Electrochemical Synthesis of Polypyrrole Nanowires**

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Semiconductor circuitry has gone through spectacular developments in the past decades, as testified by the impressive density of electronic components and very high processing speeds. Nowadays, microelectronics and molecular electronics are fields of tremendous research activity. There is accordingly a need for molecular conductors with nanometer dimensions. As an answer to that challenge, molecular wires are being developed. Several research groups are investigating doped conducting polymers such as polyacetylene, polyaniline, polypyrrole, and other polyheterocycles and attempting their confinement in appropriate porous materials.[1]

For example, polypyrrole, polythiophene, and polyaniline were recently grown in layered materials such as FeOCl and V_2O_5.[2] Zeolite molecular sieves are also good candidates for inclusion chemistry owing to their structurally well defined, nanometer-size channel structures. Several studies are concerned with the confinement of molecular conductors in zeolite host channels, and molecular wires have been obtained by chemical polymerization of pyrrole in zeolite channels in the presence of iron(III) ions.[3] Other examples include formation of filaments of conducting polymers (ca. 50–1000 nm in diameter) in the transverse pores of Nucleopore and Anopore membranes, as described by Martin,[4] whose research group synthesized 10-μm long polypyrrole and poly(3-methylthiophene) fibrils with diameters in the range of 0.03–1 μm in nucleopore membranes.[5] More recently,[6] the electrochemical synthesis of fibrils and tubules of conducting polymers and of metal tubules and rods was carried out in similar host membranes. It is noteworthy that template-synthesized polypyrrole has higher conductivity than the bulk material; this is explained by the better packing and alignment of the polymer chains.[7]

Here we report on a new electrochemical method for the synthesis of conducting polypyrrole nanowires. For the last few years, we have been interested in the electrodeposition of insulating polymer films onto metallic substrates (Ni, Fe).[8] These films are designated as "grafted films", since they have the unique property of remaining attached to the electrode surface even when they are prepared and kept in a solvent in which the polymer exhibits good solubility. This electrografting reaction was successfully achieved in appropriate solvents with some acrylic monomers, such as acrylonitrile and ethyl acrylate (EA).[9] In this work, we used this strategy to prepare a new substrate that can act as a template for the electropolymerization of pyrrole to give nanowires. Figure 1 shows a typical cyclic voltammogram for the electrografting of poly(ethyl acrylate) PEA film onto a vitreous carbon electrode in a bath containing 0.05 M tetraethylammonium perchlorate (TEAP) and 2.5 M ethyl acrylate in dimethylformamide (DMF). The potential was scanned up to the top of the first reduction wave ($E = -1.8$ V (Pt electrode), scan rate = 20 mV s^{-1}, curve 1) and held until the current decreased as the result of the growth of an insulating polymer film. A second cathodic scan (curve 2) completes the passivation of the electrode. The PEA film was carefully washed with pure DMF to remove unchanged monomer and any soluble contaminants. This modified electrode was then immersed in a solution of 0.05 M TEAP and 0.005 M ferrocene in DMF to determine whether it could be used as an anode in further experiments. Figure 2 shows the corresponding voltammogram (curve B) together with that for a pure vitreous carbon anode (curve A). The higher potential difference between the oxidation and reduction maxima of the Fe^{II}/Fe^{III} couple for curve B indicates a small increase in resistivity for the precoated electrode due to the grafted PEA film. This coating is thus not completely insulating, most likely because swelling by DMF allows ferrocene to diffuse to the surface of the carbon electrode and to react quasireversibly.

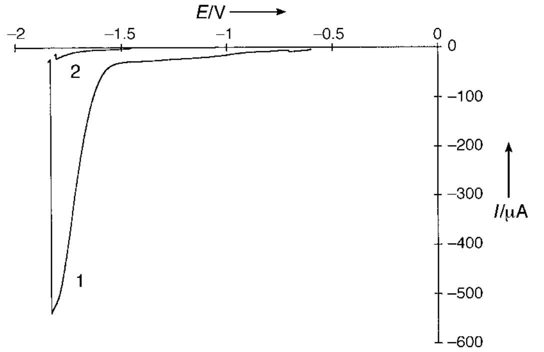

Figure 1. Cyclic voltammogram for grafting of ethyl acrylate (2.5 M in 0.05 M TEAP/DMF) onto a vitreous carbon electrode. Scanning rate = 20 mV s^{-1}; 1: first scan; 2: second scan.

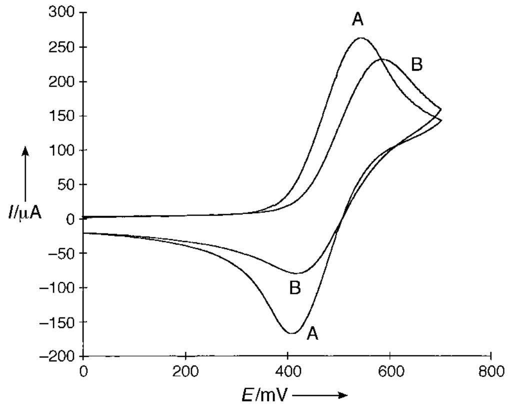

Figure 2. Cyclic voltammogram of ferrocene (0.005 M) in 0.05 M TEAP/DMF; scanning rate 20 mV s^{-1} with a pure vitreous carbon anode (A) and with a PEA-grafted carbon anode (B).

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Pyrrole was electropolymerized at a constant current of 0.5 mA in a bath containing 0.05 M TEAP and 0.1 M pyrrole in DMF. The chronopotentiogram for the PEA grafted vitreous carbon anode shows a typical behavior (Figure 3, curve A): an overpotential followed by a significant decrease in potential.

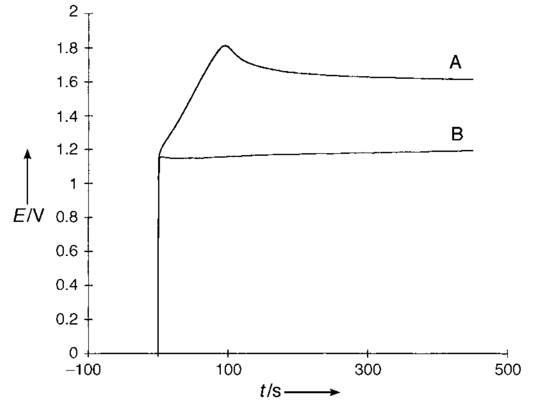

Figure 3. Chronopotentiogram of pyrrole (0.1 M in 0.05 M TEAP/DMF) with a PEA-grafted carbon anode (A) with a pure carbon anode (B). $I =$ 0.5 mA.

In the case of a pure carbon anode (curve B), a monotonous curve is observed at a lower potential. Clearly, polypyrrole (PPY) can be synthesized on a PEA-coated carbon electrode, although a higher potential is required, in particular to initiate the polymerization of pyrrole. The current density is the same as that of the pure carbon anode. X-ray photoelectron spectroscopic analysis of the PEA-grafted electrode after anodic polarization gave the composition C 71, N 1.25, O 27.5, Cl 0.23 % and thus confirmed the coexistence of PEA and PPY on the electrode. A PPY/PEA weight ratio of 33 % and a PPY doping level of 0.2 were calculated.

The composite PPY/PEA electrode was investigated by scanning electron microscopy (SEM) coupled with energy dispersive analysis of X-rays (EDAX). Figure 4 clearly shows the formation of a nanowire, which grows from the electrode surface through a hole in the PEA coating. The EDAX analysis shows a large amount of Cl on the wire, which is consistent with the perchlorate doping of PPY. Moreover, the PEA grafted film is very uniform with no visible defects or holes in the surface. Note, however, that the PEA film investigated by SEM was previously dried, whereas pyrrole polymerization was conducted with a PEA film that was swollen by DMF. Thus, diffusion of pyrrole through the swollen film allows electropolymerization to be initiated on the surface of the vitreous carbon according to the usual mechanism reported by Andrieux et al.[10] Asavapiriyanont et al.[11] studied the further stages of pyrrole polymerization, which involves an instantaneous nucleation process with three-dimensional growth on the conducting surface. Therefore, in accordance with this nucleation process, the increase in E in the first part of the chronopotentiogram would correspond to the formation and growth of nuclei, which, however, is perturbed by the grafted PEA chains. As a result, the growth of the PPY nuclei would be the rate-limiting step responsible for the increase in potential. However, since the tethered PEA chains have some mobility in DMF, they can be displaced laterally by the growing PPY, so that small channels become available and allow PPY to emerge from the PEA film with a certain diameter. Then the potential decreases until it reaches a plateau value imposed by the diffusion of the monomer through the PEA layer.

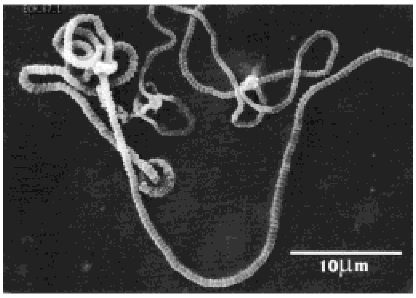

Figure 4. SEM image of a PPY wire on PEA-grafted carbon anode.

The only explanation for wire formation is that the polymerization proceeds on the surface of the electrode and thus beneath the PEA film (Figure 5). Therefore, pyrrole molecules must diffuse between the carbon surface and the foot of the growing PPY wire, so that the already formed PPY is pushed away from the electrode on further polymerization. According to this hypothesis, no oxidation of the monomer would occur on the surface of the PPY wire, and this would preserve the horizontal dimensions imposed by the channel that is driven through the PEA coating. This explanation is consistent with fundamental considerations of the potential at the wire surface. Indeed Li et al.[12] reported that the conductivity of PPY films electrochemically synthesized from solvents with high donor number such as DMF was as low as about 10^{-6} S cm^{-1}. As a result, the decrease in potential on the PPY wire can be estimated to be 500 V cm^{-1}. If the thickness

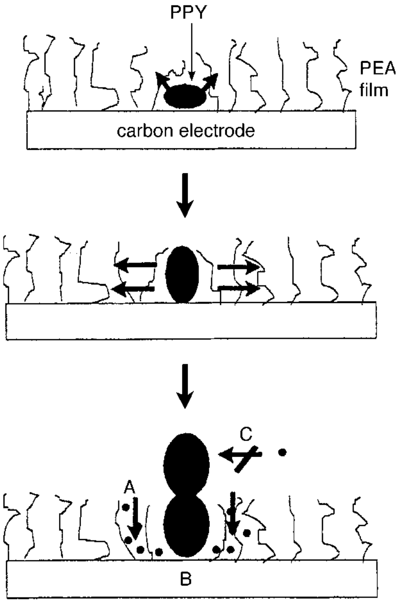

Figure 5. Schematic mechanism for PPY wire growth. 1) PPY nucleation on the C electrode in an opening in the PEA layer. 2) Channel formation in the PEA film. 3) Wire formation. A) monomer diffusion; B) PPY growth from the foot of the wire; C) No polymerization at the tip of the PPY; ● = pyrrole monomer.

of the PEA layer is assumed to be 0.5 µm, the ohmic resistance through the PPY wire within this coating is 100 Ω, and the actual potential on the PPY wire emerging from PEA film may be too small for oxidation of the monomer.

Our observations in this study are completely different from the template synthesis of nanowires by electropolymerization in nanoporous membranes.[6] In template synthesis, PPY begins to grow from the electrode surface, that is, from the foot of the pores. Then the growing PPY follows the pore wall and forms tubules, which as soon as they come out of the pores, grow as a continuous top layer. This growth mechanism is possible because the conductivity of PPY synthesized in water is sufficiently high. Moreover, the membrane is insoluble in the reaction medium, so that the monomer cannot diffuse through it to reach the electrode surface. It can only penetrate into the pores until they become completely blocked. This mechanism is thus fundamentally different from that observed in this work.

From the SEM images, the PPY wire has a diameter of approximately 600 nm and a length of about 300 µm. All the wires have an annular structure, which might be an imprint of the PEA channel through which the PPY grows. Figure 6 shows a set of wires that have grown from the electrode surface. The PPY wires are randomly dispersed on the whole electrode surface and have diameters between 400 nm and 1 µm.

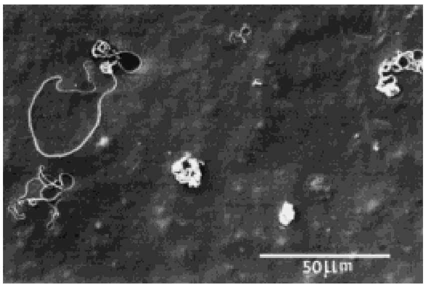

Figure 6. SEM image of PPY wires on PEA-grafted carbon.

According to the proposed PPY growth mechanism, there would be no intrinsic limit to the wire length; only the polarization time would be a limiting factor. As long as the formation of channels through the PEA film remains unexplained, the wire diameter and the density of the wires on the electrode surface cannot be predicted. Wire formation is actually controlled by the complex interaction of several parameters, including PPY conductivity, current density, PPY and Py diffusion rate through the swollen layer of grafted polymer, and hence the nature, thickness, and grafting density of the insulating polymer chains.

Experimental Section

Monomers, solvent, and conducting salt were dried before use. Electrochemical experiments were carried out in a one-compartment cell with a platinum pseudoreference electrode and a platinum counterelectrode with a PAR potentiostat (EG&G, Model 273 A) in a glovebox under a dry inert atmosphere. This technique is detailed elsewhere.[8, 9]

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[1] G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612.
[2] M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1987**, *109*, 3797; M. G. Kanatzidis, C. G. Wu, H. O. Marcy, C. R. Kannewurf, *J. Am. Chem. Soc.* **1989**, *111*, 4139.
[3] T. Bein, P. Enzel, F. Beuneu, L. Zuppiroli, *Adv. Chem. Ser.* **1990**, *226*, 433.
[4] C. R. Martin, *Acc. Chem. Res.* **1995**, *28*, 61.
[5] Z. Cai, C. R. Martin, *J. Am. Chem. Soc.* **1989**, *111*, 4138.
[6] S. Demoustier-Champagne, E. Ferain, R. Legras, C. Jérôme, R. Jérôme, *Eur. Polym. J.*, in press.
[7] R. V. Parthasarathy, C. R. Martin, *Chem. Mater.* **1994**, *6*, 1627.
[8] R. Jérôme, M. Mertens, L. Martinot, *Adv. Mater.* **1995**, *7*, 807.
[9] N. Baute, P. Dubois, L. Martinot, M. Mertens, P. Teyssié, R. Jérôme, *Eur. J. Inorg. Chem.*, submitted.
[10] C. P. Andrieux, P. Audebert, P. Hapiot, J. M. Savéant, *J. Phys. Chem.* **1991**, *95*, 10158.
[11] S. Asavapiriyanont, G. K. Chandler, G. A. Gunawardena, D. Pletcher, *J. Electroanal. Chem.* **1984**, *177*, 229.
[12] J. Ouyang, Y. Li, *Polymer* **1997**, *38*, 1971.

A Novel Class of Ruthenium Catalysts for Olefin Metathesis**

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Dedicated to Professor Heinrich Nöth
on the occasion of his 70th birthday

Transition metal catalyzed C–C bond formation is a focal issue in both organic synthesis and polymer chemistry.[1] One of these C–C coupling processes is olefin metathesis encompassing reactions such as ring-opening metathesis polymerization (ROMP), acyclic diene metathesis reaction (ADMET), ring-closing metathesis (RCM), and metathesis of acyclic olefins.[2] In this area ruthenium–phosphane complexes have conveyed much progress,[3] since they tolerate polar functional groups. Herein, we report the first ruthenium-based examples of a new class of compounds containing alkylidene groups as well as N-heterocyclic carbenes[4–6] as ligands and their application as catalysts in olefin metathesis.

The phosphane complex [$RuCl_2(PPh_3)_2(=CHPh)$] developed by Grubbs et al.[3d] reacts with 2.2 equivalents of the appropriate imidazolin-2-ylidene to yield compounds **1**–**4**

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