

# Investigation on Dendrite-Like Fiber Formation in the Electropolymerization of Pyrrole

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Durante a polimerização potencioestática ou galvanostática de pirrol em água usando surfactante como eletrólito, observamos o crescimento de fibras poliméricas a partir da superfície do eletrodo de trabalho em um processo de nucleação semelhante à formação de dendritos. Este processo ocorre depois da polimerização da primeira camada de polipirrol na superfície do eletrodo de platina e é principalmente devido à oxidação do pirrol limitada por difusão na interface polipirrol/eletrólito. A microscopia eletrônica de varredura indica uma morfologia fibrilar para estas fibras de polipirrol.

Growth of polymeric fibers from the working electrode surface, in a dendrite-like nucleation process, has been observed during potentiostatic or galvanostatic polymerization of pyrrole in water using a surfactant as electrolyte. It occurs after the polymerization of a first layer of polypyrrole on the surface of the platinum electrode and is mainly due diffusion-limited oxidation of pyrrole at the polypyrrole/surfactant electrolyte interface. Scanning electron microscopy (SEM) indicates fibrillar morphology for these polypyrrole fibers.

**Key words:** *polypyrrole, conductive polymer, electropolymerization*

## Introduction

Polypyrrole has been known since the beginning of the century as "pyrrole black". It was electrochemically synthesized as a conductive polymer, for the first time, in the form of films by Weiss *et al.* in 1965<sup>1</sup>. Later on it was extensively studied by Diaz *et al.*<sup>2</sup>. Conductive (1 to 100 S/cm) and self-supported films of polypyrrole were obtained by potentiostatic (1.2 V vs. SCE) anodic polymerization of pyrrole in acetonitrile containing a tetraalkylammonium salt. The polymer is obtained on a platinum working electrode in the form of a self-supported film of 20 to 500 micrometers thickness. Its properties depend on the polymerization conditions, such as: current density, pH, electrolyte and counter-ion. Several articles have recently reviewed polypyrrole electrochemistry<sup>3-5</sup>. It has also been reported by several authors that flexible polypyrrole films are obtained in the presence of polyelectrolytes and surfactants<sup>6-8</sup>. A systematic study of the electropolymerization conditions in the presence of surfactants has been reported<sup>9</sup>.

Electrochemical crystallization with the growth of dendrites is a well known process and is reported to occur during the discharge of lead/sulphuric acid batteries. Lead sulphate dendrites grow on lead crystal electrode surfaces after the early stages of the anodic oxidation, leading to amorphous active lead sulphate<sup>10</sup>. The dendritic formation on polypyrrole was first mentioned in the literature by Diaz when electropolymerizing pyrrole potentiostatically in the presence of p-toluenesulphonate salts<sup>11</sup>. Wegner<sup>12</sup> *et al.* also mentioned the dendrite-like electropolymerization of pyrrole in the presence of surfac-

tants at current densities higher than 5 mA/cm<sup>2</sup>. Other authors pointed out that dendrite formation on the surface of polypyrrole depends on the dopant anion used, although, according to the same authors, the anions themselves are not incorporated into the structures<sup>13</sup>. Later on, reports on the static and dynamic diffusion limited pyrrole electrochemical polymerization in the presence of p-toluenesulphonate was interpreted in terms of fractal dimensions modeling<sup>12-14</sup>. These authors worked with a two dimensional electrochemical cell under various conditions.

Our present interest is focused on studying the changes of the mechanical properties of polypyrrole obtained in aqueous electrolytes containing different concentrations of sodium dodecylsulphate (SDS) with different current densities. In this study we observed the dendrite-like formation of polypyrrole fibers when working at high current densities, i.e., greater than 5 mA/cm<sup>2</sup>. The fibrillar morphology of the dendrites was characterized by SEM.

## Experimental

For the electropolymerization we used a FAC model 200 potentiostat/galvanostat, deionized water and freshly distilled pyrrole. Commercially available SDS was extracted with dry diethylether and recrystallized from ethanol before use. As a working electrode we used a polished platinum plate coated on one side with an insoluble insulating polymer and as counter electrode a platinum wire. In a typical experiment we polymerized galvanostatically (3-7 mA/cm<sup>2</sup>) for one hour using a concentration of 0.05 M

of pyrrole and 0.025 M of SDS. Scanning Electron Microscopy, SEM, was performed on a Jeol JSM-1300 instrument at 25 kV. Film conductivities were measured by the four-point-probe method.

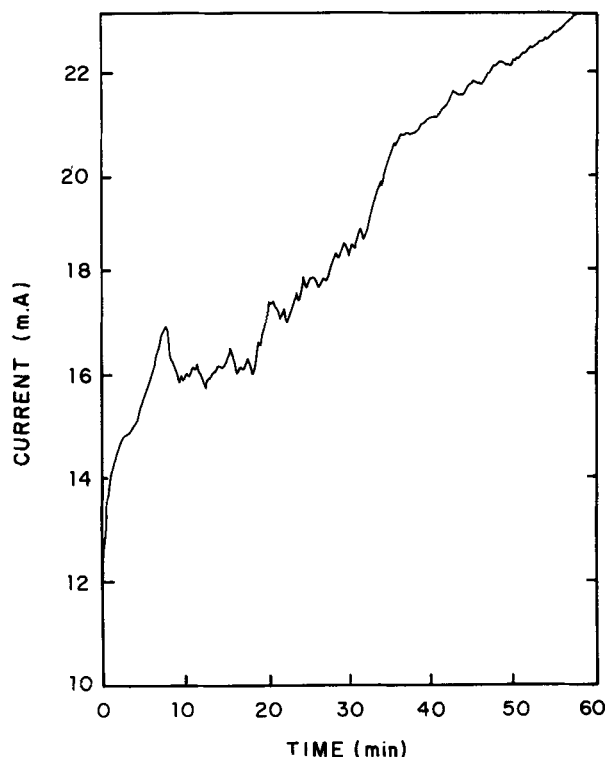
### Results and Conclusions

As reported in the literature, the electrochemical polymerization of pyrrole occurs by the anodic oxidation of the monomer, forming a cation-radical which dimerizes with the release of hydrogen. These dimers are consequently reoxidized with the subsequent formation of another cation-radical, producing oligomers and propagating the reaction with electrochemical stoichiometry and film formation.<sup>3-5</sup>

The formation of the initial layer of polypyrrole at the platinum electrode surface is undoubtedly occurring by pyrrole oxidation at the Pt/electrolyte-solution interface. However, after the polymerization of the first polypyrrole layer, experimental results show evidence that further reaction occurs at the polymer/solution interface. When potentiostatic deposition of conducting polymers is performed, a linear increase of current with time in the early stages of the reaction does suggest that the active electrode area also increases, resulting from the expansion of the conducting phase<sup>17-18</sup>.

We observed the dendrite-like formation of fibers at the electrode area covered by polypyrrole after the initial formation of a film on the electrode surface (ca. 5 mm). This occurred when performing the galvanostatic polymerization of pyrrole at current densities higher than 5 mA/cm<sup>2</sup>, in the presence of SDS as electrolyte. These fibers grow preferentially near the surface of the electrolyte solution. Fiber formation occurs despite the change of surfactant concentration (from 0.6 to 7.0 × 10<sup>-2</sup>M) at constant current densities. Also, stirring the solution, either mechanically (with a magnetic bar) or with ultrasound (40 kHz) showed little effect on fiber formation. When the polymerization is performed potentiostatically (1.15 V vs. SCE) we observe an increase in the current as a function of time (Figure 1), indicating active surface increase with fiber formation. Dodecylsulphate absorption bands are observed in the FT-infrared spectra of the films and of the fibers after extraction with water. Thermogravimetric analysis of polypyrrole/dodecylsulphate shows an initial weight loss inflection at the same temperature as observed for pure sodium dodecylsulphate. These results indicate the incorporation of the surfactant anion in the film and in the fibers, in contrast with reports of the other authors<sup>11</sup>.

We confirmed fiber formation at the polypyrrole/electrolyte interface by performing the polymerization reaction using as working electrode a previously obtained polypyrrole film with a conductivity of 20 S/cm. This film was prepared under the following conditions: SDS concentration = 0.025 M and current density = 6 mA/cm<sup>2</sup>. In this case, dendrite-like fiber growth also occurred in the regions of the polypyrrole electrode near the surface of the electrolyte solution. On the Pt electrode coated with polypyrrole the reaction on the polypyrrole interface is favoured due to the low diffusion of the electrolyte in the polypyrrole film covering the Pt electrode. On the other hand, the growth of the fiber on the solution surface is due to the higher concentration of surfactant in this region. The unidirectional growth of polypyr-

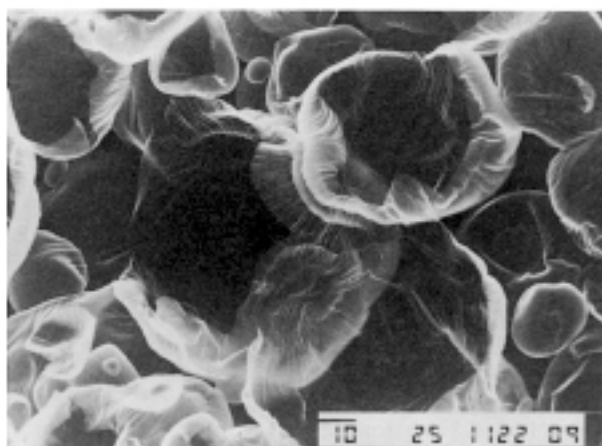
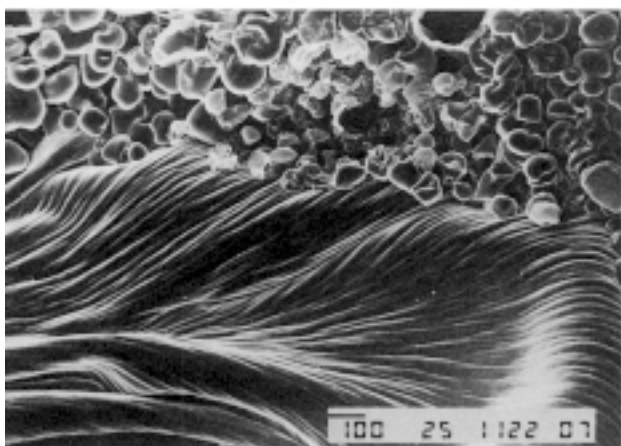
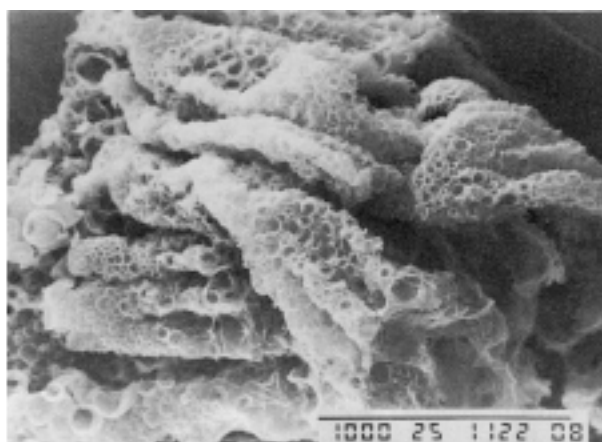
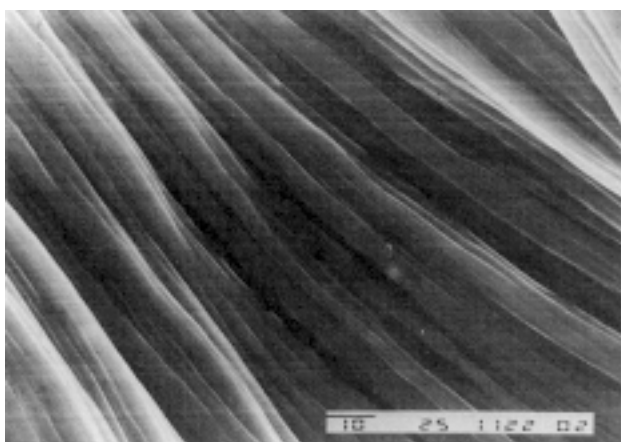


**Figure 1.** Variation of the current as a function of time during the potentiostatic (1.15 V vs. SCE) polymerization of pyrrole (0.1 M) in the presence of SDS (0.03 M).

role is probably a consequence of the electrolyte orientation induced by the applied electric field. In all cases the fibers grow in the direction of the counter electrode, short-circuiting the system after ca. one hour of reaction. Conductivity of the fibers is in the same range as that of the films. By lowering the applied potential we observe a decrease in fiber formation.

SEM pictures of the fibers confirm its fibrillar morphology, as shown in Figure 2a. The fibers grow from the working-electrode in the direction of the counter-electrode. In Figure 2b we see the position of the polypyrrole film where the fibers started to grow. The direction of growth of the fibers confirms that the electric field induces an orientation of the ionic surfactant molecules in the electrolyte solution from the working to the counter-electrode. Figures 3a and 3b show, with different magnifications, the SEM of the fiber extremity with particular emphasis on the fiber ends. These pictures and the above-mentioned results suggest that controlled dendrite growth can be used to enlarge the surface area of previously obtained polypyrrole films or to obtain polypyrrole fibers. Large surface area is highly desirable when designing battery electrodes.

We conclude that, using an appropriate current density, in order to establish a diffusion limited rate for the polymerization, the presence of the surfactant, SDS, strongly favours the dendrite-like nucleation of polypyrrole with the growth of long macroscopic fibers or formation of large surface area films.



**Figure 2.** a) SEM picture of the polypyrrole fiber, b) SEM picture of the region on the film where the fiber starts to grow.

**Figure 3.** SEM picture of the fiber extremities at different magnifications: a) bar represents 1  $\mu\text{m}$  and b) bar represents 10  $\mu\text{m}$ .

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