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## Molecular Crystals and Liquid Crystals

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## Electrochemical Synthesis of Heteroaromatic Polymers : New Compounds and Novel Substrates

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ELECTROCHEMICAL SYNTHESIS OF HETEROAROMATIC POLYMERS :  
NEW COMPOUNDS AND NOVEL SUBSTRATES

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Abstract The electrochemical deposition of polypyrrole on carbon fibers surfaces is described with the resulting morphologies and mechanical properties. The first in a family of heteroaromatic conducting polymers has been obtained from thieno [3,2-b]pyrrole.

INTRODUCTION

Considering the remarkable properties of heteroaromatic polymers, we have oriented our research in two different directions. The first <sup>a</sup> consists in depositing the polymers - in this work polypyrrole - on novel substrates, here, carbon fibers, which are a fascinating material for various applications such as composites and microelectrodes.

In the second <sup>b</sup>, we synthesize new compounds from condensed five-membered heterocycles ; we report here the first polymer , obtained from thieno [3,2-b]pyrrole.

In both cases, electrochemical methods are used.

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POLYPYRROLE-COATED CARBON FIBERS<sup>a</sup>

Polymerizations are carried out under classical conditions<sup>1,2</sup>. . . Deposition occurs at the anode, made of a 1.5 cm long carbon fiber wisp containing 10,000 single filaments.

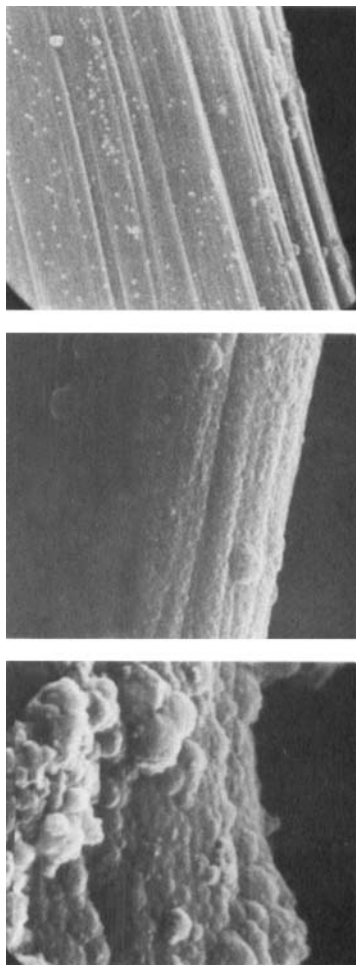


FIGURE 1 Scanning electron micrographs of polypyrrole-coated carbon fibers.

After 15 sec of polymerization, XPS spectra already present the main features of polypyrrole : some polymer "islands" start to grow on the surface, as seen on scanning electron micrographs (Fig. 1, upper part). After 10 to 15 min, a thin continuous film covers the fibers. Its thickness, determined on Figure 1, center part, is approximately  $0,5 \mu\text{m}$ . For longer times ( $> 30$  min), the coating builds up as lumps ( $5 \mu\text{m}$ ) lying over the continuous film (Fig. 1, lower part).

The adhesion between the fiber and the 30 min polypyrrole coating has been tested first by sonication with no significant changes. Tougher treatments, however, such as rubbing the wisp between two metallic plates, removes most of the polymer lumps but leaves the thin film absolutely intact, indicating strong adhesion of this coating to the fiber.

The mechanical properties of the carbon fibers are sensibly improved by this polypyrrole film. The elongation at rupture, measured on single filaments, is increased by approximately 20 % (from 1.36% up to 1.64%).

The rupture load changes from 11.5 to 14.3 grams but the properties per unit (YM,TS) - though not diminished - may not vary in the same proportion, because of the increased fiber section.

X-ray photoelectron spectra reveal that the electronic structure and the doping level of polypyrrole synthesized on carbon fibers are quite comparable with those of the gold-deposited compound<sup>3</sup>. However, the C 1s peak width is significantly larger (2.5 eV instead of 1.9 eV), due to the contribution of quasi-graphitic carbons constituting the fiber. C/N ratio (5.0) indicates a 75 % ( $\pm 10\%$ ) surface coverage by the polymer after 30 min of voltage application. This is probably due to the wisp compactness which restricts reagents diffusion (and so polypyrrole deposition) on the filaments most inside.

#### A NEW CONDUCTING POLYMER FROM THIENO [3,2-b] PYRROLE<sup>b</sup>

The electronic structure of the monomers represented in Figure 2 has been investigated by ab initio STO-3G calculations. The series appears quite promising for the synthesis of conducting polymers, as the first ionization potentials are lower than those of pyrrole and thiophene (Table I)<sup>4</sup>.

TABLE I Ab initio ionisation potentials (eV)

PYRROLE	THIOPHENE	THIENO(2,3)- PYRROLE	THIENO(3,2)- PYRROLE	PYRROLO(2,3)- PYRROLE	PYRROLO(3,2)- PYRROLE	THIENO(2,3)- THIOPHENE	THIENO(3,2)- THIOPHENE
6.28	7.02	5.47	5.39	5.07	4.89	6.02	5.95

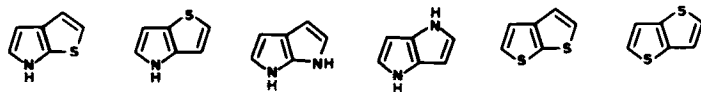


FIGURE 2 Structural formulae of monomers

The electrochemical polymerization of thieno [3,2-b] pyrrole is carried out under potentiostatic conditions (+ 0.5 V vs Ag/AgNO<sub>3</sub> 10<sup>-1</sup> M in CH<sub>3</sub>CN) in a one-compartment three-electrodes cell on a gold anode with a platinum plate as counterelectrodes. The acetonitrile solution, 10<sup>-1</sup> M in Et<sub>4</sub>NBF<sub>4</sub> and 10<sup>-2</sup> M in the monomer, is bubbled with argon before and during the reaction. Voltage application for 20 min leads to a thick black deposit (10 μm), very difficult to peel off the substrate.

At this point of the work, this prevented any precise conductivity measurements. However, no surface charge builds up during XPS analysis, giving clear evidence for effective conductivity. The XPS core levels intensities are in agreement with polythienopyrrole formulation and the N 1s/F 1s ratio indicates a doping level of about 35 %. Scanning electron micrographs of the polymer reveal an irregular film constituted of small grains (0.5 to 2 μm).

#### CONCLUSION

Promising results have been obtained, particularly for the improvement of carbon fibers properties by a conducting polymeric surface film, and for the preparation of a new series of heteroaromatic conducting polymers based on bicyclic monomers.

#### REFERENCES

1. A.F. Diaz and B. Hall, IBM J. Res. Dev., **27**, 4, 342 (1983)
2. E.M. Genies, G. Bidan and A.F. Diaz, J. Electroanal. Chem., **149** 101 (1983).
3. W.R. Salaneck, R. Erlandsson, J. Prejza, I. Lundstrom and O. Inganäs, Synthetic Metals, **5**, 125 (1983).
4. R. Lazzaroni, J.P. Boutique, J. Riga, J.J. Verbist, J.G. Fripiat and J. Delhalle, JCS Perkin Trans. II (1984) in press.