Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

Electrochemically synthesized polypyrrole nanotubules: effects of different experimental conditions

DEMOUSTIER-CHAMPAGNE SOPHIE[(a)], FERAIN ETIENNE[(a)] JEROME CHRISTINE[(b)], JEROME ROBERT[(b)] and LEGRAS ROGER[(a)]

[(a)]Université catholique de Louvain, Unité de Chimie et de Physique des Hauts Polymères, Croix du Sud, 1; B-1348 Louvain-la-Neuve, Belgium
[(b)]Université de Liège, Centre d'Etude et de Recherche sur les Macromolécules, Bâtiment B6, Sart-Tilman, B-4000 Liège, Belgium

Abstract

Nanotubules of polypyrrole (PPy) were electrochemically synthesized using the pores of nanoporous polycarbonate (PC) particle track-etched membranes (PTM) as templates. The influence of some conditions of electrosynthesis (electrochemical method, monomer concentration, electrolyte concentration and nature) on the kinetics of pyrrole electropolymerization and on the morphology of the obtained nanomaterials has been investigated. In particular, the empirical kinetics of the electrochemical generation of polypyrrole-perchlorate (PPy-ClO_4) from aqueous solution, at 0.8 V (vs SCE) was followed by electrical charges measurement. The orders with respect to pyrrole and $LiClO_4$ are 0.34 and 0.70 respectively. The electrogeneration of polypyrrole-polystyrenesulfonate (PPy-PSS) was also followed and shows that an increase of the electrolyte concentration increases the polymerization rate at constant potential. Finally, the morphology of PPy nanotubules doped with $LiClO_4$ and NaPSS has been studied by high resolution emission SEM and by TEM.

INTRODUCTION

Currently there is a considerable interest in nanos-cale materials, since they exhibit novel properties largely as a consequence of their finite small size. Moreover, nanomaterials have wide-ranging implications to a variety of areas, including chemistry, physics, electronics, optics, materials science and the biomedical sciences. A possible chemical approach for building such nanoscale objects involves the use of nanoporous host materials as templates [1]. In particular, Martin *et al.* [2,3] described a new method for preparing organic microtubules which consists in using a microporous membrane as a template during tubules synthesis. Until now, most of their work has focused on the synthesis of polypyrrole, poly(3-methylthiophene) and polyaniline inside the pores of a polycarbonate Nucleopore 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 reported, once on the electrochemical synthesis of pyrrole, Martin *et al.* essentially used the chemical way consisting in using a template membrane as a dividing wall between a solution of monomer and a ferric salt polymerization agent [4]. The monomer and oxidizing agent diffuse toward each other through the pores in the template membrane, and react to yield the polymer. Recently, in parallel to the development of preparation process and characterization techniques of nanoporous particle track etched membranes (nano PTM) [5-7], we consider the use of these nano PTM as templates for the synthesis of nanoscale polymers. We started with the electropolymerization of pyrrole inside the pores of polycarbonate (PC) nano PTM. 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 different synthesis parameters (the applied potential, the monomer concentration, the electrolyte nature and concentration) influence the pyrrole electropolymerization process and the morphology of the obtained materials.

EXPERIMENTAL

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. Pyrrole (Janssen) was distilled under low pressure prior to use. The poly (sodium-4-styrenesulfonate) (NaPSS, Acros) and the lithium perchlorate ($LiClO_4$, Aldrich) were used without any prior purification.
The microporous polycarbonate particle track-etched membranes (PTM) used in this work were

obtained by the following way. A 10 *μm* thick crystalline bisphenol-A polycarbonate (PC) film from Bayer was irradiated in the accelerator of the Cyclotron Research Centre of Louvain-la-Neuve with energetic heavy ions (Ar^{9+}, 5.5 MeV/amu) at a fluence of 4.5 x 10^8 ions per cm^2. This irradiation is carried out under vacuum at room temperature. The ion irradiated film is then UV irradiated to increase the selectivity [5] of the chemical etching which is performed with a NaOH aqueous solution at a controlled temperature (70°C) [6,7]. For this study, we prepared and used micro-porous PC PTM with pore diameters of 200 nm.

Polymer synthesis

A layer of about 500 nm of gold was deposited on one side of the template membrane using a vacuum coating. This metal film was used as an anode to electrochemically synthesize the polymer within the pores of the membrane. All experiments were carried out in a conventional one compartment cell with a Pt counter electrode and a saturated calomel reference electrode, at room temperature. The different electrochemical techniques employed for synthesis of polypyrrole were accomplished using an EG and G Princeton Research Model 273A potentiostat/galvano-stat. The electrosynthesis described above yields a composite of the porous polycarbonate PTM and the polypyrrole fibers (PC/PPy).

Electron microscopy

Scanning electron microscopic images were obtained using a high resolution FEG Digital Scanning Microscope 982 Gemini from Leo. For morphological studies using SEM, the PC membrane has been dissolved in dichloro-methane and PPy fibers have been collected by filtration.
Transmission electron microscopy studies were carried out using a Philips EM 301 Transmission Electron Microscope. The TEM samples were prepared as follows: the PPy/PC composite was immersed in a 2% (w/v) aqueous OsO_4 solution for 1 h. This treatment selectively stains the PPy. The stained membrane was then embedded in an epoxy resin and cut with an LKB Ultramicrotome III at room temperature, following the microtoming procedure described by Martin *et al. [8]*.

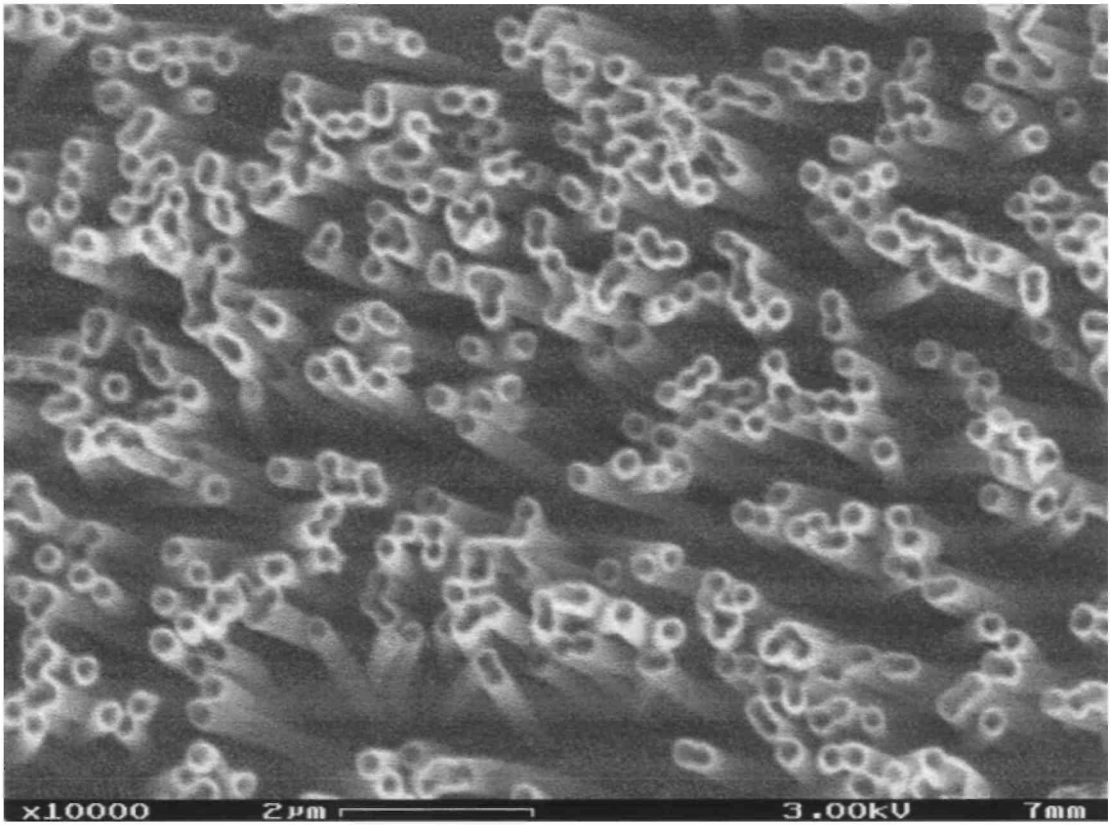

Fig. 1. Scanning electron microscopic image of polypyrrole nanotubules obtained by electrochemical synthesis at 0.8 V in a bath containing an aqueous solution of 0.1 M pyrrole and 0.1 M $LiClO_4$.

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

RESULTS AND DISCUSSION

In order to investigate the influence of electrochemical synthesis parameters on the electropolymerization of pyrrole inside the pores of a PC nano PTM and on the morphology of the obtained polypyrrole nanostructures, the following initial conditions were used: polymerization potential of 0.8 V vs calomel reference electrode in a 0.1 M pyrrole aqueous solution containing 0.1 M of $LiClO_4$. The polymerization was performed at 25°C. SEM micrographs of the template synthesized polypyrrole nanostructures obtained after dissolution of the polycarbonate template membrane are shown in Fig. 1. These images clearly show that nanotubules are obtained when polypyrrole is synthesized within the pores of the template membrane. That nanotubules are obtained by template synthesis is also proven by the TEM image shown in Fig. 2. This picture shows pores containing rings of stained polypyrrole.
It is interesting to note that electrochemical deposition of polymer naturally leads to the formation of tubules while it produces solid wires in the case of metal deposition. Martin *et al.* [1]. who already reported on the formation of conducting polymer tubules propose to explain this phenomenon by the electrostatic attraction between the growing polyca-tionic polymer and anionic sites along the pore walls of the polycarbonate membrane.

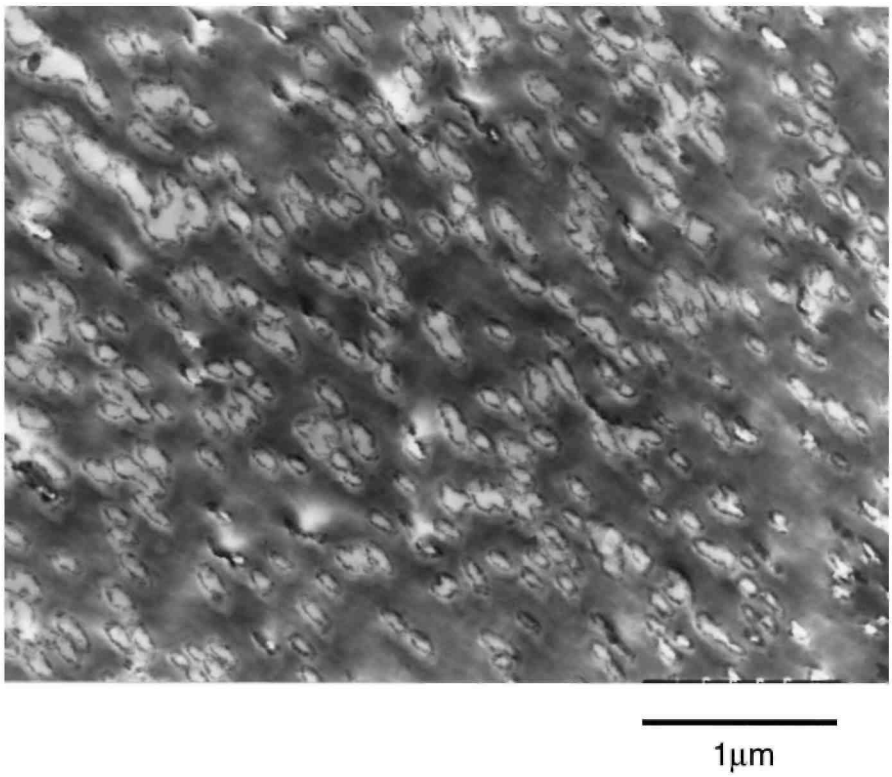

Fig. 2. Transmission electron micrograph of ultramicrotomed sections of the PC membrane after electrosynthesis of polypyrrole tubules within the pores of the membrane.

Although, we agree that the electrostatic attraction surely contributes to the formation of the polymer tubules, we found interesting to study carefully the influence of different synthesis parameters on the growing of polypyrrole inside the pores of a template membrane. To our knowledge, the only reported study on the influence of some pyrrole polymerization conditions inside the pores of microporous membranes concerns the effect of monomer and electrolyte concentration on the electrical conductivity of polypyrrole fibers [9]. However, in that work there was no information on the rate of electropolymeri-zation nor on the morphology of the obtained materials.

Influence of the electrochemical method

One of our hypothesis is that the formation of tubules could also result from a limited diffusion of the monomer and the electrolyte inside the pores. Indeed, at the beginning of the electropolymeriza-tion process, the monomer contained in the pores is rapidly consumed. As the growing of the chain along the pore walls is very fast, the first tubules emerge rapidly from the surface and progressively cover the

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

opening of the pores. When the pores are completely corked with polypyrrole, the diffusion of the reagents is stopped and consequently it is no more possible to thicken the tubules walls. The first parameter studied to test this hypothesis was the electrochemical method employed to electrogenerate polypyrrole inside the pores of PC nano PTM. We used the pulsed chronoamperometry technique in order to let the monomer and electrolyte periodically diffuse inside the pores. The different pulsed time t_1 (time during which a potential of 0.8 V vs calomel reference was applied) and delay time t_2 (time during which no polarization was imposed) employed in these experiments are summarized in Table 1. The electropolymerizations were carried out at room temperature in a bath containing an aqueous solution of pyrrole (0.1 M) and $LiClO_4$ (0.1 M). The morphologies of the polypyrrole nanostructures obtained after dissolution of the host membrane were analyzed using a FEG microscope. In each case, polypyrrole nanotubules of the same thickness than those obtained using the conventional chronoamperometry technique and presented in Fig. 1 were observed. This seems to indicate that the diffusion of the monomer and electrolyte inside the pores of the membrane is not the determinant parameter leading to the formation of tubules, at leas tusing membranes with pores diameters equal or larger than 200 nm.
The influence of other important electrosynthesis parameters such as the monomer and electrolyte concentration was then investigated. We reported here the results of our kinetic and morphology studies.

Table 1. Pulsed and delay times used during pulsed electropoly-merization of pyrrole

t_1(s)	t_2(S)	Number of pulses
5	20	20
5	50	20
10	20	10
10	50	10
20	50	5

Influence of the monomer and electrolyte concentration

The dependence of the rate of polymerization on monomer and electrolyte concentration, or the order of reaction, can be studied from gravimetric or electrical data [9-13]. In this paper we only report on electrical kinetics. From the influence of monomer or electrolyte concentration, an empirical gravimetric kinetics can be obtained:

$$R_p = k[\text{pyrrole}]^{\alpha}[\text{electrolyte}]^{\beta} \qquad (1)$$

where R_p is the polymerization rate, α, β reaction orders and k the kinetic constant.
From the chronoamperograms obtained during each electropolymerization, the concomitant polymerization charges (electrical charge consumed during polymerization) can be obtained. From the evolution of that charge with polymerization time, an empirical kinetics can be achieved. If we assume a linear relation between consumed electrical charge
and produced polymer weight of the form

$$Q = k'M \qquad (2)$$

where Q is the electrical charge consumed to generate the polymer (in mC), M is the polymer weight generated during polarization (in mg) and k' is the current productivity (electrical charge consumed to generate a unit of polymer mass, in mC mg^{-1}). The slopes of the straight lines are:

$$dQ/dt = k'\, dM/dt = k'R_p \qquad (3)$$

where R_p is the polymerization rate which has been defined in equation (1). Therefore:

$$dQ/dt = k''[\text{pyrrole}]^{\alpha}[\text{electrolyte}]^{\beta} \qquad (4)$$

where $k'' = kk'$
Taking the logarithms, we have:

$$\log dQ/dt = \log k'' + \alpha \log[\text{pyrrole}] + \beta \log[\text{electrolyte}] \qquad (5)$$

A representation of log dQ/dt against log[pyrrole] or log[electrolyte] will give a straight line, the slope of which is the order of the reaction related to the monomer or electrolyte concentration.
The electrogeneration of PPy/PC composite was followed from solution having different concentrations of monomer or different concentrations of electrolyte.

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

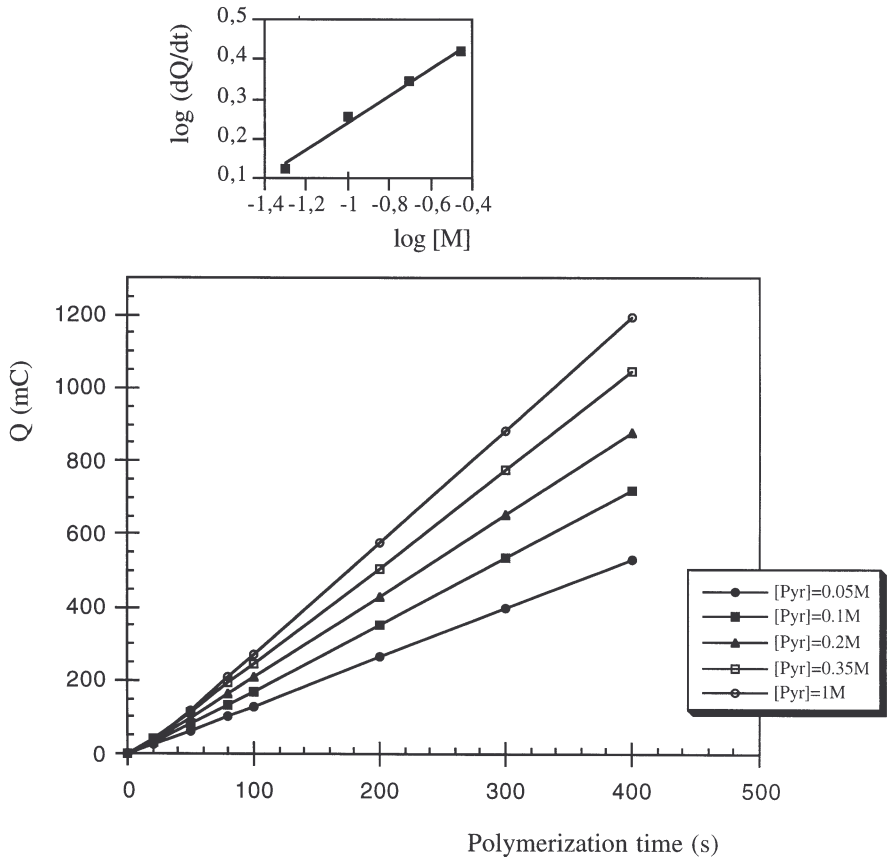

Fig. 3. Determination of the reaction order to pyrrole concentration from electrical charges results. R_p values were obtained from slopes of electrical charges-polymerization time straight lines for different pyrrole concentrations at 0.8 V polymerization potential and 0.1 M $LiClO_4$.

Electrogeneration at different concentrations of monomer

Aqueous solutions containing 0.1 M $LiClO_4$ and different concentrations of monomer ranging from 0.05 M to 1 M were used as electropolymerization solutions. Polypyrrole was generated by polarizing the working electrode at 0.8 V for different polarization times lower than the time required for the whole filling of the pores of the template membrane. The filling of the pores can be easily monitored by measuring the plating current. Indeed, as the first polypyrrole tubules emerge from the surface, the current increases very rapidly due to the formation of caps associated to a three-dimensional deposition. All the electropolymerizations done for the kinetics study were stop before this stage. The electrical charge *(Q)* consumed to generate the polymer was obtained by integration of the chronoamperograms recorded during electropolymerization.

As shown on Fig. 3, the charge consumed vs polymerization time gives a straight line at each concentration of monomer. Each slope *(dQ/dt)* has the meaning of a polymerization rate R_p: charge consumed to generate the polymer per unit of polymerization time. A double logarithmic plot of the slopes *(dQ/dt)* obtained with pyrrole concentration ranging from 0.05 to 0.35 M, gives a straight line (Fig. 3):

$$\log(\mathrm{d}Q/\mathrm{d}t) = \log R_\mathrm{p} = 0.58 + 0.34[\mathrm{Pyrrole}] \quad r = 0.9957$$

the empirical kinetics from electrical parameters being:

$$R_\mathrm{p} \% [\mathrm{Pyrrole}]^{0.34}$$

The value of pyrrole reaction order obtained for electrogeneration inside the pores of a host membrane (0.34) is slightly lower than the value obtained for the electrogeneration of pyrrole on a bare platinum electrode (without any restricted accessibility of the monomer/electrolyte solution to the electrode) which is 0.5 [10].

The morphologies of the template synthesized polypyrrole nanostructures obtained by electropolymerization using different monomer concentration were analyzed by SEM after dissolution of the PC

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

membranes. For pyrrole concentration ranging from 0.05 to 0.35 M, we observed similar PPy nanotubules than those shown on Fig. 1. At 1 M monomer concentration, the number of initiation sites of new chains is greatly increased compared to propagation sites, hindering chain growth along the pore walls. The observed morphology presented on Fig. 4, seems to indicate that the creation of nuclea-tion sites is so fast that it breaks the template membrane leading almost immediately to the formation of a nearly continuous but very rough polypyrrole film.

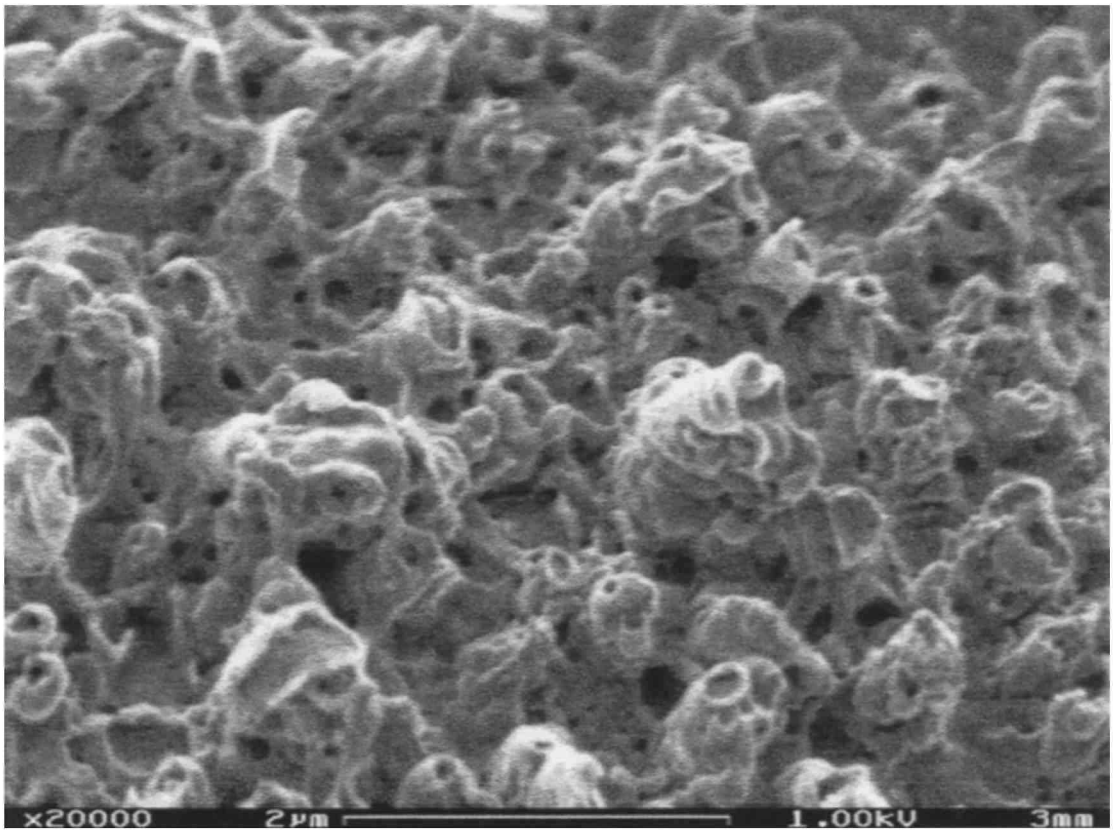

Fig. 4. Scanning electron microscopic image of polypyrrole nanotubules obtained by electrochemical synthesis at 0.8 V in a bath containing an aqueous solution of 1 M pyrrole and 0.1 M $LiClO_4$.

Electrogeneration at different concentrations of electrolyte

Following a similar procedure to that described above, electrical kinetics was obtained from 0.1 M pyrrole in aqueous solutions containing different concentrations of $LiClO_4$ ranging from 0.01 to 1 M. A linear variation of the electrical charge with polymerization time was obtained at each concentration of electrolyte (Fig. 5). Increasing slopes (increasing polymerization rates) were obtained when the concentration of electrolyte was raised. The double logarithmic plot of these slopes *(dQ/dt)* vs the concentration of electrolyte gives a straight line (Fig. 5):

$$\log(\mathrm{d}Q/\mathrm{d}t) = \log R_\mathrm{p} = 0.99 + 0.83[\mathrm{ClO}_4^-] \quad r = 0.9976$$

with the concomitant empirical kinetics from electrical parameters being:

$$R_\mathrm{p} \% [\mathrm{ClO}_4^-]^{0.83}$$

The value of electrolyte (ClO_4^- anions) reaction order obtained for electrogeneration inside the pores of a host membrane (0.83) is slightly higher than the value obtained for the electrogeneration of polypyrrole on a platinum electrode (without any restricted accessibility of the monomer/electrolyte solution to the electrode) which is 0.7 [10].
The morphologies of the template synthesized polypyrrole nanostructures obtained by electropolymerization using different $LiClO_4$ concentration were analyzed using SEM after dissolution of the PC membranes. For $LiClO_4$ concentrations ranging from 0.05 to 1 M, we always observed similar PPy nanotubules than those presented on Fig. 1.
Influence of the electrolyte nature

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

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 a polyelectrolyte (NaPSS) instead of a small size anion (ClO_4^-) as doping agent during the electropolymerization of pyrrole inside the pores of a PC membrane. Aqueous solutions containing 0.1 M pyrrole and different concentrations of NaPSS ranging from 0.01 M to 0.2 M were used as electropolymerization solutions. Polypyrrole was generated by polarizing the working electrode at 0.8 V for a denned polarization time. As shown on Fig. 6, a linear variation of the electrical charge with polymerization time was obtained at each concentration of electrolyte. Increasing slopes (increasing polymerization rates) were obtained when the concentration of electrolyte was raised.

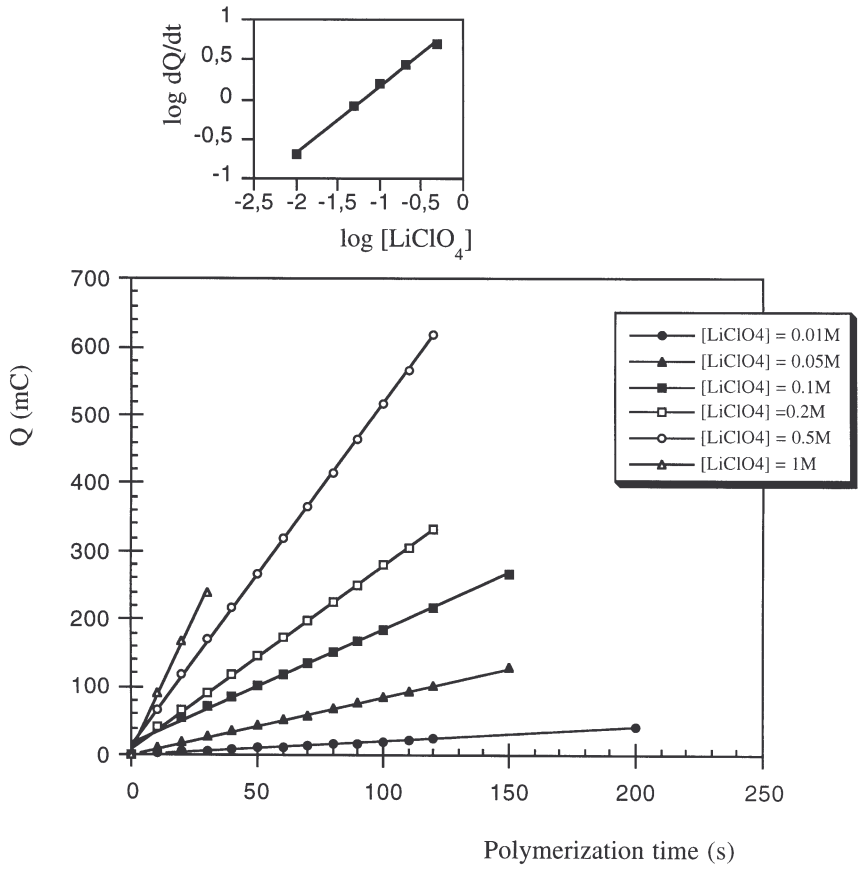

Fig. 5. Determination of the reaction order to $LiClO_4$ concentration from electrical charges results. R_p values were obtained from slopes of electrical charges-polymerization time straight lines for different $LiClO_4$ concentrations at 0.8 V polymerization potential and 0.1 M pyrrole.

Published in: European polymer journal (1998), vol. 34, iss. 12, 1767-1774
Status: Postprint (Author's version)

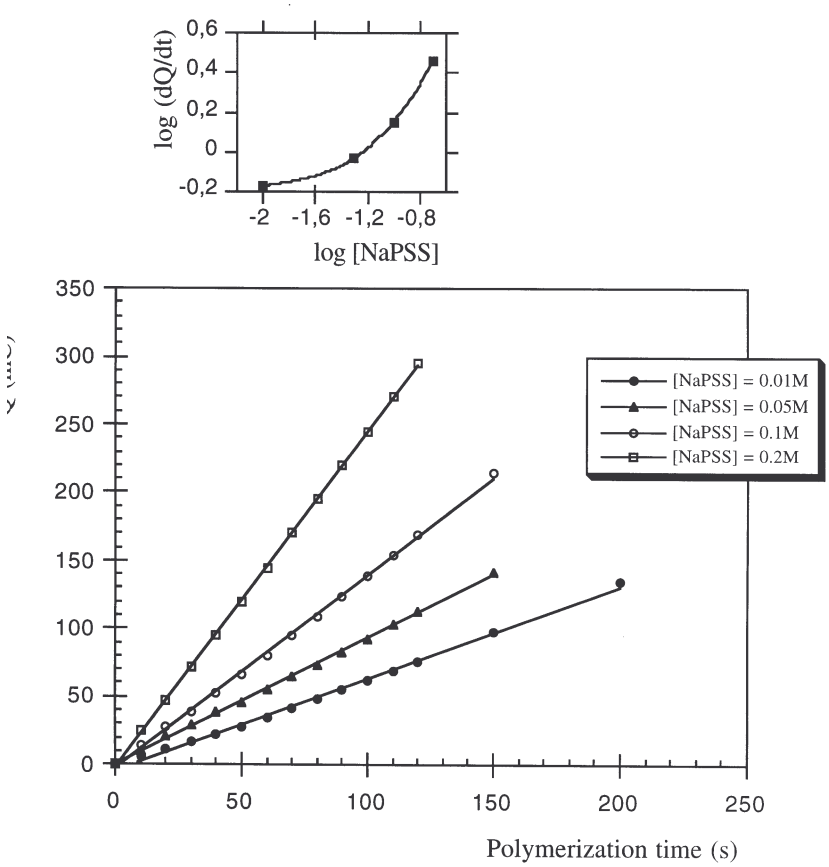

Fig. 6. Evolution of the electrical charge (Q) with polymerization time for different NaPSS concentrations at 0.8 V polymerization potential and 0.1 M pyrrole. The insert shows the double logarithmic plot of the slopes (dQ/df) vs the concentration of NaPSS.

However, the double logarithmic plot of these slopes *(dQ/dt)* vs the concentration of electrolyte does not give a straight line anymore but fits better with an exponential curve (Fig. 6). This is surely a consequence of the large size and polyanionic nature of PSS used as counter anion. As shown by Otero *et al* [14] who studied the electrogeneration of PPy-PSS on platinum electrode, the polyelectrolyte is firstly adsorbed on the electrode and thus retards the monomer oxidation-polymerization process. However, once the monomer oxidation is initiated, this process is much faster for increased polyelectro-lyte concentration.
The morphologies of the template synthesized polypyrrole nanostructures obtained by electropoly-merization using different NaPSS concentrations were analyzed using SEM after dissolution of the PC membranes. In each case, we observed polypyr-role nanotubules with much thicker walls than when we used $LiClO_4$ as electrolyte. On Fig. 7, we present a SEM micrograph of the polypyrrole nano-tubules obtained by electrosynthesis at 0.8 V in an aqueous bath containing 0.1 M pyrrole and 0.1 M NaPSS.

CONCLUSION

The overall objective of this investigation was to determine the effects of different synthesis parameters (electrosynthesis method, monomer concentration, electrolyte nature and concentration) on pyrrole electropolymerization inside the pores of PC PTM and also their effects on the morphology of the nanostructures obtained.
Using a pulsed technique, in order to let monomer and electrolyte regularly diffuse inside the pores, instead of the chronoamperometry method to electrosynthesize polypyrrole does not change the morphology of the obtained nanomaterials. In both cases, polypyrrole nanotubules of similar thickness were observed. So, the diffusion of the monomer and electrolyte inside the pores of the membrane is not the determinant parameter leading to the formation of tubules, at least using membranes with pores diameters equal or larger than 200 nm.
A kinetics study of the PPy-ClO_4 and PPy-PSS electrogeneration was followed by electrical charges measurement. The increase of the monomer concentration or of the electrolyte ($LiClO_4$ or NaPSS)

concentration increases the polymerization rate at constant polarization voltage.

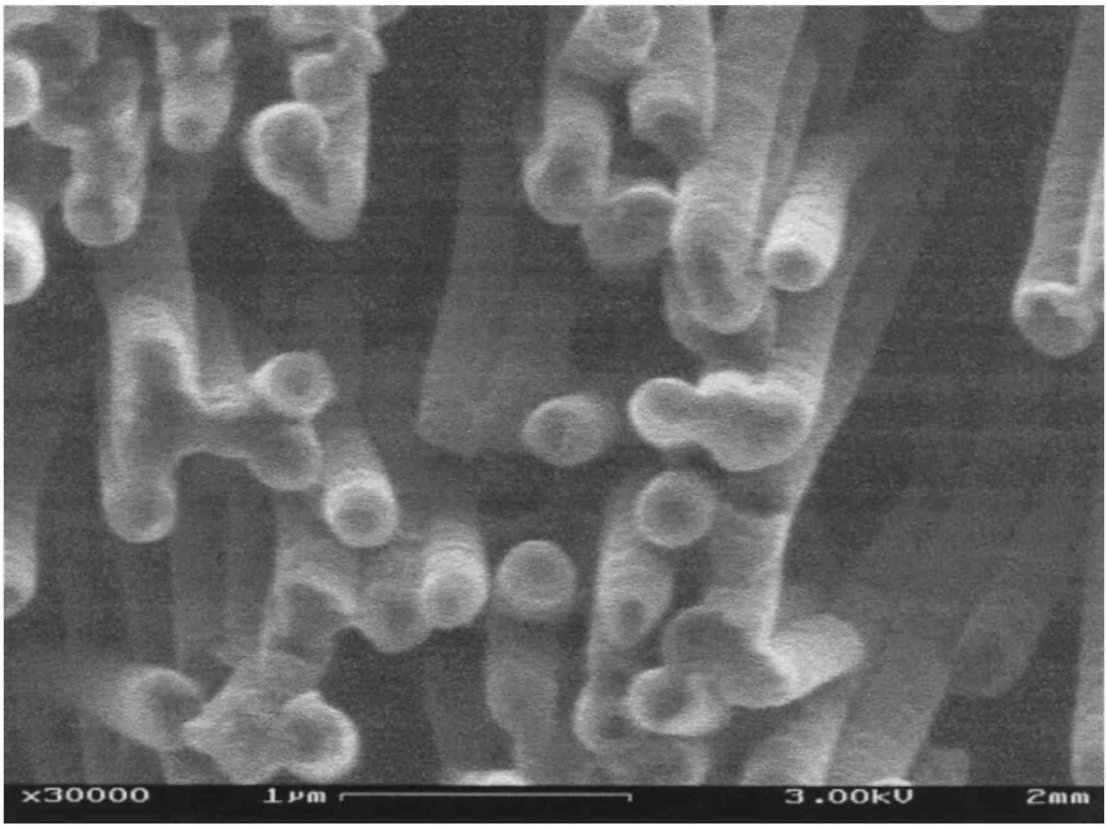

Fig. 7. Scanning electron microscopic image of polypyrrole nanotubules obtained by electrochemical synthesis at 0.8 V in a bath containing an aqueous solution of 0.1 M pyrrole and 0.1 M NaPSS.

The electrogeneration of PPy-ClO_4 inside the pores of a PC PTM from aqueous solutions at constant potential (0.8 V) follows the empirical electrical kinetics: $R_p\%[Pyrrole]^{0.34}[ClO_4^-]^{0.83}$. By changing the pyrrole concentration from 0.05 to 0.35 M, or the $LiClO_4$ concentration from 0.01 to 1 M, PPy nanotubules of the same thickness than those obtained using our initial conditions ([pyrrole] = 0.1 M and [$LiClO_4$ = 0.1 M) were always obtained. However, changing the nature of the electrolyte (a polyanion NaPSS instead of a small size anion) used for the electrogeneration of polypyrrole leads to the formation of much thicker PPy-PSS nanotubules.
The influence of other synthesis parameters and of the size of the membrane pores on the growing of polypyrrole inside the pores of PC PTM membranes is now under investigation. Currently, conductivity measurements of different electrosynthesized nanomaterials composites presenting different morphologies are also carried out and will be reported later.

Acknowledgements

The authors thank the "Services Fédéraux des Affaires Scientifiques Techniques et Culturelles" for their financial support in the frame of the "Pôle d'Attraction Interuniversitaires". Thanks also go to P. Lipnik for TEM analysis.

REFERENCES

[1]. Ozin, G. A., *Adv. Mater.,* 1992, 4, 612.
[2]. Martin, C. R., *Science,* 1994, 266, 1961.
[3]. Martin, C. R., *Chem. Mater.,* 1996, 8, 1739.
[4]. Martin, C. R., Van Dyke, L. S., Cai, Z. and Liang, W, *J. Am. Chem. Soc,* 1990, 112, 8976.
[5]. Ferain, E. and Legras, R., *Nucl. Instrum. Methods Phys. Res. B,* 1993, 82, 539.
[6]. Ferain, E. and Legras, R., *Nucl. Instrum. Methods Phys. Res. B,* 1994,84,331.

[7]. Ferain, E., and Legras, R., *Nucl. Instrum. Methods Phys. Res. B,* 1997, 131, 97.
[8]. Martin, C. R. and Parthasarathy, R. V., *Chem. Mater.,* 1994, 6, 1627.
[9]. Granström, M, Carlberg, J. C. and Inganas, O, *Polymer,* 1995,36,3191.
[10]. Rodriguez, J., Grande, H.-J., Otero, T. F., *Handbook of Organic Conductive Molecules and Polymers,* ed. H. S. Nalwa, Vol. 2. John Wiley & Sons, 1997, Chap. 10.
[11]. Otero, T. F. and Santamaria, C, *Electrochim. acta,* 1992, 37, 297.
[12]. Otero, T. F., Rodriguez, J., Angulo, E. and Santamaria, C, *Synth. Met.,* 1991, 43, 2831.
[13]. Otero, T. F. and Angulo, E., J. *Appl. Electrochem.,* 1992, 22, 369.
[14]. Otero, T. F. and Sansifiena, J. M., J. *Electroanal. Chem.,* 1996, 412, 109.