Chem. Mater. **1999,** *11,* 829−834

Effect of Electrolyte Concentration and Nature on the Morphology and the Electrical Properties of Electropolymerized Polypyrrole Nanotubules

Sophie Demoustier-Champagne* and Pierre-Yves Stavaux

Université Catholique de Louvain, Laboratoire de Physique et de Chimie des Hauts Polymères,
Place Croix du Sud, 1. B-1348 Louvain-la-neuve, Belgium

Received October 13, 1998. Revised Manuscript Received December 16, 1998

Polypyrrole (PPy) with four different counterions was electrochemically synthesized in homemade polycarbonate particle track-etched membranes with different pore sizes. A dependence of the PPy growing rate on the pore size and on the electrolyte nature and concentration has been observed. The morphology of the different template-synthesized nanostructures has been carefully analyzed by field-emission scanning electron microscopy. In all cases, nanotubules were observed. However, their thickness depends on the pore diameter of the template membrane and on the nature of the supporting electrolyte. The electrical conductivity of PPy in such a structure is known to increase compared to the bulk conductivity, which is also shown here. In addition Raman spectroscopy showed that the relative conjugation length increases with decreasing pore size.

Introduction

There is now a large interest in nanoscale materials since they not only have potential applications in various areas such as chemistry, physics, electronics, optics, material science, and biomedical science, but they are also of fundamental interest. When restricted to the field of material sciences, the main interest is that the physical properties of a material can change in the transition between the bulk scale and the nanoscale. Among the different strategies to synthesize nanoscopic materials reported in the literature, template synthesis is an elegant approach.[1] This technique consists of including metallic or organic constituents inside the void spaces of nanoporous host materials. Though there now exists a huge range of hosts, track-etched membranes present a significant advantage, because they lead to the production of different kinds of nanotubules and nanowires with monodisperse diameters and lengths. At present, a number of companies (Nuclepore, Poretics, and Whatman[2]) sell microporous polymeric filtration membranes with a wide range of pores diameters (0.03−12 μm) and pores densities (10^5−10^9 pores/cm^2).

Martin et al.[3−5] have used these commercial membranes as templates to prepare nanofibrils composed of metals, semiconductors, and conducting polymers. Until now, concerning the preparation and the characterization of conducting polymers nanofibrils, most of their work has focused on the synthesis of polypyrrole, poly(3-methylthiophene), and polyaniline inside the pores of a polycarbonate Nuclepore membrane. These polymers can be synthesized by oxidative polymerization of the corresponding monomer. This may be accomplished either electrochemically or with a chemical oxidizing agent. Although they once reported the electrochemical synthesis of pyrrole,[6] Martin et al. essentially used the chemical method.[7,8] They showed that the electrical conductivity of the so obtained conducting polymer tubules could be an order of magnitude higher than in the bulk form of the polymer.

Recently, in parallel to the development of a preparation process and characterization techniques for nanoporous particle track-etched membranes (nano-PTM),[9−11] we considered the use of these nano-PTM as templates for the synthesis of nanoscale polymers.[12−14] In particular, we focused our attention on the electropolymerization of pyrrole inside the pores of polycarbonate (PC) nano-PTM.[13,14] Until now, not much attention has been paid to the study of the influence of the synthesis parameters on the electropolymerization of pyrrole in confined medium. The aim of this paper is to determine how the electrolyte nature and concentration as well as the diameter of the nanopores in the template can influence the pyrrole electropolymerization process and

---

* Corresponding author. Tel: 0032/10 473560. Fax: 0032/10 451593. E-mail: demoustier@poly.ucl.ac.be.

(1) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.
(2) Nuclepore Corp. Pleasanton, CA; Poretics Corp. Livermore, CA; Whatman sa, Louvain-la-Neuve, Belgium.
(3) Martin, C. R. *Science* **1994**, *266*, 1961.
(4) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739.
(5) Hulteen, J. C.; Martin, C. R. *J. Mater. Chem.* **1997**, *7*, 1075.
(6) Penner, R. M.; Martin, C. R. *J. Electrochem. Soc.* **1986**, *133*, 2206.
(7) Martin, C. R.; Van Dyke L. S.; Cai Z.; Liang W. *J. Am. Chem. Soc.* **1990**, *112*, 8976.
(8) Menon, V. P.; Lei, J.; Martin, C. R. *Chem. Mater.* **1996**, *8*, 2382.
(9) Ferain, E.; Legras, R. *Nucl. Instrum. Methods Phys. Res. B* **1993**, *82*, 539.
(10) Ferain, E.; Legras, R. *Nucl. Instrum. Methods Phys. Res. B* **1994**, *84*, 331.
(11) Ferain, E.; Legras, R. *Nucl. Instrum. Methods Phys. Res. B* **1997**, *131*, 97.
(12) Duchet, J.; Legras, R.; Demoustier-Champagne, S. *Synth. Met.* **1998**, *98*, 113.
(13) Demoustier-Champagne, S.; Ferain, E.; Legras, R.; Jérôme, C.; Jérôme, R *Eur. Polym. J.* **1998**, *34*, 1767.
(14) Demoustier-Champagne, S.; Legras, R. *J. Chim. Phys. PCB* **1998**, *95*, 1200.

10.1021/cm9807541 CCC: $18.00

the morphology and electrical conductivity of the obtained nanomaterials.

In this work, we present our study on the electrochemical growth of polypyrrole (PPy) inside the pores of homemade PC nano-PTM. This study has been performed using four types of doping agents: perchlorate (ClO_4^-), dodecyl sulfate (DS), toluenesulfonate (TS) and polystyrenesulfonate (PSS). The morphology of the different nanostructures has been carefully analyzed using field-emission scanning electron microscopy (FE-SEM). The relative conjugation length in the PPy chains has been determined using Raman spectroscopy, and a two-probe method has been used to measure the electrical conductivity of template-synthesized polypyrrole nanostructures.

Experimental Section

Materials. The present work was carried out in aqueous solutions. Purified water obtained by passing distilled water through a milli Q (Millipore) water purification system was used as solvent (σ < 18 $M\Omega^{-1}cm^{-1}$). Pyrrole (Acros) was distilled prior to use. Poly(sodium 4-styrenesulfonate) (PSS, Acros), lithium perchlorate (ClO_4^-, Aldrich), dodecyl sulfate sodium salt (DS, Acros), and *p*-toluenesulfonic acid sodium salt (TS, Acros) were used without any prior purification. PC PTMs with a thickness of 20 μm, a pore density of 10^9 pores/cm^2, and different pore diameters ranging from 35 to 100 nm prepared by a our own procedure[15] were used as template membranes for the synthesis of PPy nanostructures.

Polypyrrole Electrochemical Synthesis. A metallic layer serving as an electrode is evaporated onto one side of the membrane: a 10−20 nm adhesion layer of Cr is applied first, followed by a Au film with a thickness from 500 nm to 1 μm. The electropolymerization was performed, at room temperature, in a conventional one-compartment cell with a Pt counter electrode and an Ag/AgCl reference electrode. The solutions contained 0.1 M pyrrole and various concentrations of one type of supporting electrolyte: ClO_4^-, DS, TS, or PSS. The synthesis solutions were deoxygenated with N_2 before polymer electrodeposition. Polymers were grown potentiostatically at 0.8 V using an EG&G Princeton Research Model 273A potentiostat/galvanostat.

Characterization of Polypyrrole Nanostructures. A field-emission gun digital scanning electron microscope (DSM 982 Gemini from Leo) with an accelerating voltage of 1 kV was used to characterize the polypyrrole nanostructures. For the morphology observation, the host membrane was dissolved in dichloromethane, and the isolated PPy nanotubules were collected by filtration on a silver filter. The PPy tubules were then repeatedly rinsed with copious quantities of dichloromethane to remove any traces of the PC template membrane.

Raman spectra were recorded on a dispersive Dilor spectrophotometer with an incorporated microscope employing a He−Ne$^+$ laser emitting at 632.8 nm.

The electrical conductivity of the PPy nanostructures established inside the pores was obtained by measuring the bulk resistance across the filled membrane by a two-probe method. The metalized side of the membrane was held on a copper electrode, and two copper wires contacted the other side of the membrane. Silver paste ensured a good contact and allowed determining a well-defined cross section for calculating the conductivity. The conductivity along a single fibril can be calculated from the resistance measurement that provides the bulk resistance of the composite membrane, *R*, which can be written as:

$$1/R = 1/R_f + 1/R_m \tag{1}$$

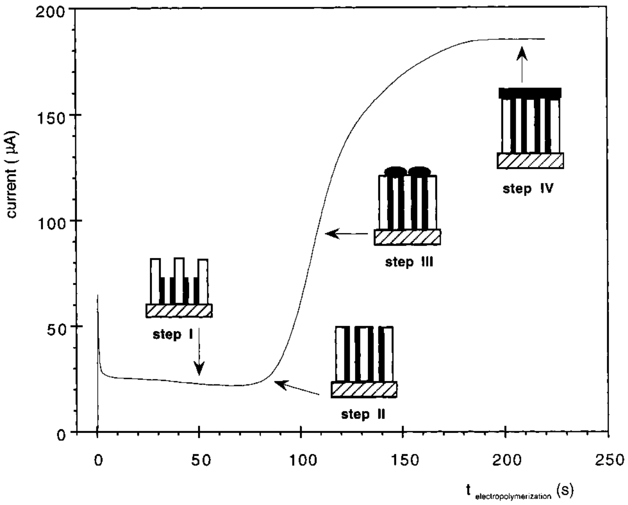

Figure 1. Typical chronoamperogram obtained for the electropolymerization of pyrrole in pores of a homemade PC track-etched membrane. The schematics display four different stages of the growth process: step I, PPy tubules are growing in the pores of the template membrane; step II, the pores are just completely filled (this point corresponds to $t_{filling}$); step III, PPy tips are appearing on the membrane surface; step IV, PPy growth appears over the whole membrane surface.

Where R_f is the parallel sum of the resistances of the conductive polymer tubules and R_m is the resistance of the PC membrane. R_m can be neglected because $R_m \gg R_f$. So we can write the following equation:

$$1/R = 1/R_f = n/R_i \tag{2}$$

Where *n* is the number of tubules in the measurement area and R_i is the resistance of an individual tubule. From the area measurement determined by optical microscopy and from the known pore density of the membrane, the number of contacted tubules can be estimated. So, R_i can be calculated from *R*. Knowing the length (*L*) of the pores and the outside (ϕ_o) and the inner diameter (ϕ_i) of the tubules and from the calculated value of R_i, the tubule conductivity (σ) can be determined by

$$\sigma = L/[R_i\pi(\phi_o^2 - \phi_i^2)/4] \tag{3}$$

Results and Discussion

Electrosynthesis of PPy Nanostructures. It is well-established that the supporting electrolyte used to synthesize a conducting polymer affects its morphology and some of its properties. For this reason, we used different types of electrolytes as doping agents during the electropolymerization of pyrrole inside the pores of a PC membrane. In each case, polypyrrole was generated by polarizing the working electrode at 0.8V vs Ag/AgCl for a defined polarization time. One of the advantages of the electrochemical method compared to the chemical one is that the growth rate and the tubules length are easily controlled. Indeed, with short electropolymerization times, short tubules can be obtained. Alternatively, by depositing large quantities of PPy, long tubules can be prepared. Figure 1 shows a potentiostatic electric current vs time, *i*−*t* curve, characteristic for the oxidation of pyrrole in nano-PTM.

In the same figure, two pores are schematically drawn in cross section at three different stages of the growth process. During the first stage, the polymer is growing in the pores (step I). Growth proceeds in the pores until they are filled up to the top surface of the membrane

---

[15] To be patented.

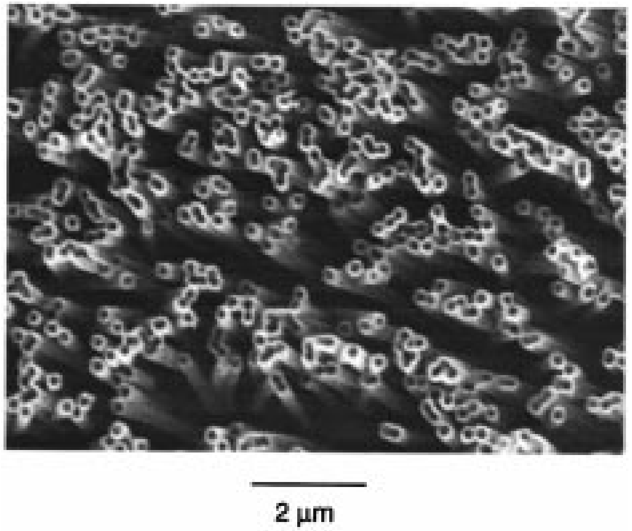

Figure 2. FE-SEM image of PPy/ClO_4 tubules obtained after dissolution of the PC membrane.

(step II). Beyond this, growth can continue in three-dimensionals and hemispherical caps form on the top of the tubules (step III), which grow in size. Since the effective electrode area increases rapidly during this stage, the electrochemical current increases. Once growth proceeds on the whole membrane surface (step IV), the current approaches an asymptotic value.

To investigate the influence of salt concentration and nature, PPy was synthesized using four types of electrolytes: ClO_4^-, DS), TS, and PSS, in different concentrations ranging from 0.1 to 0.5 M, while the pyrrole concentration was kept fixed at 0.1 M. Electrochemical syntheses was also performed using homemade PC nano-PTM with different pore diameters: 35, 65, and 110 nm.

Morphological Study. The morphology of the different template-synthesized PPy nanostructures obtained by electropolymerization inside nanopores of different sizes and using the four different doping anions in various concentrations were analyzed using FE-SEM after the dissolution of the PC host membrane. In all cases, nanotubules were obtained. Martin et al.,[16] who already reported on the formation of PPy tubules in the case of PPy chemical template synthesis, propose to explain this phenomenon by the electrostatic attraction between the growing polycationic polymer and anionic sites along the pore walls of the PC membrane. A picture representative of the obtained nanostructures is presented in Figure 2.

We observed that the thickness of the nanotubules does not vary with the concentration of the electrolyte used during the electrosynthesis. However, as shown in Figure 3, the thickness of the nanotubules is a function of the pore diameter of the template membrane and of the nature of the supporting electrolyte.

Indeed, for pores diameter of 110 nm, thicker tubules are obtained when using a large polymeric counterion (PSS), and the thinner ones are yielded when using a surfactant agent as counterion (DS). The difference of thickness between the different PPy/counterion tubules decreases when the pore diameter is reduced. Finally, for the narrowest nanopores (i.d. = 35 nm), all the types of PPy tubules have the same thickness.

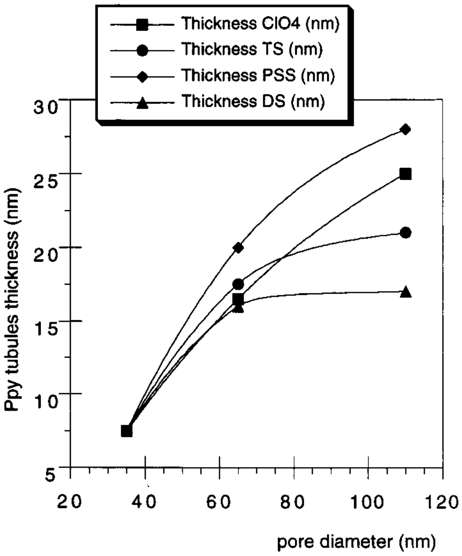

Figure 3. Dependence of the PPy thickness on pore diameter in terms of the electrolyte nature; [pyrrole] = 0.1 M, [electrolyte] = 0.1 M.

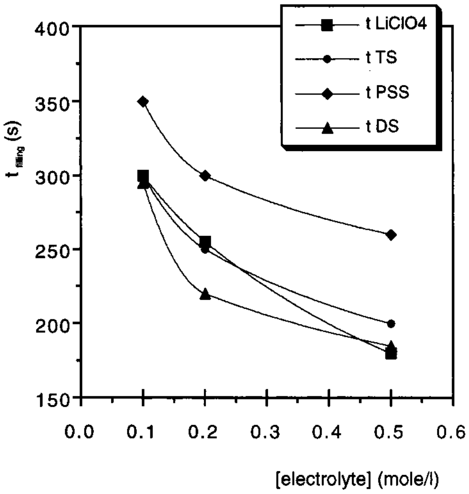

Figure 4. Evolution of the time of electropolymerization corresponding to the emergence of the PPy tubules from the membrane surface ($t_{filling}$) in terms of the electrolyte concentration and nature. Pore diameter of the template membrane = 110 nm.

Effect of the Nature and Concentration of the Electrolyte. For each electrosynthesis, the charge ($Q_{filling}$) consumed after a period of electropolymerization ($t_{filling}$) corresponding to the emergence of the PPy tubules from the surface of the membrane was determined. By keeping the pore diameter constant at a value of 110 nm while varying the electrolyte concentration, one may study the influence of this parameter on $Q_{filling}$ and $t_{filling}$. Our results are presented in Figures 4 and 5.

A decrease of $t_{filling}$ corresponding to an increase in polymerization rate is observed when the electrolyte concentration rises (Figure 4). This phenomenon has already been reported for the electrosynthesis of conducting polymer films[17–19] and has been explained in different ways: (a) an increase in the conductivity of the electrolyte solution, (b) the stabilization of the growing

---

(16) Martin, C. R. *Adv. Mater.* **1991**, *3*, 457.

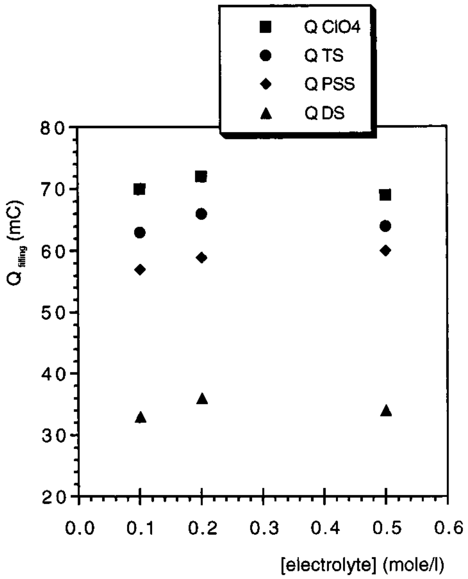

Figure 5. Evolution of the charge consumed at the emergence of the PPy tubules from the membrane surface (Q_{filling}) in terms of the electrolyte concentration and nature. Pore diameter of the template membrane = 110 nm.

radical cations by the anions of the electrolyte, their coupling being favored over secondary reactions, and (c) the effect of electrolyte concentration on the formation of oxides on Pt electrode which catalyze the monomer oxidation.[20] Finally, some authors have suggested that the polymerization process can be initiated by the oxidation of the anion.[21]

Although the filling of the pores is more rapid when increasing the electrolyte concentration, Figure 5 shows that Q_{filling} remains constant. That means that the amount of electrodeposited PPy does not vary in terms of the electrolyte concentration. This result is closely related to the morphological observations showing that the thickness of the nanotubules also does not vary in terms of the electrolyte concentration.

Influence of the Pore Diameter. The influence of the pores diameter on Q_{filling} and t_{filling} has also studied by keeping the electrolyte concentration fixed at a value of 0.1M. The results of this study for the 4 different electrolytes are reported in Figures 6 and 7.

For all the electrolytes, we observed that Q_{filling} increases with pore diameter (Figure 6). Consequently, the more the pore diameter increases, the more the amount of electrodeposited PPy increases. This observation perfectly correlates with the fact that the tubule thickness increases with the pore diameters in the template membrane (Figure 3). Moreover, the fact that similar Q_{filling} are obtained for the four types of electrolytes when the electrosynthesis of PPy is performed in nanopores of 35 nm diameter is also in perfect agreement with the observation of nanotubules of identical thickness under these conditions (Figure 3).

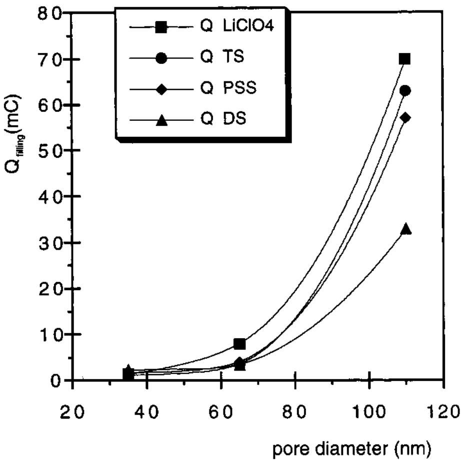

Figure 6. Dependence of the Q_{filling} on pore diameter in terms of the electrolyte nature; [pyrrole] = 0.1 M, [electrolyte] = 0.1 M.

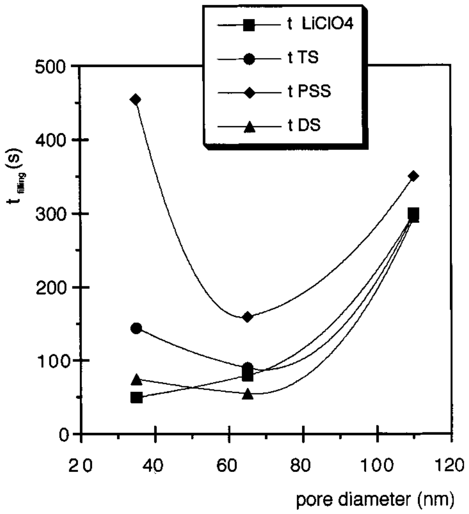

Figure 7. Dependence of the t_{filling} on pore diameter in terms of the electrolyte nature; [pyrrole] = 0.1 M, [electrolyte] = 0.1 M.

The evolution of t_{filling} in terms of the pore diameter is more complex. Indeed, as illustrated in Figure 7, t_{filling} is not only a function of the pore size but also of the electrolyte size and charge. As already mentioned, the morphological analysis of PPy tubules revealed that the larger the pore diameter is, the greater the PPy deposited amount is. This should lead to an increase of t_{filling} with pore size. That is the behavior observed when using a small counterion, such as ClO_4^-. However, with larger counterions, DS and TS, t_{filling} first decreases in the 110−65 nm pore diameter range and then slightly increases for smaller diameters. This phenomenon is even more pronounced with PSS, a polyelectrolyte. In that case, an important increase of t_{filling} is measured when using membranes with narrower pores ($\phi < 60$ nm). We think that this effect can be attributed to mass transport limitations in the pores, which are more significant for smaller pores than larger ones. Of course, the limited diffusion of the counterion inside the pores results in a decrease of the PPy growing rate along the pore walls, leading to an increase of t_{filling}. Moreover, the relative surface coverage of filled pores is found to be reduced for membranes with narrow pores. This stresses the difficulty in getting all pores wetted by water prior to electrodeposition.

---

(17) Otero, T. F.; Rodriguez, J.; Angulo, E.; Santamaria, C. *Synth. Met.* **1991**, *43*, 2831.

(18) Otero, T. F.; Angulo, E. *J. Appl. Electrochem.* **1992**, *22*, 369.

(19) Otero, T. F.; Rodriguez, *J. Electrochim. Acta* **1994**, *39*, 245.

(20) Otero, T. F., Santamaria C. *Electrochim. Acta* **1992**, *37*, 297.

(21) Prejza, J.; Lundstrom, I.; Skothein, T. *J. Electrochem. Soc.* **1982**, *129*, 1685.

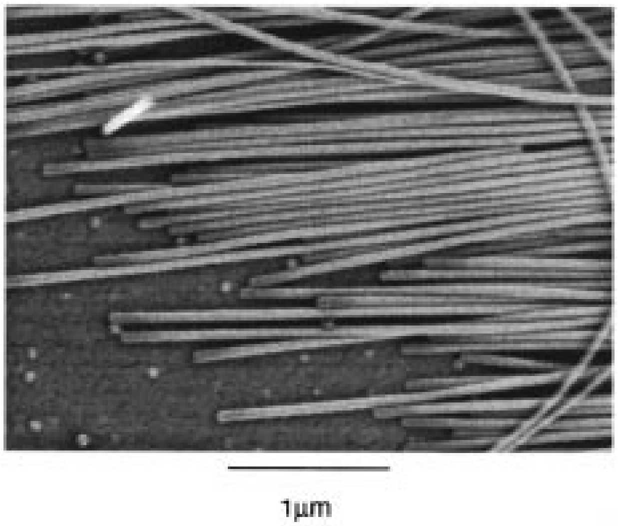

Figure 8. FE-SEM picture showing typical cylindrical-shaped PPy nanotubules obtained by electropolymerization in homemade PC nano-PTM

Conductivity Measurements. The conductivity of the different electrosynthesized PPy nanotubules has been measured using the two-probe method described in the Experimental Section. Calculation of PPy tubule conductivity requires the accurate knowledge of the pores' diameter, shape, and density and of the membrane's thickness. In all the published papers [8,22–24] dealing with this topic, the authors assume that the pores of the commercial membranes are cylindrical with a diameter corresponding to the one tabulated by the manufacturer, called the nominal diameter. This hypothesis has now been challenged by different groups[11,12,25,26] who found that the pores shape of commercial membranes are cigarlike and that real pore diameters can be larger by up to a factor of 3 compared to the nominal diameter. So, with respect to the effective wires' cross section the area can be on average up to a factor of 10 larger than what is assumed if the nominal values are used. This can, of course, drastically influence physical parameters, in particular, the electrical conductivity derived from measurements on these tubules and wires. Moreover, the pores in the commercial membranes are not aligned parallel but have a considerable angular distribution of ± 34°. For this reason, depending on the pore diameter and pore density of the PTM, a number of pores may actually intersect within the membrane. Consequently, the length of the pores, measured through the membrane, is not constant. In this work, we have used homemade PTM with a perfectly cylindrical pore shape and with pores aligned perfectly parallel. So, in this case, we obtain PPy tubules without any intersections and with constant diameter on their whole length. In Figure 8 we present a FE-SEM image showing the perfectly cylindrical shape of PPy tubules electrosynthesized in homemade PC membranes. Another difference with already reported results on the conductivity of PPy tubules is that here we have taken into account the tubular nature of the PPy nanostructures in the calculations of their electrical conductivity. Until now, this parameter had always been neglected.

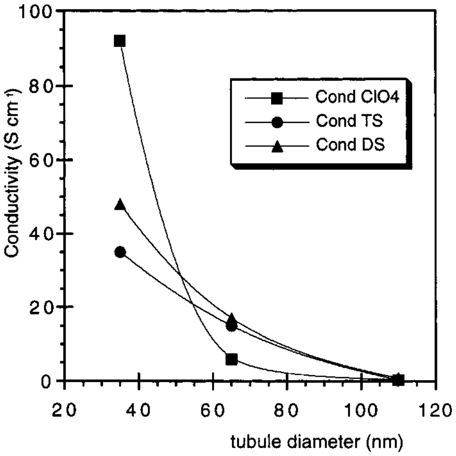

Figure 9. Plot of PPy tubules conductivity in terms of their outside diameter for three different PPy counterion combinations.

Figure 9 shows the relationship between the tubules outside diameter and the conductivity for the different PPy/counterion combinations.

In complete analogy with previous results, the conductivity increases as diameter of the tubule decreases. It is clear that there is a dependence on the size and type of the counterion, since the conductivity increases more rapidly and reaches higher values for the samples made with small counterions. This is in perfect agreement with the results reported by Inganas et al.[24] The narrowest tubules show the highest conductivity because such tubules contain a higher portion of ordered chain material. Note, however, that the values of conductivity are much lower than those found by Martin et al.[22–23] Indeed, they report enhancement of conductivities to values of approximately 10^3 S cm^{-1}.

This could result from the multiple differences between the two works: (1) PPy nanotubules have not been synthesized the same way. Martin et al. performed electrical measurements on chemically synthesized PPy nanotubules, we did it on electrochemically synthesized PPy nanotubules. (2) The syntheses have not been performed using the same template membranes; commercial membranes (Nuclepore) were used in the case of Martin et al., and homemade track-etched membranes were used in our case. (3) The parameters (nominal or real pore diameter, PPy wires or tubules, etc.) taken into account in the calculation of the conductivity are not the same. (4) To reduce the contact resistance, they applied pressure to their samples to perform the electrical measurement. We did not do that in order to avoid any possibility of PPy tubular nanostructure destruction. However, we have probably higher contact resistance. (5) They estimated the number of contacted PPy nanotubules from the pore density of the template membrane considering that 100% of the pores are filled. This assumption is rather unrealistic, especially in the case of small pore diameters. On the basis of electrochemical data, we have corrected this number

---

(22) Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. *Chem. Mater.* **1991**, *3*, 960.

(23) Cai, Z.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138.

(24) Granström, M.; Inganäs, O. *Polymer* **1995**, *36*, 2867.

(25) Chlebny, I.; Doudin, B.; Ansermet, J.-Ph. *Nano-Struct. Mater.* **1993**, *2*, 637.

(26) Schönenberger, C.; van der Zande, B. M. I.; Fokkink, L. G. J.; Henny, M.; Schmid, C.; Krüger, M.; Bachtold, A.; Huber, R.; Birk, H.; Staufer, U. *J. Phys. Chem. B* **1997**, *101*, 5497.

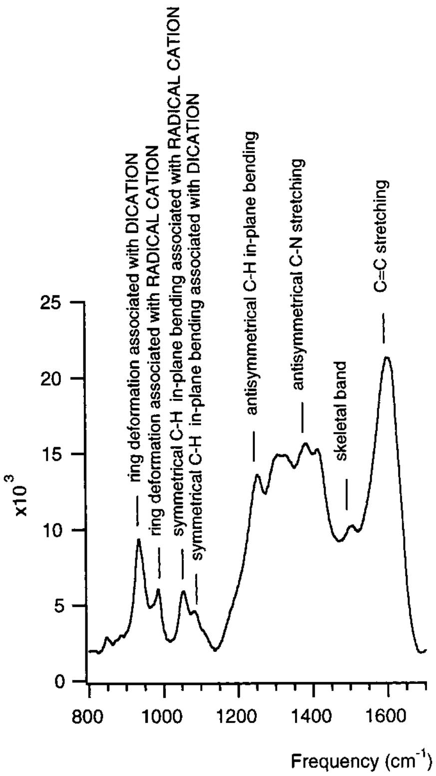

Figure 10. Raman spectrum of PPy/ClO$_4$ (i.d. = 35 nm) tubules, and bands assignment based on the works of Furukawa et al.[27]

by estimating the percentage of filled pores, called the filling ratio. The filling ratio can be estimated by making a ratio between the Q_{filling} measured experimentally (Figure 6) and the theoretical Q_{filling} calculated by the Faraday law assuming that all pores are filled. Nevertheless, even by doing this correction, incertitude still remains on the exact number of contacted PPy tubules. Therefore, to solve this problem and get reliable absolute values of the electrical conductivity of PPy nanotubules, we are now developing a method allowing the measurement of the conductivity of only one nanotubule.

Raman Spectroscopy. Raman spectroscopy is a unique tool in providing information on the structural and electronic properties of polyconjugated materials, since it shows features peculiar to the delocalization of the π electrons. It is usually thought that there is a direct relationship between the conductivity of a polymer and its state of conjugation. For that reason, we determined the relative conjugation length in the PPy tubules using Raman spectroscopy. By conjugation length we mean the length of the polyene segment along which the delocalization can take place. The fact that Raman spectroscopy is based on scattering phenomena leads to the possibility of analysis of insoluble samples without any specific preparation. The Raman analyses were performed on the different PPy/counterion nanotubules of different diameters after dissolution of the PC membrane. This allowed us to get the characteristic spectrum of polypyrrole, which is presented in Figure 10 with the assignment of the bands based on the works of Furakawa et al.[27]

Table 1. Raman Bands Intensity Ratio in Terms of PPy Tubule Diameter for Different Electrolytes

PPy tubule diameter (nm)	I_{1595}/I_{1500}			
	PPy/ClO$_4^-$	PPy/DS	PPy/TS	PPy/PSS
110	1.4	1.3	1.4	1.2
65	1.9	1.4	1.5	1.3
35	2.4	1.5	1.7	1.4

The peaks at 934 and 1086 cm^{-1} have been associated with the bipolaron structure and those at 968 and 1055 cm^{-1} with the polaron structure. The C=C stretching peak at 1595 cm^{-1} is considered to be an overlap of the two oxidized structures. More information can be extracted from Raman spectra. By calculating the bands ratio between the intensity of a band sensitive to the oxidation state of the polymer (the band at 1595 cm^{-1}) and the intensity of the skeletal band (the band at 1500 cm^{-1}), we determined the relative conjugation length. As reported in Table 1, we observed an increase of this band ratio when the PPy tubule diameter decreases. This effect is particularly well -marked for PPy/ClO$_4^-$ tubules.

We must notice that for the three other electrolytes, the samples showed small fluorescence, which perturbed the recording of the Raman spectra. The increase of the intensity of the C=C stretching band vs the intensity of the skeletal band means that the polarizability of the system is higher for narrower PPy tubules or, in other words, that the conjugated length increases. These results are in perfect agreement with the observed increase of conductivity for narrower PPy tubules. One should mention that the conclusions of our Raman work are identical to the conclusions reached by Martin et al. from polarized infrared absorption spectroscopy.[8]

Acknowledgment. The authors wish to thank Prof. R. Legras, Dr. E. Ferain, Prof. L. Piraux, and Dr. J-L. Duvail for helpful discussions. Thanks also go the "Services Fédéraux des Affaires Scientifiques Techniques et Culturelles" for their financial support in the frame of the "Pole d'Attraction Interuniversitaires".

CM9807541

---

(27) Furukawa, Y.; Tazawa S.; Fujii, Y.; Harada, I. *Synth. Met.* **1988**, *24*, 329.