

Effect of the Temperature on the Electrochemical Synthesis of Polypyrrole Dodecylsulfate

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Desenvolvemos um estudo sistemático do efeito da temperatura na síntese eletroquímica do polipirrol dodecilsulfato. Estes efeitos foram detectados seguindo as mudanças na eletroatividade e na morfologia dos filmes obtidos, usando voltametria cíclica, cronoamperometria, perfilometria e microscopia eletrônica de varredura. Filmes de poli(pirrol) preparados a 5 e 10 °C mostram uma melhor eletroatividade, uma superfície homogênea e morfologia superficial globular. Como consequência destas propriedades, a sua eletroatividade é reproduzível. Aumentando a temperatura de síntese acima destes valores obtêm-se filmes com baixa eletroatividade, superfície irregular e morfologia superficial heterogênea.

A systematic study of the effect of the temperature on the electrochemical synthesis of polypyrrole dodecylsulfate was performed. The effect was detected by following the changes in the electroactive and morphological properties of the polymer, using cyclic voltammetry, chronoamperometry, profilometry and scanning electron microscopy. Polypyrrole films prepared at 5 and 10°C show better electroactivity, a homogeneous surface and globular surface morphology. As a consequence their electroactive properties are reproducible. By increasing the synthesis temperature above these values, the films present a loss of electroactivity, an irregularly shaped surface and heterogeneous surface morphology.

Key words: *polypyrrole films; polypyrrole-DDS; polymer morphology.*

Introduction

Recently, intrinsically conductive polymers have been intensively studied due to their potential technological applications and to the extremely interesting challenges they present to chemists. The electrochromic properties of these materials place them as potential candidates for use in electrochromic devices^{1,2}. On the other hand, recently published work pointed to the possibility of using these materials in photogalvanic cells. For these applications the polymer should be prepared by the electrodeposition method and it is essential to have materials with reproducible properties. The properties of conductive polymer films obtained by electrochemical polymerization are influenced by several variables: polymerization method (galvanostatic, potentiostatic or potentiodynamic), electrolyte type and concentration, monomer concentration, solvent and temperature^{3,4}. By changing the synthesis temperature, the polymerization kinetics are affected and, as a consequence, morphology differences are expected. For poly(thiophene), the polymerization charge efficiency increases as the synthesis temperature decreases⁵.

Among conductive polymers, polypyrrole is the one which has attracted the most attention⁶⁻¹⁰. Its stability to repeated

electrochemical redox cycles and its electrochromic contrast are enhanced by using surfactants as counter ions in its synthesis¹¹. However, a significant effect of the synthesis temperature was observed when preparing these films. This motivated us to systematically study this effect in the temperature range of 5 to 50 °C.

Experimental

Polypyrrole films were electrodeposited on ITO electrodes (indium doped tin oxide coated glass slides, Nippon Sheet Glass, lot. No IM12, 100Ω) in a three electrode single cell with a cooling jacket. An aqueous 0.05M pyrrole (Aldrich, distilled) and 0.05M sodium dodecylsulfate (Fluka) solution under a current density of 0.1 mA.cm⁻² for 6.0 min. was used. A platinum sheet was used as counter electrode. Samples were prepared in triplicate for the characterizations.

Electrochemical characterization was carried out by cyclic voltammetry and chronoamperometry using an aqueous 0.5 M KCl solution. An Omnimetra PG-05 Potentiostat interfaced to a PC/AT computer was used for all measurements. An Alpha-Step Profilometer and a JEOL Scanning Electron Microscope were used to characterize the surface morphol-

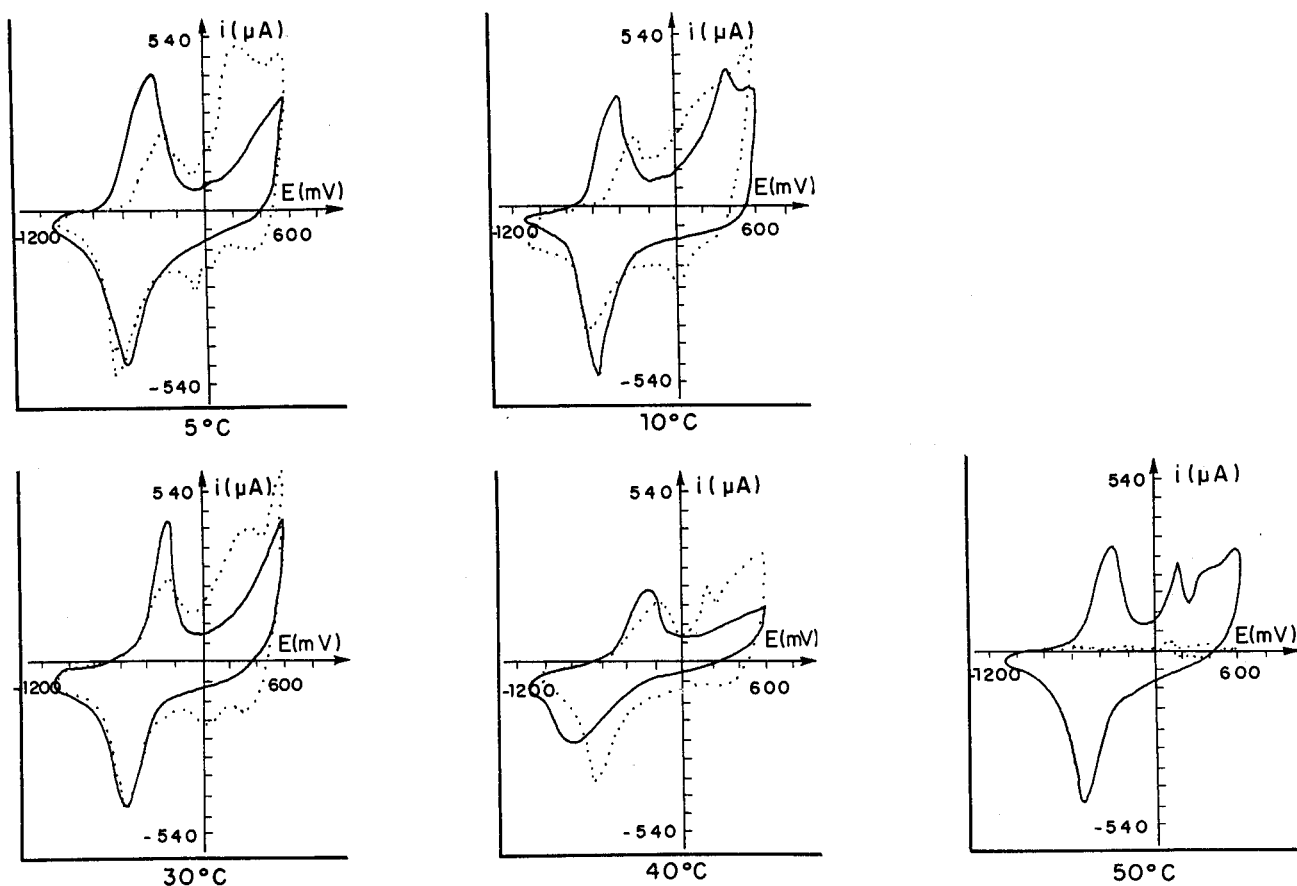


Figure 1. Cyclic voltammetry of the PPyDS films obtained at the temperatures indicated. Initial CV (—) and CV after 1000 double potential steps (....).

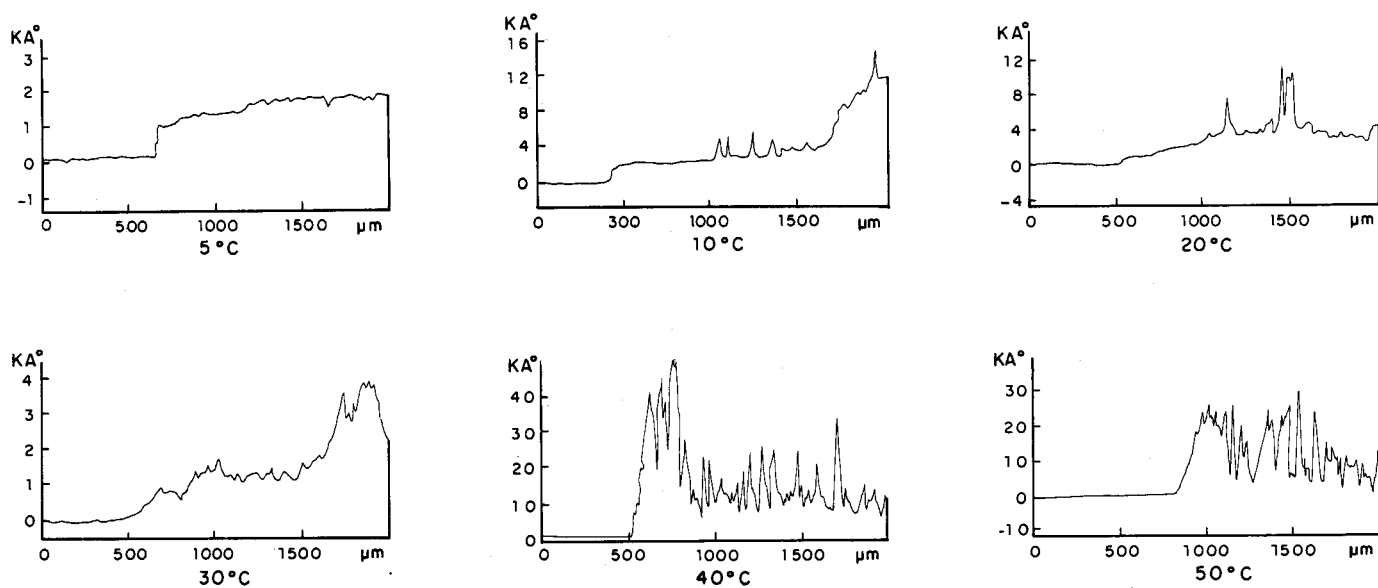


Figure 3. Profiles of PPyDS films obtained at the temperatures indicated.

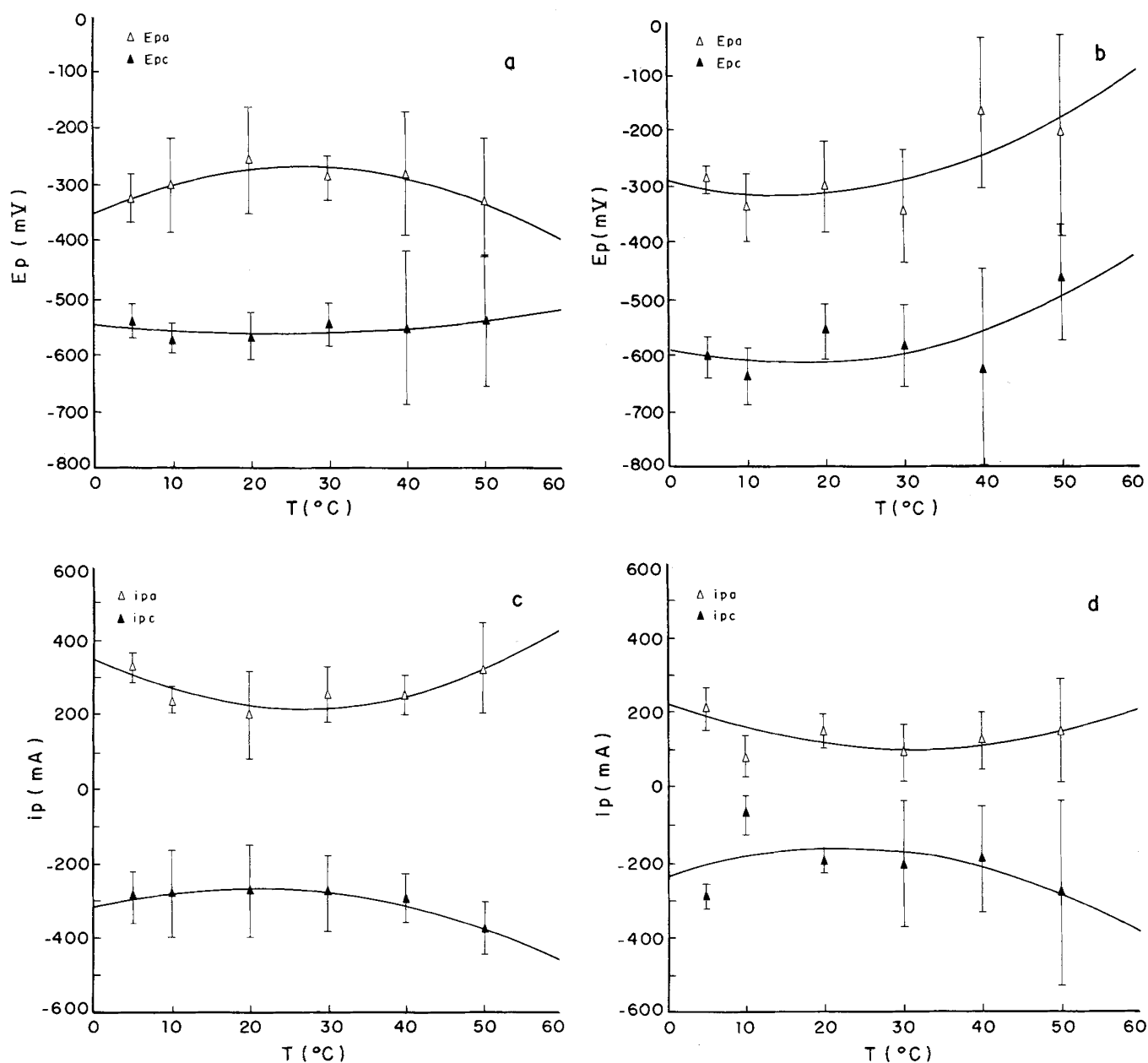


Figure 2. Variation of anodic and cathodic peak potentials and anodic and cathodic peak currents (E_{pa} , E_{pc} , i_{pa} and i_{pc} , respectively) as a function of synthesis temperature. Curves **a** and **c** contain data obtained from the initial CV and **b** and **d** are from CV measured after 1000 double potential steps.

ogy of the films. For the microscopy the samples were coated with gold.

Results and Discussion

Electrochemical characterization. In order to characterize each of the films obtained at the different temperatures, we measured an initial cyclic voltammogram at $50 \text{ mV}\cdot\text{s}^{-1}$ and subsequently submitted it to 500 double potential steps at $\Delta E = -0.90$ and 0.1 V (7 and 5 s, respectively). After this, we again measured the cyclic voltammogram in order to control

the redox stability of the material and resubmitted it to another 500 double potential steps with a final cyclic voltammetry measurement. The cyclic voltammograms are shown in Figure 1. From these curves we obtained the anodic and cathodic peak potentials and the anodic and cathodic peak currents; E_{pa} , E_{pc} , i_{pa} and i_{pc} respectively. In Fig. 2 we show the variation of these parameters as a function of the synthesis temperature, together with the calculated standard deviation (three films). We observe that samples obtained at temperatures lower than $30 \text{ }^\circ\text{C}$ show only a small shift of the peak potentials, even after the two series of double step chronoam-

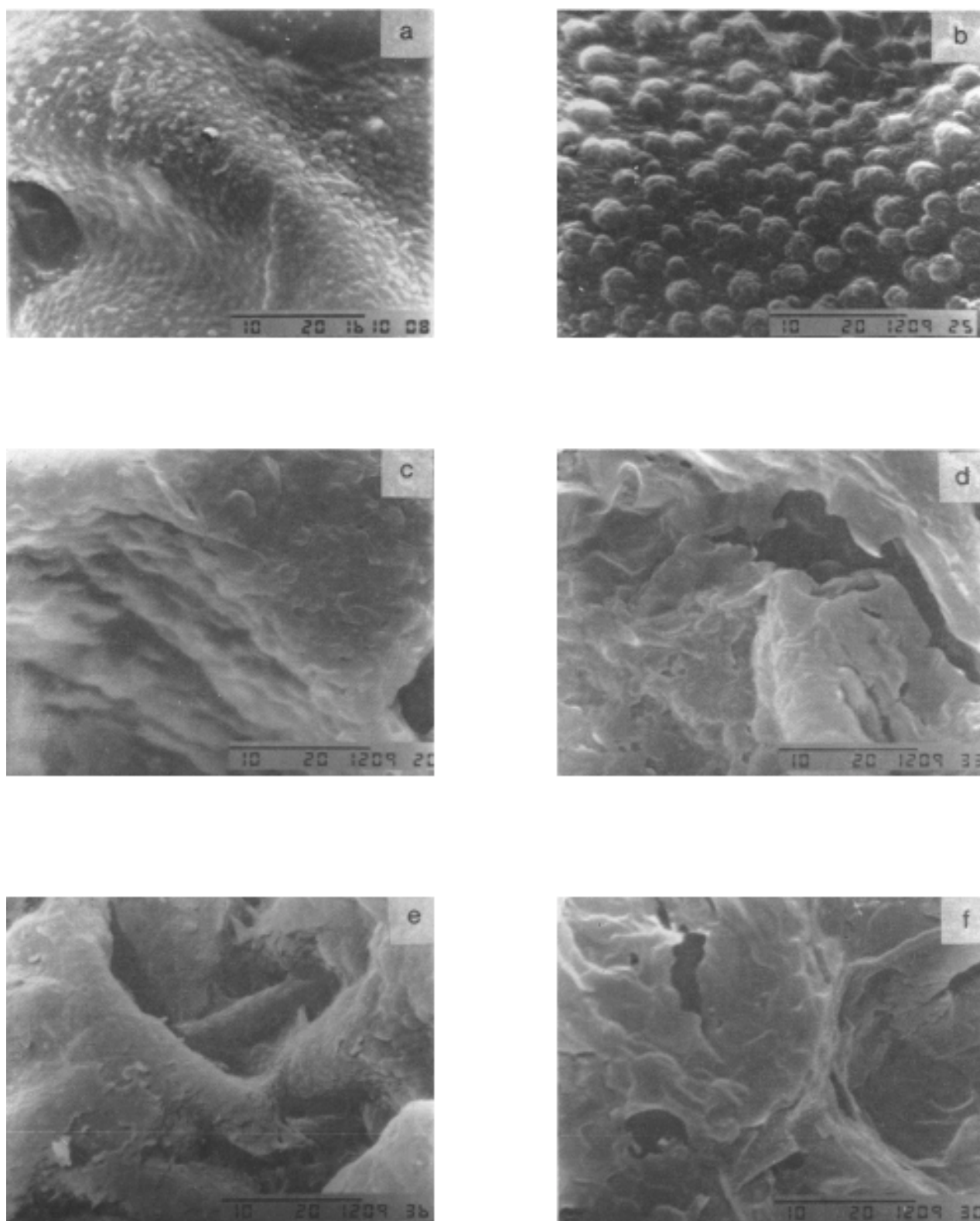


Figure 4. Scanning electron micrography of the PPyDS films obtained at the temperatures: a) 5, b) 10, c) 20, d) 30, e) 40 and f) 50 °C. Bar indicates the scale in μm .

perometry experiments. In particular, films prepared at 5 °C show a 10% shift with a standard deviation of the same order of magnitude. The reproducibility of the electrochemical parameters for films prepared at temperatures above 30 °C is considerably lower, as observed by the increase in the standard deviation shown in the curves.

The standard potential E_0 , characteristic for each chemical compound, is constant (-0.45V) after the double potential chronoamperometry experiments only for films prepared at 5 and 10 °C. For higher synthesis temperatures the shift of the standard potential indicates a chemical modification of the material after the double potential step experiments.

Surface morphology characterization. The profiles of the films obtained at different temperatures are shown in Fig. 3. The region of the film measured was near to its edge in order to evaluate the thickness variation. A pronounced increase in the surface rugosity of the films is observed as the synthesis temperature increases. This causes an increase in the surface area of the films; as a consequence the current densities used in the synthesis decrease markedly as a function of time. This rugosity increase is also responsible for the irreproducibility of the electrochemical parameters for films prepared at temperatures above 30 °C.

In Fig. 4 we show the scanning electron micrographs, SEM, at similar magnification degrees for PPyDS films. These show significant modifications of the surface morphology as a function of synthesis temperature. Films prepared at 5 and 10°C show a globular morphology. The globules are densely and uniformly distributed with an average diameter of 2.5µm and a cauliflower shape. The globules are constituted of smaller cauliflower shaped globules in a fractal fashion. The globules can still be seen in the SEM of films prepared at 20 °C. However, for films prepared at temperatures above 20 °C no globules can be observed; the surface of the films are covered with scales. The film prepared at 50°C shows microcracks on its surface.

Conclusions

The surface morphology measurements indicated that films of PPyDS with a regular shape can be obtained only at synthesis temperatures below 10 °C. This is confirmed by the reproducibility of the electrochemical parameters for different films prepared at these temperatures.

Upon increasing the synthesis temperature there is an alteration of the growth rate of the polymeric chains and also a change in the macroscopic nucleation and growth steps for the polymer film. The smoother surface of the films prepared at lower temperatures suggest a bidimensional growth parallel to the electrode surface. The nucleation occurs homogeneously on all the electrode surface. By increasing the temperature the reaction rate increases and the film growth seems to be three-dimensional with concomitant nucleation and growth producing a loss of the initial globular morphology.

We conclude that polypyrrole films prepared in the presence of dodecylsulfate surfactant present a homogeneous and uniform surface morphology and reproducible electrochemical properties only when synthesized at temperatures below 10 °C.

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