

## Electrochemical formation of polypyrrole nanowires

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### Abstract

This paper aims at approaching the mechanism of formation of polypyrrole (PPy) nanowires by an all-electrochemical process, which consists in electrografting a poly(alkylacrylate) film onto the surface of a cathode, followed by the anodic electropolymerization of pyrrole (Py) at the surface of this organomodified electrode. The experimental conditions for the pyrrole oxidation, including solvent and concentrations of monomer and supporting electrolyte, have been changed with the purpose to tune the characteristic features of the polypyrrole nanowires. The polyacrylate template has also been modified, all other conditions being the same, in an effort to design the shape and size of the wires. The electrochemical behavior of the as-prepared PPy wires has been characterized.

**Keywords:** Electrochemical oxidation; Polypyrrole nanowires; Poly(alkylacrylate) film

### 1. Introduction

Since their discovery 20 years ago, a great attention has been paid to electronically conducting polymers because of potential application in various fields, such as electrochromic and electroluminescent devices, electromagnetic interference shielding, sensors, etc. [1]. Polypyrrole (PPy) and polythiophene (PTh) are typical conducting polymers which are synthesized by electrochemical oxidation of the parent monomer, which is an easy way to tune the chemical, electrical, and electrochemical properties of the polymer [2]. Nowadays, remarkable progress in electronic and sensing devices is reported, which requires the availability of nanosized conducting dots and wires [2]. In an effort to prepare conducting polymer nanowires, membranes have been used as templates for the electrosynthesis of nanotubules of polypyrrole [3] and polyaniline (PAni) [4]. Microtubules of PPy [5a] and PAni [5b] have also been prepared by a template-free technique by using  $\beta$ -naphthalenesulfonic acid as a conducting salt.

Recently, we have reported on a new method to prepare PPy wires, which consists in electropolymerizing pyrrole (Py) at the surface of an anode premodified by a grafted polyethylacrylate (PEA) film [6]. Actually, ethylacrylate is first reduced into species that initiate the formation of polymer chains chemisorbed at the surface of the cathode even in a good solvent for them [7]. This premodified electrode is used as an anode for the pyrrole oxidation [8,9]. More information about the cathodic electrografting of acrylates can be found elsewhere [7-10]. Although the pyrrole polymerization at the surface of a neat carbon electrode forms a PPy film with a cauliflower-like morphology, PPy wires with a diameter in the range of 400 nm- 1  $\mu$ m and a length controlled by the polarization time are grown through the PEA film pregrafted to the carbon electrode. A reasonable explanation for this observation is that pyrrole diffuses through the PEA film for being oxidized at the anode surface and that PPy, which emerges from holes in the PEA coating, cannot grow laterally because of a too low conductivity [6]. In this paper, the experimental conditions for the pyrrole oxidation have been changed, including solvent, concentration of monomer and supporting electrolyte and anode precoat-ing, in order to give credit to the proposed mechanism and to identify key parameters for the control of conductivity and thus morphology of PPy.

### 2. Materials

Acetonitrile and dimethylsulfoxide (DMSO) were dried over  $\text{CaH}_2$ . Propylene carbonate (PC) was dried with molecular sieves for 24 h, and *N,N'*-dimethylformamide (DMF) was dried over phosphorus pentoxide. All these solvents were recovered by distillation, under reduced pressure at 70 °C in case of DMF and DMSO. Tetraethylammonium perchlorate (TEAP) was heated in vacuo at 80°C for 12 h. Sodium *para*-toluene sulfonate (Na-*p*TS) and lithium per-chlorate were used as received. Pyrrole and thiophene (Th) were distilled in vacuo before use. Ethyl acrylate (EA), acrylonitrile (AN)

and *tert*-butyl acrylate (tBuA) were dried over  $\text{CaH}_2$  for 1 day and distilled under reduced pressure. In cathodic experiments, cyclic voltammetry (CV) was carried out with a monomer solution (0.5—3 M) added with TEAP ( $5 \times 10^{-2}$  M) as a conducting salt. The water content of this solution was measured by the Karl—Fischer method (Tacussel aquaprocessor) and had to be lower than 5 ppm for getting rid of a parasitic electrochemical signal. These experiments were carried out in a glove box under a dry inert atmosphere at room temperature. The anodic experiments, i.e., chronopotentiometry (CP) and chronoamperometry (CA), were carried out under inert atmosphere, with a previously degassed solution. The working electrode was placed between the reference electrode and the counter-electrode (both platinum foils). The potentiostat was a PAR-EG&G model 273A. The glassy carbon (Carbone Lorraine) was mechanically polished with paper of different grain sizes followed by polishing with diamond pastes, then cleaned with heptane and acetone in an ultrasonic bath and dried in vacuo overnight at 150 °C.

The morphology of PPy was observed by scanning electron microscopy (SEM) with a high resolution FEG Digital Scanning Microscope 982 Gemini from Leo, operating at 1kV.

### 3. Results and discussion

In the previous paper, [6] formation of PPy wires was observed under the following conditions. EA (2.5 M) was dissolved in DMF together with TEAP (0.05 M) and reduced at the surface of a glassy carbon cathode at the potential (at the top) of the first reduction peak (i.e., ca. -1.6 V). The PPy wires were then formed by chronopotentiometry ( $I = 0.5$  mA) in DMF (solvent) with TEAP (0.05 M) as a conducting salt, pyrrole (0.1 M) as the monomer and the PEA modified glassy carbon as the anode. Fig. 1A shows a typical chronopotentiogram recorded under these conditions. An overpotential is first observed followed by a plateau at ca. 1.9 V. Fig. 2A shows the wires accordingly formed (diameter of ca. 2  $\mu\text{m}$ ). The cross-section of nascent objects have been observed, which confirms that they are wires rather than tubules. Fig. 2B shows that the wires have a ringed structure, which suggests a helicoidal growth.

The major question addressed in this work is how to control size, shape, and properties (conductivity) of the PPy wires. In a first step, the experimental parameters that may influence the pyrrole electropolymerization have been changed i.e., solvent, conducting-salt, monomer concentration, polarization method, etc. while using the same C/PEA template which basically dictates the diameter of holes through which the wires are emerging and growing. In the second step, the template (conducting substrate, cathodi-cally grafted polymer, etc.) has been modified and pyrrole has been oxidized under the optimized conditions, in order to understand better the templating role of the polymer electrografted to the conducting surface.

#### 3.1. Effect of the polarization technique

Chronoamperometry has been used rather than chronopotentiometry for the pyrrole electrooxidation and polymerization.

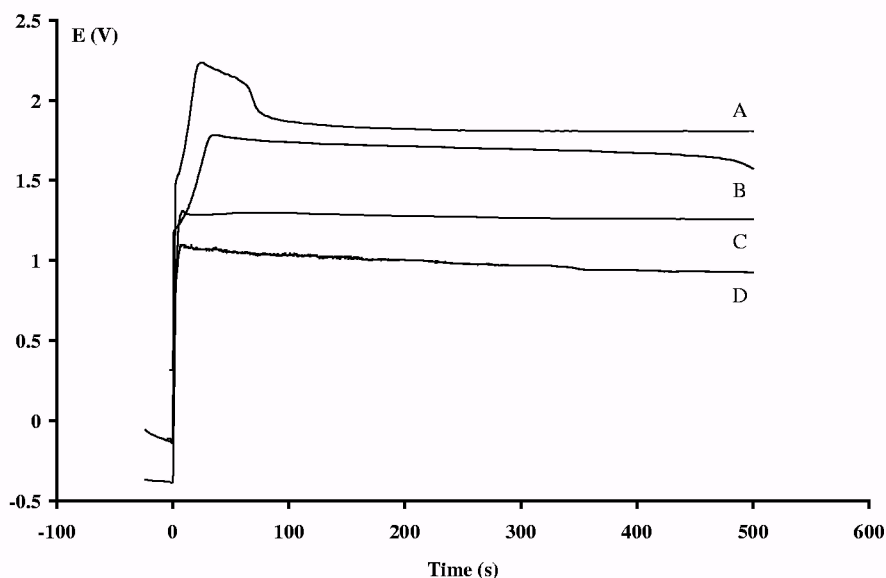


Fig. 1. Chronopotentiogram (0.5mA, 500s) recorded on a C/PEA template dipped in a Py (0.1M)/TEAP

(0.05M) solution in (A) DMF, (B) DMSO, (C) PC and (D) ACN.

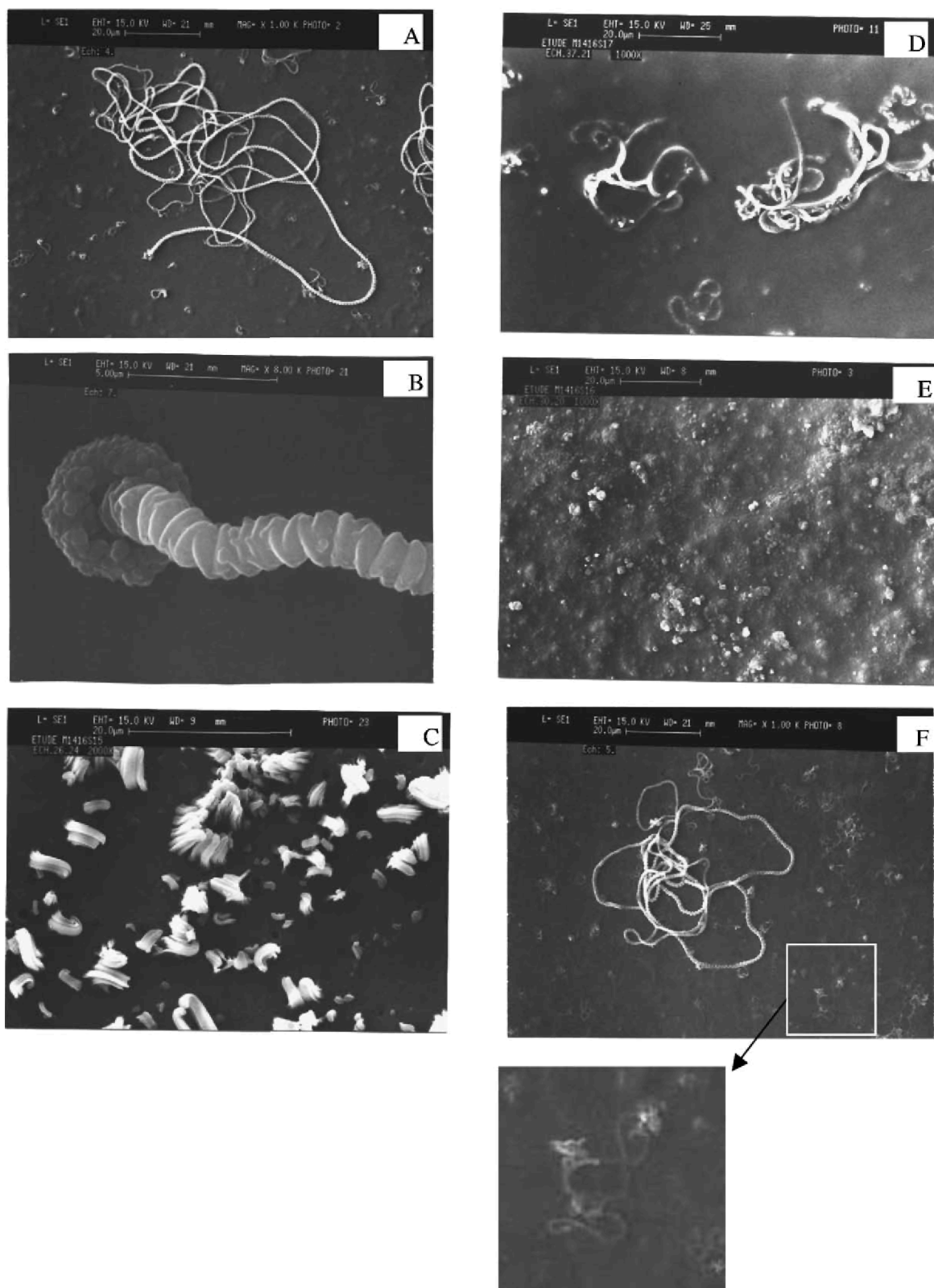


Fig. 2. SEM micrographs of wires prepared under standard conditions: full wires (A) and their microstructure (B). Wires prepared by CA (C), by CP in DMSO (D), by CP in ACN (E), by CP in DMF with  $[TEAP] = 0.15 M$  (F).

*Table 1 Morphology and conductivity of PPy according to the solvent donor number*

Solvent	Donor number [12]	PPy conductivity (S/cm) [13,14]	PPy morphology
DMF	26.6	$10^{-4}$	Wires
DMSO	29.8	$10^{-6}$	Wires
PC	15.1	55	Cauliflower-like
ACN	14.1	80	Cauliflower-like

The potential is indeed better controlled with the benefit to prevent PPy from being overoxidized and, thus, to be more conductive. The potential was fixed at 1.7 V/Pt, thus lower than the potential at the plateau observed in the CP experiments (Fig. 1A). The time was 55 s and the current was ca. 0.45 mA, which is comparable to the current used in CP. Fig. 2C shows the formation of short length wires in relation to the short polarization time. These nascent wires tend to aggregate, which is less desirable than the formation of individual wires by the CP technique, which remains accordingly the preferred technique.

### 3.2. Effect of the solvent

The PPy wires were prepared until now in DMF, i.e., a good solvent for the PEA template, which is accordingly swollen and makes easier the diffusion of Py and the counter-ion to the carbon surface. Several good solvents for PEA [11] have been substituted for DMF, i.e., dimethyl-sulfoxide, propylene carbonate, and acetonitrile. These solvents have been chosen because of a difference in the donor number (DN) (Table 1), [12] which is known to influence the conductivity of PPy [13,14]. This conductivity is indeed higher whenever pyrrole is anodically polymerized in solvents of low DN, such as PC and ACN, than in solvents of higher DN (e.g., DMF and DMSO) (Table 1). Fig. 1 compares the chronopotentiograms recorded in the three additional solvents (Fig. 1B-D for DMSO, PC, and ACN, respectively) with respect to that in DMF (Fig. 1A). In the two solvents of high donor number (DMF and DMSO), the polymerization occurs at a higher potential ( $>1.75$  V/Pt), and a well-marked and long lasting nucleation (until  $\sim 50$  s in DMSO) is observed, more likely as result of a regular decrease in conductivity of the growing PPy. In case of PC and ACN, no overpotential is observed and the potential at the plateau is lower than in DMF and DMSO (ca. 1.1—1.2 V/Pt) because PPy is more conductive. Although wires are formed upon polarization in DMSO (Fig. 2D), it is no longer the case in PC and ACN (Fig. 2E). In this case, the roughening of the surface is observed, whereas Cl (from the  $\text{ClO}_4^-$  counter-ion) and N are detected by EDAX. Pyrrole has thus polymerized in a 3D space rather than in a 2D one. As summarized in Table 1, any attempt to improve the PPy conductivity by using low DN solvents results in the three dimensional growth of the polymer [13,14] with loss of the wire structure, which supports the proposed mechanism.

### 3.3. Effect of the conducting salt

Concentration of the conducting salt has been increased in order to modify the PPy conductivity, which is known to increase at conducting salt concentrations higher than 0.1M [15]. No striking difference is observed in the chronopotentiogram when the TEAP concentration is increased from 0.05 (Fig. 3A) to 0.15 M (Fig. 3B). However, SEM analysis shows a large number of short wires that seem to be beneath the surface (diameter of ca. 0.3  $\mu\text{m}$ ; length:  $<20$   $\mu\text{m}$ , zoomed Fig. 2F) together with a few long wires on top of it (diameter of ca. 1.25  $\mu\text{m}$ ;  $L > 100$   $\mu\text{m}$ ) (Fig. 2F).

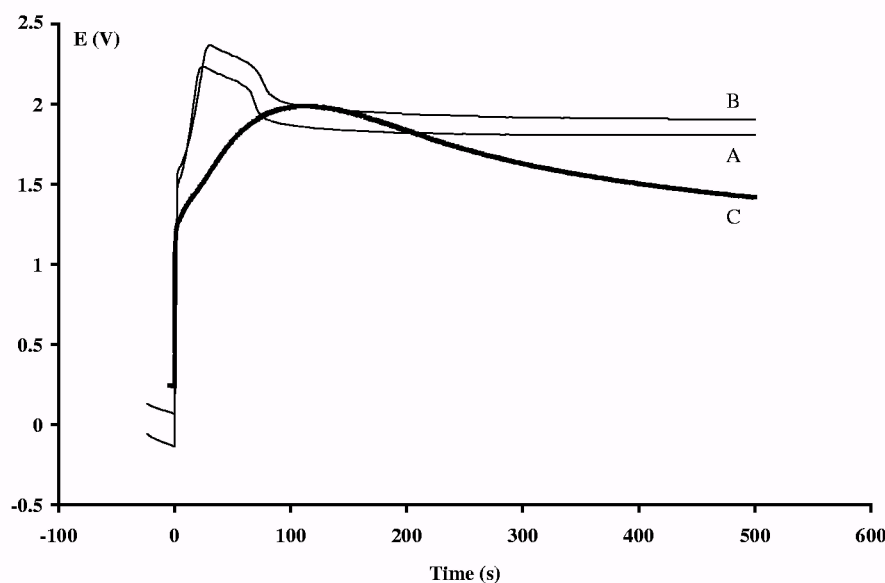


Fig. 3. Chronopotentiogram (0.5 mA, 500 s) recorded on a C/PEA template dipped in a DMF solution of Py (0.1M) containing TEAP 0.05 M (A), TEAP 0.15M (B) and *p*TS 0.05M (C).

Sodium *p*-toluene sulfonate (*p*TS) has been substituted for TEAP as a conducting salt. The *p*TS counter-ion is known indeed to impart a tubule-like structure to PPy, [16] when prepared in aqueous solution by chronoamperometry. This morphology is explained by the preferential growth of PPy in one direction as result of either ionic repulsion between the dopant and the electrolyte [16] or the alignment of the  $\pi$ -electrons of *p*-toluene sulfonate with the delocalized  $\pi$ -electrons of PPy [17]. In this study, no PPy wire is formed in the presence of Na-*p*TS.

In order to understand better the crucial role of the salt and the associated counter-ion, an additional experiment has been carried out that consists in preparing first PPy wires in the presence of TEAP dissolved in DMF and dipping then the electrode in a *p*TS solution in DMF followed by anodic polarization. The surface of the electrode has been analyzed by EDAX after the two-step modification. No Cl is detected in contrast to S, which confirms that most of the  $\text{ClO}_4^-$  anions contained in the PPy formed during the first step have been easily exchanged by *p*TS anions when the polymer was dipped in a solution of the Na-*p*TS salt [18]. The length of the wire has not increased as result of the second polarization step. Rather a granular structure is imparted to the surface.

The chronopotentiogram has been recorded in the presence of TEAP and *p*TS, respectively, at the same concentration (0.05 M). Comparison of Fig. 3A–C shows that the overpotential extends over a much larger time scale in case of Na-*p*TS and that the polymerization occurs at lower potential, however with formation of a rather granular morphology instead of wires. The conducting salt has thus an important effect on the growth of PPy, to the point where wires can be formed or not, depending on the salt used. The easy exchange of the  $\text{ClO}_4^-$  counter-ions of PPy wires raises the interesting prospect of incorporating counter-ions with a catalytic or biological activity in the wires.

#### 3.4. Effect of the monomer

Fig. 4A shows the curve recorded for a solution of Py (0.5M) and TEAP (0.15M) in DMF. As aforementioned, PPy wires are formed under these conditions. When the Py concentration is five times higher, polymerization occurs at a lower potential and nucleation and overoxidation are not observed on the CP curve (not shown). Consistent with formation of PPy of a much higher conductivity, no wire but rather dots of  $400 < \varphi < 700$  nm are formed.

##### 3.4.1. Nature of the monomer

It is worth investigating whether wires of other conjugated polymers could be prepared similarly to PPy. When thiophene is substituted for pyrrole in DMF, no overpotential is observed but rather a plateau at a high potential close to 2.6 V/Pt (Fig. 4B). No polymer wire is however observed at the surface by SEM. The surface is merely more granular as result of the thiophene polymerization. As a rule, electropolymerization of thiophene requires more acidic solvents than pyrrole because thiophenyl radical-cations are more reactive than the pyrrole radical-cations towards nucleophilic species [19]. During thiophene electropolymerization, colored soluble oligomers are formed and dissolved in the

electrolytic solution.

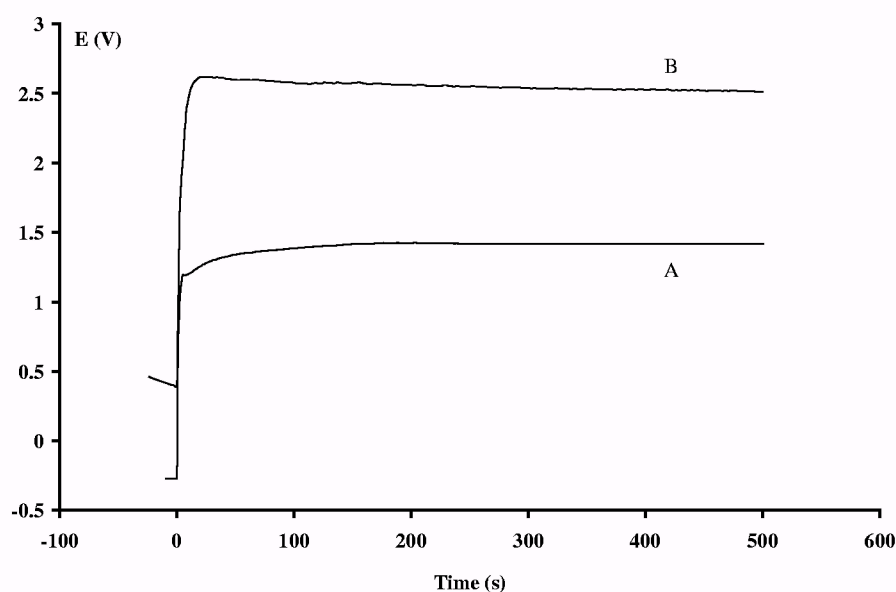


Fig. 4. Chronopotentiogram (0.5 mA, 500 s) recorded on a C/PEA template dipped in a DMF solution of Py (0.5M) and TEAP (0.15M) (A), thiophene (0.1 M) and TEAP (0.05M) (B).

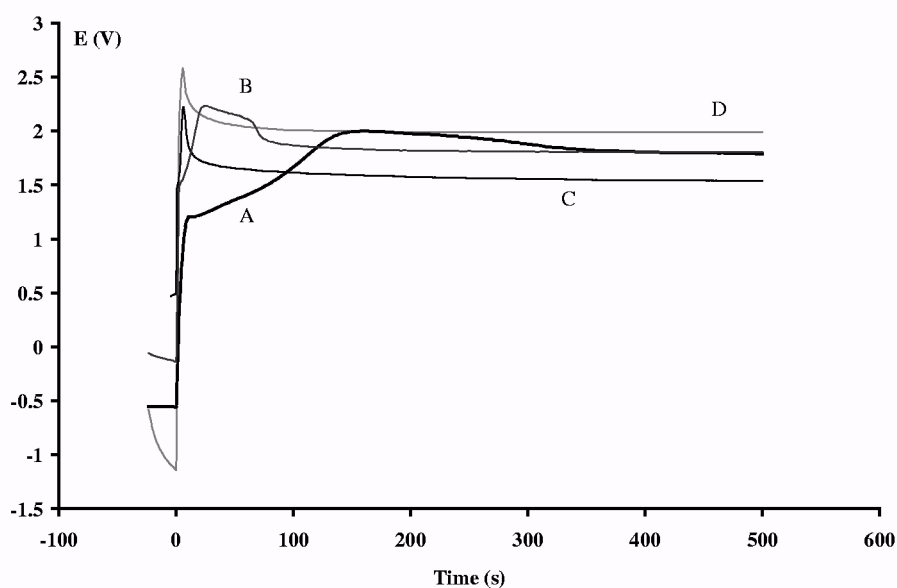


Fig. 5. Chronopotentiogram (0.5 mA, 500 s) of a Py (0.1 M) and TEAP (0.05M) solution in DMF on a template consisting of a PEA grafted onto non-polished glassy carbon (A), polished glassy carbon (B), platinum (C) and ITO glass (D).

As result of this first series of experiments, it appears that any effort to increase the PPY conductivity (increase of the monomer concentration, decrease of the DN of solvent, etc.) has a detrimental effect on the wire formation, which gives credit to the previously proposed growth mechanism [6]. Although not clearly understood yet, changing the conducting salt can deeply affect the PPY morphology. The best conditions for PPY wire formation are thus: CP ( $I = 0.5$  mA and  $t = 500$  s) of a Py (0.1 M) and TEAP (0.05M) solution in DMF. These conditions have been used in the next sections devoted to the effect of the template.

### 3.5. Effect of the substrate

The template used until now was a carbon electrode modified by a grafted polyethylacrylate film (C/PEA). Fig. 5 compares first the chronopotentiograms recorded in case of glassy carbon that has been



mechanically polished or not (curves B and A, respectively) and coated with PEA. Over-potential occurs at a longer time whenever the substrate is non-polished (Fig. 5A), but no wire is observed by SEM. However, polishing of glassy carbon before electrografting of PEA results in an overpotential in the CP profile and formation of PPy wires (Fig. 5B). A decrease in the surface roughness is known to improve the homogeneity of polarization. Onto a rough surface, the characteristic features of the voltammograms recorded for the acrylate electrografting are attenuated, and a less homogeneous organic film should be deposited.

Platinum is an attractive substrate because of inertness in anodic experiments. Fig. 5C shows a chronopotentiogram with a short overpotential, whereas no wire but rather ten-taculantly and hemispherically shaped PPy has grown on the surface, respectively on the edge and in the center of the electrode, respectively (Fig. 6A and B, EDAX:Cl and N).

ITO-glass has also been used as a conducting substrate. The chronopotentiogram shown in Fig. 5D is the same as on Pt except for a higher potential. Non-adhering PPy film is formed instead of wire. It must be noted that the surface of neat ITO was very rough (AFM analysis) and possibly responsible for a template of poor quality.

### 3.6. Effect of the electro grafted polymer

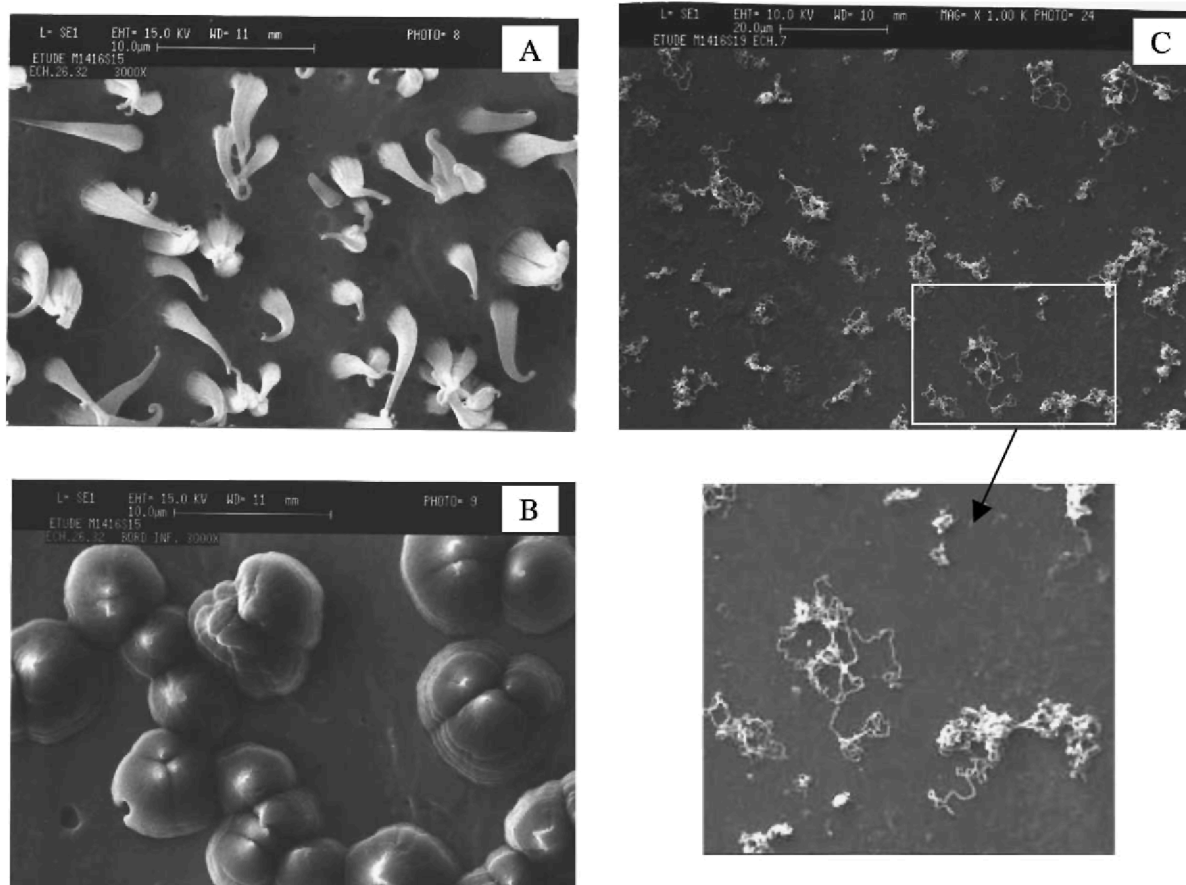
#### 3.6.1. Film thickness

As reported elsewhere, [10c,20] the thickness of the electrografted PEA layer changes with the monomer concentration, e.g., from 40 to 120 nm when the EA concentration is increased from 0.5 to 2 M with a Ni cathode. Fig. 7 shows the curves recorded for the pyrrole oxidation with a PEA template prepared at three different EA concentrations. Thickness of the PEA film has been measured by ellipsometry for the dry films [20] as reported in Table 2.

Table 2 Characteristics of the wires according to the thickness of the PEA template

[EA] (M)	Thickness (nm) [20]	Diameter ( $\mu\text{m}$ )	Length ( $\mu\text{m}$ )	Density ( $\text{N}^\circ$ wires/ $\text{cm}^2$ )	Homogeneity
0.5	40	5	60	7,500	Misshapen wires
1.5	100	4	100	50,000	~ Same size
3	120	3-5	80-100	18,000	Long wires

Fig. 6. SEM micrographs of PPy prepared with a Pt/PEA template. Tentacles on the edge of the electrode (A); dots in the center of the electrode (B). PPy prepared with a C/PtBuA template (C).



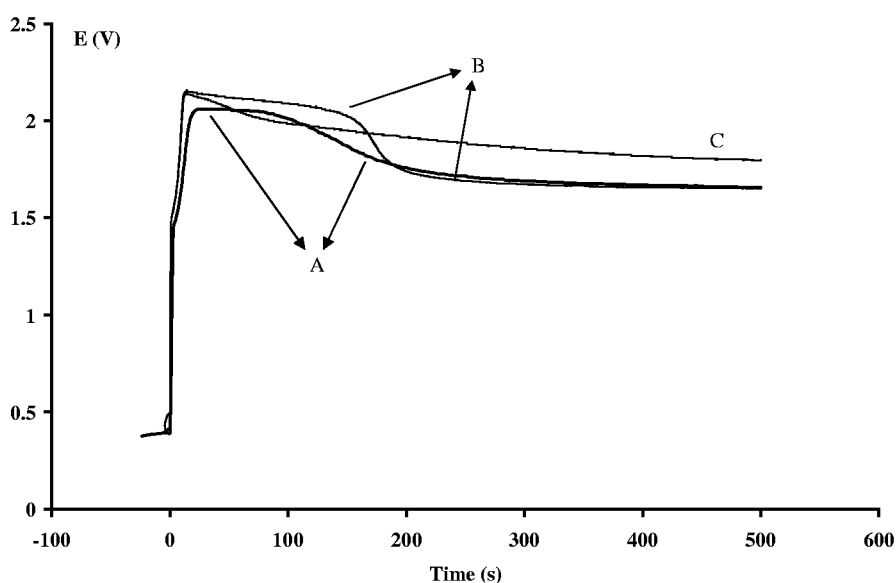


Fig. 7. Chronopotentiogram (0.5 mA, 500 s) of a Py (0.1 M) and TEAP (0.05M) solution in DMF on a C/PEA template. PEA was electrografted with  $[EA] = 0.5$  M (A), 1.5 M (B) and 3 M (C).

A rather long overpotential is first observed (Fig. 7A), whose intensity increases with the film thickness (Fig. 7B) and finally disappears when the template is thicker (Fig. 7C). In all cases, PPy wires are formed. They are, however, misshapen with a larger diameter, a shorter length, and a lower density when the template is thinner. Upon increasing the thickness of the PEA film, regular wires are formed, their length increases from 60 up to 100  $\mu\text{m}$ , their diameter does not change significantly and their density at the surface increases first and then decreases. The low density in case of a thin film might result from a weak attachment of the wires to the surface, which are partly lost during the washing step. Conversely, less defects are available to the growth of PPy wires throughout thicker PEA films. In parallel, length and diameter of the wires are more scattered.

### 3.6.2. Electrografted polymer

In addition to PEA, polyacrylonitrile (PAN) and poly(*t*-butylacrylate) (PtBuA) have been used as the electrografted film. In sharp contrast to PEA, PAN prevents PPy wires from being formed under the same conditions [21]. A granular surface is observed in accordance with the chronopotentiogram that shows a lower steady potential (Fig. 8, curve C). This observation was attributed to the better coating properties of PEA that limits the pyrrole diffusion to the electrode surface, in line with the overpotential observed [6]. PAN and PEA being swollen by a good solvent (DMF), a lower grafting density in case of the templating PAN chains could explain the nodular morphology of PPy. Indeed, when there are only few grafting sites on the surface, the grafted chains do not overlap, they preserve their random-walk conformation, and they leave space available on the surface. In the extreme case of high grafting density, the grafted chains tend to orient themselves perpendicularly to the surface [22]. Based on the current quantity measured for the reduction of acrylonitrile (Ni cathode) and electrografting of PAN, Mertens et al. calculated a grafting density of 0.2 chain/ $\text{\AA}$  [2]. Under the same conditions, except for the cathode (glassy carbon instead of Ni), the current quantity is ca. eight times higher for EA compared to AN and so should be the grafting density of PEA versus PAN. Therefore, the PEA coating is thought to provide the growing PPy chains, and thus wires, with a network of "canals", accordingly for wire formation. The much weaker constraint imposed by the (swollen) PAN chains onto growing PPy is consistent with the formation of "mushrooms" rather than wires. This type of structure was also observed in case of the electroreduction of bithiophene at the surface of a PAN grafted Ni electrode [21].

When poly(*tert*-butyl acrylate) (PtBuA) is the template all the other conditions being the same, a small overpotential is observed (Fig. 8, curve B) and the steady potential is higher compared to PAN, but still lower than for PEA. In addition to few wires of a large diameter (ca. 2–3  $\mu\text{m}$ ), wires with a diameter in the 100–300 nm range are observed (Fig. 6C). The current quantity noted for the PtBuA electrografting peak is at least two times higher compared to PEA. Therefore, a higher density of



grafted PtBuA chains is in line with a decrease in the wire diameter.

### 3.7. Electroactivity

The electroactivity of the PPy wires has been tested by cyclic voltammetry in an aqueous solution containing lithium perchlorate (0.1 M) as a conducting salt (Fig. 9,  $\nu = 20\text{mV/s}$ ). A rapid loss of the electroactivity confirms the low conductivity of PPy prepared in DMF.

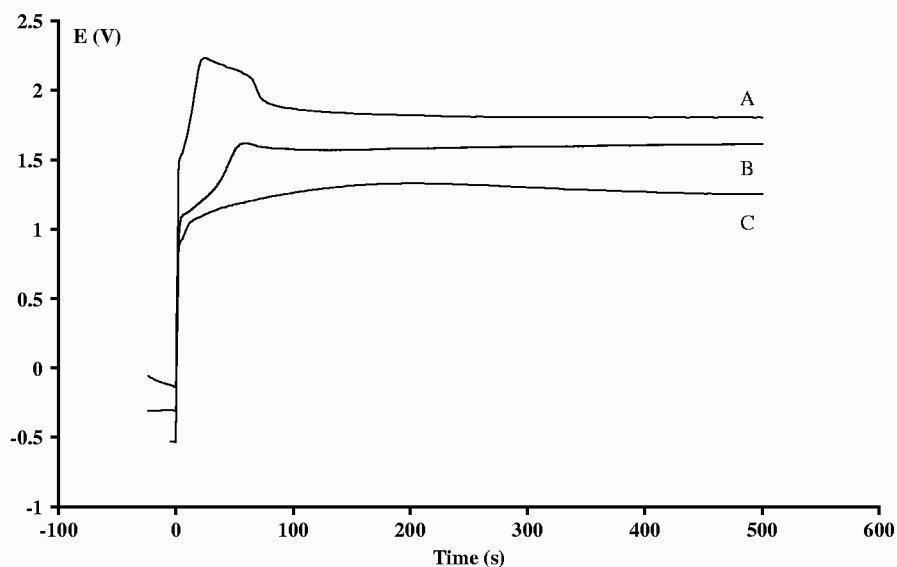


Fig. 8. Chronopotentiogram (0.5 mA, 500 s) of a Py (0.1 M) and TEAP (0.05M) solution in DMF on a glassy carbon grafted with PEA (A), PtBuA (B) and PAN (C).

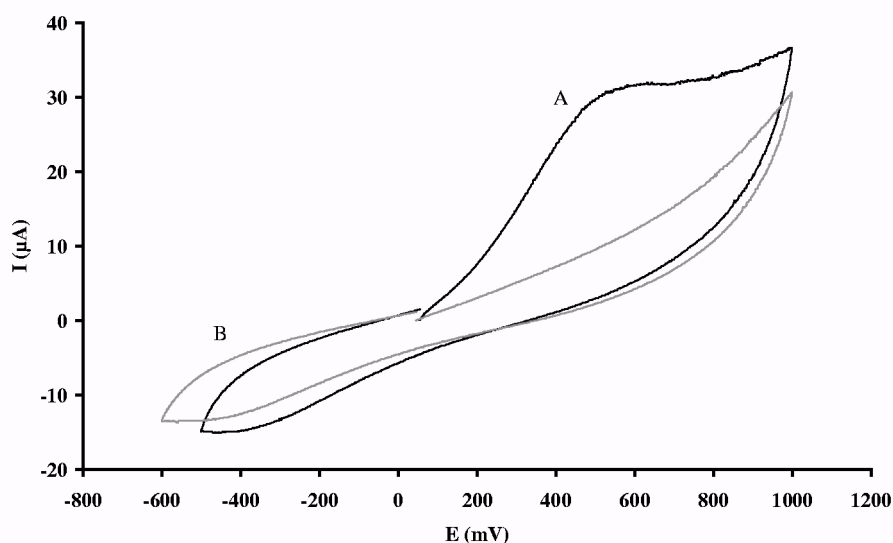


Fig. 9. Electroactivity of PPy wires in an aqueous  $\text{LiClO}_4$  (0.1 M) solution. (A) First scanning, (B) second scanning (20mV/s).

## 4. Conclusions

Experimental parameters that control the morphology of PPy grown from the surface of a precoated glassy carbon anode have been investigated. First of all, a low conductivity for PPy is a prerequisite for the formation of the wires. A solvent of high donor number and a low monomer concentration must accordingly be used. The conducting salt has also an important role, because PPy wires are formed in the presence of TEAP and not at all when *p*TS is used. The easy exchange of the  $\text{ClO}_4^-$  counter-ions of PPy wires by ions of a specific activity is worth being recalled. When the characteristics of the

template are concerned, several criteria must be met, i.e., the surface of the conducting substrate must be smooth, the organic coating must be thick enough (~ 100 nm) and, above all, the grafting density of the templating chains must be as high as possible. Then, wires with a diameter of 100–300 nm can be prepared, whose the length is merely controlled by the polarization time. The wire density is regulated by the thickness of the grafted polymer and its nature can control the morphology of the wires, including the diameter. The length of the wires is merely controlled by the polarization time. At the time being, [Py] = 0.1 M, [TEAP] = 0.05 M, DMF, CP with  $I = 0.5$  mA and electrografted PtBuA onto polished glassy carbon are the best conditions for the production of nanosized PPy wires. Low conductivity and electroactivity of the PPy wires is a pending problem, that could however be tackled by the wire metallization by insertion of metallic ions in PPy and further chemical reduction [23]. Finally, the counter-ions exchange could provide the PPy wires of quite a large surface area, with valuable catalytic properties [24].

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