Electrochemical Synthesis of Conjugated Polymer Wires and Nanotubules

Christine Jérôme,[a] Sophie Demoustier-Champagne,[b] Roger Legras,[b] and Robert Jérôme*[a]

Abstract: Two electrochemical methods designed for the synthesis of polypyrrole (PPy) wires and nanotubules are the topic of this paper. The concept that allows the morphology of PPy to be controlled is discussed for each method, and the performances of the two complementary techniques are compared in terms of dimension, shape and conductivity of PPy.

Keywords: conducting materials · electropolymerization · membranes · nanostructures · template synthesis

Introduction

Nowadays, the synthesis of molecular conductors is a field of intensive research, the purpose being to produce objects on the nanometric scale. Therefore, the control of the morphology of conducting polymers, such as polypyrrole (PPy) and polyaniline, is a very stimulating challenge, the production of molecular wires and tubules being a very actively pursued target.

The confined polymerization of these conducting polymers is a very pertinent way to give them controlled shape and dimension, which addresses the question of the availability of appropriate templates. Kanatzidis et al.[1] reported on the polymerization of conjugated polymers in layered materials, such as FeOCl and V_2O_5. Bein et al.[2] used zeolite molecular sieves for the chemical synthesis of polyaniline.

However, in addition to chemical synthesis, conducting polymers are commonly synthesized by electropolymerization as films deposited on anodes. These layered conducting materials are very well-suited for electrochemical applications, such as sensors.[3] Nevertheless, the use of microtubules of PPy rather than films is by far more efficient for the immobilization of biologically active species such as glucose oxidase and, in this case, for the direct electron transfer between the enzyme and the conducting polymer so improving the electrochemical detection.[4] This example also emphasizes the need for increasing substantially the surface/volume ratio of electrochemically prepared conjugated polymers.

Martin et al.[5–7] used commercially available particle track-etched membranes (PTM's) as templates for the preparation of nanofibrils of metals, semiconductors, and conducting polymers. They concentrated on the synthesis of three main conducting polymers, namely polypyrrole, poly(3-methylthiophene), and polyaniline, within the pores of a polycarbonate (PC) Nucleopore membrane. Although the oxidative polymerization of the parent monomers can be initiated either electrochemically or by a chemical oxidizing agent, Martin et al. essentially used the chemical technique,[8–9] except for one example of electrochemical synthesis of pyrrole.[10] They showed that the electrical conductivity of the tubules was one order of magnitude higher than the bulk polymer.

The purpose of this paper is to give a survey of the recent contribution of electrochemistry to the formation of PPy nanotubules and PPy nanowires. Although PTM's are the templates in the former case, anodes previously grafted by an insulating polymer are used in the latter one.

Discussion

Particle track-etched membranes and PPy nanotubules: In all the published papers[5–10] dealing with the use of PTM's as templates, the authors assume that the pores of the commercially available membranes are cylindrical with a diameter that has been tabulated by the manufacturer, called nominal diameter. This hypothesis is now challenged by several research groups[11–13] who found that the pores in commercial membranes are cigar-like and that the actual diameter can be larger by up to a factor of 3 compared with the nominal diameter. Accordingly, the actual cross section area of the wires can be on average up to a factor of 10 larger than calculated on the basis of the nominal value. This observation

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[a] Prof. Dr. R. Jérôme, Dr. C. Jérôme
University of Liège
Center of Education and Research on Macromolecules (CERM)
B6 Sart-Tilman, 4000 Liège (Belgium)
E-mail: rjerome@ulg.ac.be

[b] Dr. S. Demoustier-Champagne, Pr. Dr. R. Legras
Université catholique de Louvain
Unité de Physique et de Chimie des Hauts polymères (POLY)
Croix du Sud, 1, 1348 Louvain-la-Neuve (Belgium)
E-mail: demoustier@poly.ucl.ac.be

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has a drastic influence on the physical parameters, mainly the electrical conductivity extracted from measurements on these tubules and wires. Moreover, the pores in the commercial membranes are not aligned parallel but they have a considerable angular distribution of ±34°. For this reason, depending on the pore diameter and pore density of the PTM's, a number of pores may actually intersect within the membrane, and their length is not constant. Recent developments in the POLY laboratory at the "Université catholique de Louvain" has tackled this problem and can now produce reliable and reproducible nanoporous membranes.[14] The samples produced at the laboratory-scale exhibit a series of well controlled characteristic features, that is mean pore size in the range of 15 to 100 nm, narrow pore size distribution, and perfectly cylindrical pores with smooth walls and parallel arrangement across the membrane. As result of these optimized features, nanoporous PTMs are excellent templates for the preparation of controlled nanometric materials.[12, 13] Recently, Demoustier-Champagne et al. reported on the use of these nanoporous PTM's as templates for the chemical and electrochemical synthesis of nanoshaped conducting polymers, particularly PPy nanostructures.[13, 15–17] Prior to the electrochemical deposition of PPy within the pores, a metallic layer (Au) serving as electrode is evaporated onto one side of the membrane. The electropolymerization is performed, at room temperature, in a conventional one-compartment cell with a Pt counter electrode and an Ag/AgCl reference electrode. The solutions containing the monomer and one conducting salt are deoxygenated with N_2 before polymer electrodeposition. Polymers are grown potentiostatically at +0.8 V.

Figure 1 illustrates PPy nanotubules that have been prepared according to this general method. The nascent polymer is preferentially deposited as thin layer on the pore walls, so forming hollow polymer tubules that cross the whole thickness of the membrane. It must be noted that the electrochemical deposition of PPy, and conducting polymers in general, results in tubules, whereas solid wires are formed in the case of metal deposition. Martin et al.[18] suggested that the electrostatic attraction between the growing polycationic polymer and the anionic sites along the pore walls of the polycarbonate membrane would be at the origin of this difference.

It is well established that the supporting electrolyte used to electrosynthesize conducting polymers affects their morphology and conductivity. Therefore, the electrochemical synthesis of polypyrrole has been carried out in the presence of different electrolytes (perchlorate (ClO_4^-), dodecylsulfate (DS), toluenesulfonate (TS), and polystyrene sulfonate (PSS)) and thus of different counterions. Furthermore, PC nano-PTM's with different pore diameters have been used in order to cover a wide range of geometrical constraints.[17] One of the advantages of the electrochemical method compared with the chemical one is that the growth rate and the length of the tubules are easily controlled. Indeed, the filling of the pores is easily monitored by the measurement of the plating current. As the PPy tubules emerge from the membrane template, the current increases very rapidly as result of a 3D deposition. In each experiment, the charge (Q_{filling}) consumed and the time (t_{filling}) required for the PPy tubules to emerge from the membrane surface were measured. The influence of the pores diameter on Q_{filling} and t_{filling} was studied by keeping the electrolyte concentration constant at 0.1 M. For all the supporting electrolytes considered, it was observed that Q_{filling} increases with the pore diameter. So, the larger the pore diameter, and the higher the amount of electrodeposited PPy. This observation is in complete agreement with the observation that the thickness of the tubule increases with the diameter of the pores in the template membrane.

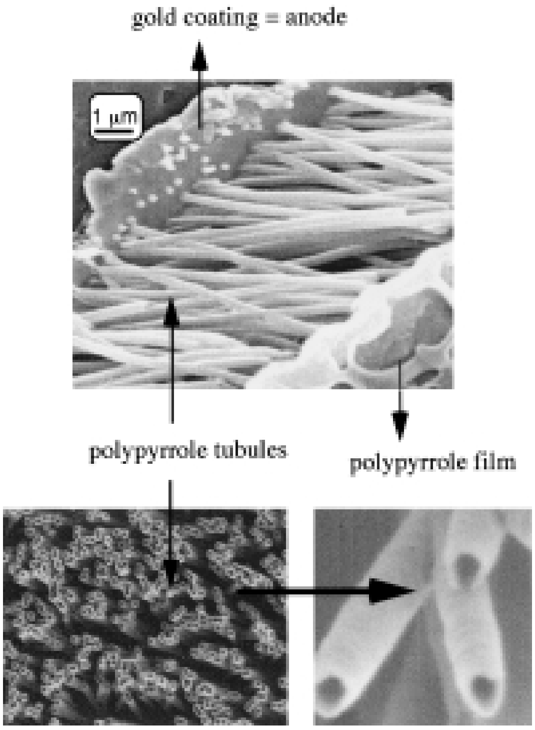

Figure 1. FE-SEM image of PPy/ClO_4 tubules collected after dissolution of the PC membrane.

Abstract in French: *Cet article décrit deux méthodes électrochimiques de synthèse de fils et de nanotubes de polypyrrole (PPy). Les bases conceptuelles qui permettent de contrôler la morphologie du PPy sont discutées pour chaque méthode et les performances de ces deux techniques complémentaires sont comparées en termes de dimension, de forme et de conductivité du PPy.*

The dependence of t_{filling} on the membrane porosity is more complex. Indeed, t_{filling} changes not only with the porosity but also with the size and charge of the anion in solution. Since more PPy is deposited in larger pores, t_{filling} should increase with the size of the pores. This behavior is actually observed in the presence of small counterions, such as ClO_4^-. However, when larger anions are used, for example dodecylsulfate and toluenesulfonate, the reverse dependence is observed in membranes with pores in the 110 to 65 nm diameter range, although it increases slightly for smaller pores. This effect is even more pronounced with a polyelectrolyte, such as polystyrene sulfonate, since an important increase of t_{filling} is observed with membranes of narrow pores ($\phi_{\text{pores}} < 60$ nm). This phenomenon has been attributed to limitation of the mass transport, which is more drastic for smaller pores than for larger ones. Of course, the limited diffusion of the counterion within the pores results in a decrease of the PPy growing rate along the pore walls, leading to increased t_{filling}. Moreover, the relative coverage of the internal surface of the filled pores is found to be smaller for membranes with narrow pores. This observation points out that all the pores are not wetted by water prior to electrodeposition.

The conductivity of the electrosynthesized PPy nanotubules has been measured by a two-probe technique. Figure 2 shows the relationship between the outer diameter of the tubules and the conductivity of PPy doped by various counterions.

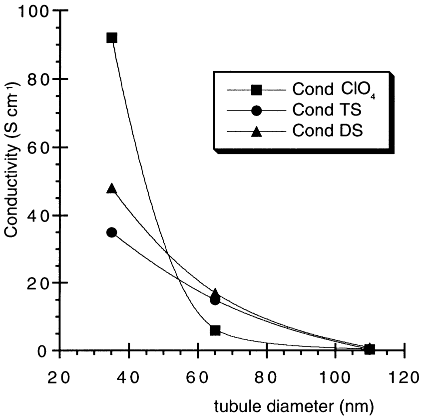

Figure 2. Plot of the conductivity of PPy tubules vs the outer diameter for 3 different PPy/counterion combinations.

In complete analogy with previous studies,[5, 6] the electronic conductivity is enhanced in the case of narrow PPy tubules. The effect of the size and type of the counterion is also clear, since the conductivity increases more rapidly and reaches higher values in the case of small counterions. These observations are consistent with the data reported by Inganas et al.,[19] who came to the conclusion that the conductivity of the narrowest tubules is the highest because they contain more ordered chain material.

Since the intrinsic conductivity of synthetic polymers is usually related to the chain conjugation, the relative conjugation length of PPy in the tubules has been analyzed by Raman spectroscopy. These Raman analyses were performed for nanotubules of different diameters containing various counterions. Based on Furakawa's assignment of the PPy bands,[20] the relative conjugation length was estimated from the ratio between the intensity of a band sensitive to the PPy oxidation state (at 1595 cm^{-1}) and the intensity of the skeletal band (at 1500 cm^{-1}). This band ratio actually increases when the diameter of the PPy tubules is decreased; this indicates that the polarizability of PPy, and thus the conjugation length, are higher in the case of the narrower tubules. This structural feature can explain the increase in conductivity observed for this family of tubules' The conclusion drawn from this Raman study completely agrees with the work by Martin et al. based on polarized infrared absorption spectroscopy.[18]

Conductive substrates grafted by insulating polymers and PPy nanowires: Recently, a strategy for the preparation of polypyrrole nanowires has been reported by the CERM at the University of Liege.[21] It consists of a two-step all electrochemical process. The starting point is a conducting substrate, such as a glassy carbon plate, onto which an insulating polyethylacrylate (PEA) film has been first electrografted under negative potential. This modified carbon electrode is then used as an anode, for the polypyrrole electrosynthesis. The PEA grafted carbon actually behaves as a template for the PPy growth and triggers the wire formation.

From previous studies,[22] it is known that the cathodic polarization of a glassy carbon plate (or a metal plate) dipping in a solution of ethyl acrylate (2 M) and tetraethylammonium perchlorate (0.05 M) in dimethylformamide (DMF) allows for the grafting of a PEA film by holding the potential at the top of the first reduction wave for a few seconds. A second cathodic scan shows a dramatic decrease of the current intensity which is the signature of the grafting reaction. The as-prepared PEA film is quite thin (≈100 nm) and remains attached onto the electrode surface even when dipped in a good solvent for the polymer (e.g., DMF) for a long time. Moreover, electroactive species (e.g., ferrocene) can diffuse through the previously swollen PEA chains and reach the carbon surface where they react electrochemically. More details about this electrografting process and the characteristics of the as-prepared films have been reported elsewhere.[22]

When a good solvent for PEA is used, the carbon plate grafted by PEA can be used as an anode for the galvanostatic polymerization of pyrrole ($I = 0.5$ mA cm^{-2}). The chronopotentiogram then shows an overpotential as soon as the polymerization starts, followed by stabilization at a potential higher than the one measured onto the bare carbon electrode (Figures 3A and B). This increase in potential clearly indicates that the PEA grafted film is an obstacle to the PPy growth and the pyrrole diffusion.

After the anodic polarization, scanning electron microscopy shows the formation of quite long PPy wires that have grown from the electrode surface through the PEA film (Figure 4). These PPy wires have a regular annular micro-

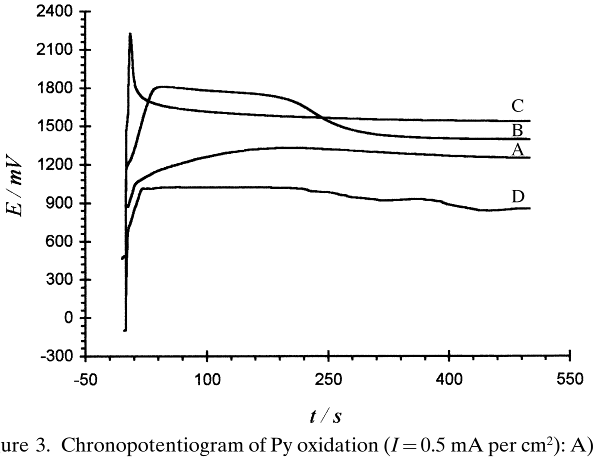

Figure 3. Chronopotentiogram of Py oxidation ($I = 0.5$ mA per cm^2): A) in DMF onto bare carbon, B) in DMF onto PEA grafted carbon, C) in DMSO onto PEA grafted carbon, D) in ACN onto PEA grafted carbon.

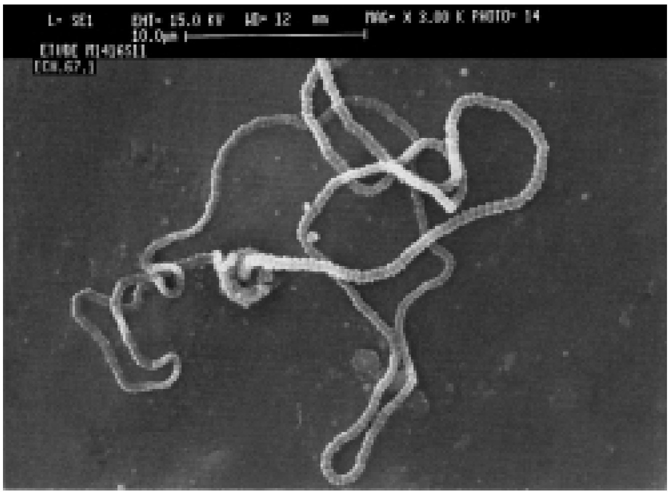

Figure 4. SEM image of PPy/ClO_4 wires grown from a PEA grafted carbon electrode.

structure and a diameter in between 350 nm and 4 μm. The length of these wires can be controlled by the polarization time, a polarization of 500 s leading to 100 μm to 300 μm long wires. The fracture of these wires shows that they are full wires and not tubules as it was the case for PPy synthesized in the pores of PTM's.

The morphology of the PPy wires is modified by the thickness of the grafted PEA films. Too thin PEA films (<60 nm) are at the origin of misshaped wires; this indicates that a lower limit in the film thickness beyond which nanowires are properly formed. When the grafted PEA films are too thick (>100 nm), the average diameter and length of the wires are increased, as well as their dispersity. Thus, the insulating film that covers the anode appears to act as a template, which governs the wire formation, the highest density of wires (50000 wires per cm^2) and the best homogeneity in size being observed for about 100 nm PEA grafted film, at least under the experimental conditions used in this study.[23]

The wire formation is also dependent on the insulating polymer which is previously grafted on the anode. When polyacrylonitrile is electrografted instead of PEA, the chronopotentiogram does not go through an overpotential, and polymerization occurs at a lower potential. Instead of nanowires, PPy with a more commonly observed granular morphology is then formed on the electrode surface. So the structural characteristics of PPy are deeply affected by the insulating polymer which acts as a template for the Py polymerization. Compared with PAN, PEA appears to be more efficient in restricting the diffusion of Py to the electrode and the growth of PPy from the electrode surface, to very local spots.

The solvent used for the pyrrole polymerization has also a deep influence on the polymer morphology.[23] Indeed, PPy wires are formed in solvents with high donor number (DMF or dimethylsulfoxide (DMSO)), whereas the more traditional cauliflower-like morphology is observed in solvents of low donicity (acetonitrile; ACN). Once again, an overpotential at the first stage of the polymerization is the signature for the growth of PPy wires as shown in Figure 3 (curves B, C, and D). All the solvents in which PPy wires can be formed are not only good solvents for PEA, but also solvents of high donicity known for imparting limited conductivity to PPy.[24] At the time being, the measurement of the conductivity of the PPy wires is a problem which explains why no data have been made available until now.

Although the formation and growth of PPy wires remain amazing under the experimental conditions used, a mechanism has been tentatively proposed which relies upon the major experimental observations. Initially, pyrrole diffuses through the swollen PEA film and it is oxidized at the carbon surface with formation of PPy nuclei according to the mechanism of nucleation and growth known for PPy.[25] As soon as the electrode is polarized, oligomers start to be formed so near the surface, by repeated dimerization so leading to dimer, tetramer, octamer etc. Above a critical length, the oligomers are insoluble and are deposited as nuclei on the surface thus beneath the solvated PEA chains. The next step for the PPy polymerization would be a solid state polymerization at the origin of the nuclei growth. Since PEA chains have some mobility in DMF, they can be displaced laterally by the growing PPy nuclei so making a small channel available and allowing PPy to come out of the PEA film with a certain diameter. The further growth occurs by polymerization at the surface of the electrode thus beneath the PEA film (Figure 5). Pyrrole diffuses in between the carbon surface and the foot of the growing PPy wire, so that the already formed PPy is pushed away from the electrode. According to the observation that the PPy wires are formed in solvents in which PPy is usually of a limited conductivity, no monomer oxidation would occur directly on the surface of the PPy wire, which would preserve the lateral dimensions of the wire imposed by the channel driven through the PEA coating.

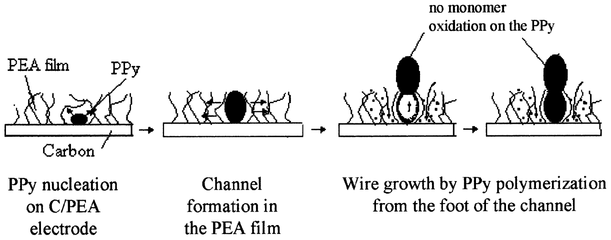

Figure 5. Schematic growth mechanism for PPy wires from a PEA grafted carbon anode.

The growth of PPy nanowires through a thin insulating template previously grafted to the electrode does not appear to proceed according to the same mechanism as in the case of PTM's templates. Indeed, in PTM's, Py polymerization is initiated at the electrode surface, thus at the foot of the pores, PPy then grows along the pore walls, and as soon as the tubules come out of the pores, PPy grows as a continuous top layer. It must be noted that this reaction occurs in water, in which PPy is formed with high conductivity and the PTM's are completely insoluble so preventing pyrrole from diffusing to the underlying electrode.

Conclusion

Two complementary electrochemical methods have been reviewed that allow the shape of PPy to be designed, the key points being the template and the solvent used in each of these techniques.

In the case of PTM templates, PPy is synthesized in a confined medium filled with an aqueous solution of Py. It takes up the shape and size of the pores of the template membrane. The conductivity of the PPy tubules accordingly formed is enhanced when the membrane porosity is decreased.

The second type of template used is an insulating polymer grafted onto the electrode. The growing sites are templated expectedly by defects in the polymer coating, such that the polymerization of Py, that has to occur in an organic solvent of high donicity (and good solvent for the template), can be initiated at the electrode/template interface and propagate through the template. The choice of the solvent more likely accounts for the lack of Py oxidation onto the surface of the PPy wires emerging from the template. The length of the wires is only limited by the polarization time.

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