumed electrical charge and produced polymer weight of the form

$$Q = kM$$

where Q is the electrical charge spent during polarization (mC), M is the polymer weight generated during polarization (mg), and k is the electrical charge spent to generate a unit of polymer mass (C g^{-1}). The slopes of the straight lines are

$$\frac{dQ}{dt} = k \frac{dM}{dt} = kR_p$$

where R_p is a polymerization rate (polymer weight generated by unit of time).

Now as we are seeking an order dependence from the expression

$$R_p = k' [\text{pyrrole}]^a$$

then we must take the double logarithmic representation given by R_p against monomer concentration. From the above expression for the slopes, taking logarithms, we have

$$\log R_p = \log \frac{dQ}{dt} - \log k$$

Therefore,

$$\log \frac{dQ}{dt} = \log k + \log k' + a \log [\text{pyrrole}]$$

Hence, a representation of $\log dQ/dt$ against $\log [\text{pyrrole}]$ will give a straight line, the slope of which is the order of the reaction related to the monomer concentration. This is shown in Fig. 8 where an average reaction order of 0.4 is obtained. The slight curvature of the experimental points is related to a small increase observed in the current efficiency when the monomeric concentration rises. The subsequent empirical kinetics may be written as

$$R_p = k [\text{pyrrole}]^{0.4}$$

From the electrical charge consumed during polymerizations carried out at different electrolyte concentrations, an order dependence of 0.5 was obtained. The subsequent empirical kinetics are written as

$$R_p \propto [\text{ClO}_4^-]^{0.5}$$

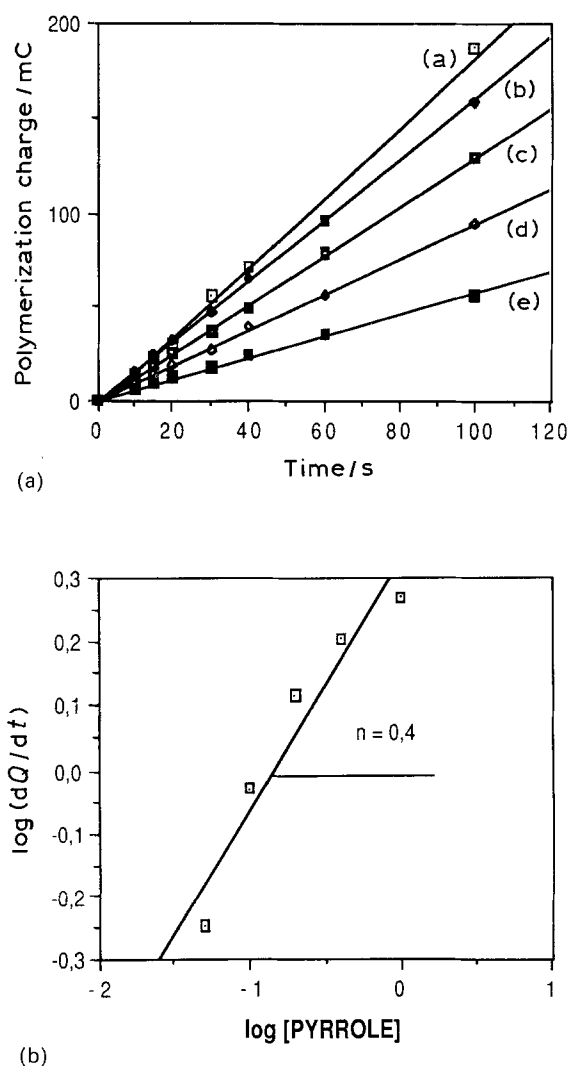


Fig. 8. (a) Evolution of the charge involved in polypyrrole film generation processes at 800 mV with polymerization time for different pyrrole concentrations employed in synthesis. [Py]: (a) 1, (b) 0.4, (c) 0.2, (d) 0.1 and (e) 0.05 M. ([LiClO₄] = 0.1 M, *T* = 25°C. (b) Determination of the reaction order relative to pyrrole concentration from the charges consumed in film generation.

These reaction orders relative to monomer and electrolyte concentrations are depicted in Table 1, along with gravimetric reaction orders, as well as correlation coefficients of the straight lines.

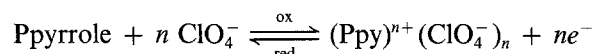
3.5. Order dependence from stored charge

The polypyrrole films electrogenerated on the platinum electrode can be oxidized and reduced in the background electrolyte [34]. It is accepted that the oxidation process takes place by accumulation of a positive

Table 1. Reaction orders with correlation coefficients (*r*), relative to pyrrole and LiClO₄ concentrations obtained from gravimetric and polymerization charge measurements

| | Gravimetric | <i>r</i> | Generation charge | <i>r</i> |
|-----------------------|-------------|----------|-------------------|----------|
| [Pyrrole] | 0.5 | 1.00 | 0.4 | 0.96 |
| [LiClO ₄] | 0.5 | 0.99 | 0.5 | 0.99 |

charge every four monomeric units:



Accepting this redox process the electrical charge consumed during an oxidation or reduction process must be proportional to the amount of polymer electrogenerated. Thus,

$$Q_{\text{redox}} = k' M$$

where Q_{redox} is the electrical charge implicated in the oxidation or reduction process, M is the electrogenerated polymer (mg), and k' is the electrical charge stored/mg of polymer (storage efficiency).

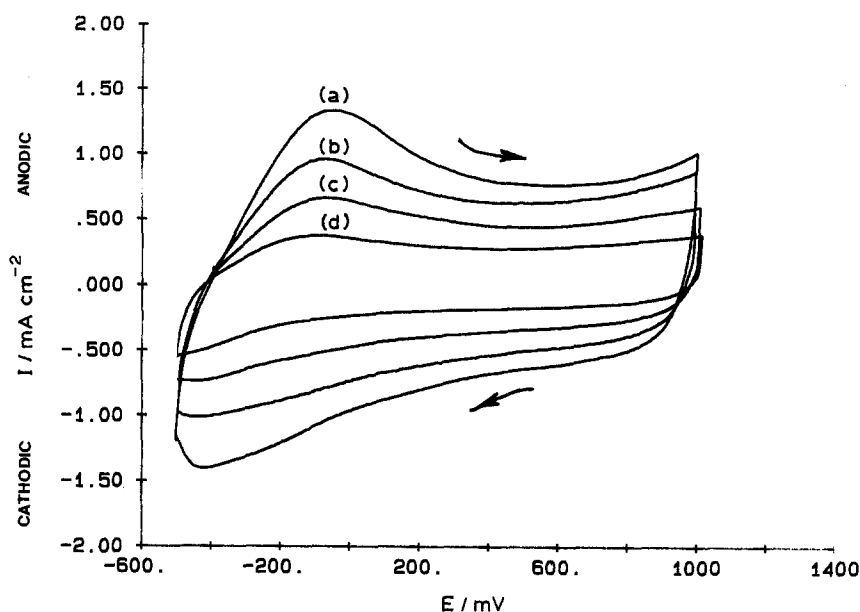
If we check all the polymer films, after synthesis, in the background solution by cyclic voltammetry (or potential steps), choosing adequate potential limits (or anodic and cathodic potentials), the electrical charge needed to oxidize or reduce the polymer film can be obtained. The variation of the redox charges between polymer films obtained at different polarization times is given by

$$\begin{aligned} \frac{dQ_{\text{redox}}}{dt} &= k' \frac{dM}{dt} = k' R_p \\ &= k' k'' [\text{pyrrole}]^a [\text{ClO}_4^-]^b \end{aligned}$$

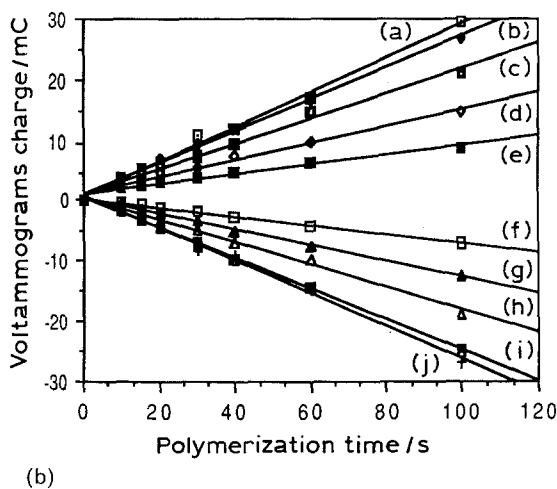
In this way reaction orders could be obtained from the stored charge in films generated, at different polarization times, from solutions with different monomer concentrations or different electrolyte concentrations, and checked in the background electrolyte. Figure 9a shows the voltammograms of control of polypyrrole films electrogenerated by polarization at 800 mV during 100 s in 0.1 M LiClO₄ solutions and different pyrrole concentrations: (a) 0.4 M, (b) 0.2 M, (c) 0.1 M and (d) 0.05 M. The electric potential was swept between -500 mV and 1000 mV/SCE at 50 mV s⁻¹ in 0.1 M LiClO₄ acetonitrile solution. Increasing current densities were obtained from polymer films electrogenerated at increasing monomer concentrations. By integration of the area under the anodic voltammogram and the line of zero current density, the stored charge (Q_{ox}) was obtained. The integration of the area between the cathodic branch and the line of zero current density give us the reduction charge (Q_{red}).

All the Q_{ox} and Q_{red} charges obtained from the control voltammograms of the polypyrrole films weighed on Fig. 2 are shown on Fig. 9b. The oxidation and reduction charges grow linearly when the checked polymer films were generated at increasing polarization times and constant electrical and chemical parameters. At constant generation times, increasing charges were implicated in the oxidation and reduction of the polymer films generated at higher monomer concentrations.

The representation for the log of the slopes dQ_{ox}/dt or dQ_{red}/dt against the log of the pyrrole concentration gives two straight lines, the slopes (order of dependence) of which are shown on Table 2. The order dependencies relative to the electrolyte were



(a)



(b)

Fig. 9. (a) Control voltammograms (between -500 and 1000 mV at 50 mV s $^{-1}$) of polypyrrole films in the background electrolyte (0.1 M LiClO $_4$ acetonitrile solution). These films were generated at 800 mV during 100 s. Polymerizations were carried out in 0.1 M LiClO $_4$ and different pyrrole concentrations (a) -0.4 M; (b) -0.2 M; (c) 0.1 M; (d) -0.05 M) in acetonitrile solutions. (b) Evolution of the charge involved in voltammetric controls (from -500 to 1000 mV at 50 mV s $^{-1}$) of polypyrrole films with polymerization time. These films were generated at 800 mV in LiClO $_4$ 0.1 M and different monomer concentrations (see figure) in acetonitrile solutions. [M]: (a) 1, (b) 0.4, (c) 0.2, (d) 0.1, (e) 0.05, (f) 0.05, (g) 0.1, (h) 0.2, (i) 0.4, (j) 1 M.

obtained from the control voltammograms, and the order dependencies relative to the electrolyte and monomer from the control chronoamperograms. In the same table are given the correlation coefficients for the straight lines from which the different reaction orders were obtained.

A general view of the table shows good agreement between order dependence obtained by different methods. The best correlation coefficients were obtained from the gravimetric results. This fact may be due to the presence of parallel discharge reactions on the electrode promoting a drop in the current efficiency [26, 29] or a polymer passivation [37]. The

relatively close coincidence between order dependence obtained from the different ways is a consequence of the working conditions: that is a potential distant from the electrolyte discharge (2.7 V/SCE) and in presence of a very low water content (0.06%). These facts lead to relatively constant current efficiency (6.7×10^{-4} mg mC $^{-1}$) and a storage efficiency of 2.5×10^2 mC mg $^{-1}$. The independence of those parameters with the polymer thickness (polarization time) in the range of thicknesses studied allow for the determination of precise empirical kinetics parameters by the different methods. Those conditions are not attained by many of the electropolymerization processes in other media and a tendency to stabilization of the produced polymer weight at long polarization times [26, 35] or high temperatures [25] is observed.

Table 2. Reaction orders and correlation coefficients (r), relative to pyrrole and LiClO $_4$ concentrations obtained from the stored charge data (voltammetric and potential step controls)

| | Volt. oxid. | r | Volt. red. | r | Step. oxid. | r | Step. red. | r |
|---------------|-------------|------|------------|------|-------------|------|------------|------|
| [Pyrrole] | 0.4 | 0.96 | 0.4 | 0.94 | 0.4 | 0.95 | 0.4 | 0.96 |
| [LiClO $_4$] | 0.5 | 1.00 | 0.4 | 0.99 | 0.4 | 0.99 | 0.4 | 0.99 |

4. Conclusions

The electrogeneration of polypyrrole from acetonitrile solution followed by microgravimetry gives an order dependence of 0.5 which is related to both the

monomer and the electrolyte concentrations.

$$R_p = k[\text{pyrrole}]^{0.5}[\text{ClO}_4^-]^{0.5}$$

The kinetic parameters were also calculated from the electrical charge consumed during polymerization. Supposing a linear dependence between the produced polymer weight and the polymerization charges, the order dependencies were found to be 0.4 relative to pyrrole and 0.5 relative to ClO_4^- . Thus,

$$R_p = k'[\text{pyrrole}]^{0.4}[\text{ClO}_4^-]^{0.5}$$

A good agreement was found between order dependence obtained from gravimetric results and polymerization charges. This coincidence is related to the employed potential of polarization distant from the electrolyte discharge. No significant parallel reactions take place on the electrode and the current efficiency remains practically constant during polymerization.

The current storage efficiency also stays constant when the thickness of the polymer layer increases. That means there is no presence of parallel reactions, producing polymer degradation and passivation, during polymerization. Under these conditions the order dependencies can be obtained from the contuse voltammograms or chronoamperograms of the polymer film in the background solution. But the best of the correlations was obtained from the gravimetric measurements thus pointing to the presence of not very fast parallel or consecutive reactions giving no polymeric products, that is when polypyrrole is electrogenerated in acetonitrile having water contents lower than 0.06% in weight.

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