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Laforgue, Alexis; Robitaille, Lucie

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HIGHLY CONDUCTIVE PEDOT NANOFIBERS OBTAINED BY COMBINATION OF ELECTROSPINNING AND VAPOUR-PHASE POLYMERIZATION

Alexis Laforgue and Lucie Robitaille

Functional Polymer Systems Group,
 Industrial Materials Institute - National Research Council Canada,
 75 de Mortagne Blvd., Boucherville (Quebec) Canada J4B 6Y4

Introduction

Since their discovery thirty years ago, intrinsically conducting polymers (ICPs) have been the subject of an intense research effort worldwide, both to better understand and control their remarkable properties and to use these in diverse applications such as organic electronics, sensors, corrosion protection, energy dissipation, magnetic shielding, light-emitting devices, solar cells, etc. Besides, the new century has brought the development of nanosciences and the production of new materials defined and controlled at the molecular level. This science of nanomaterials opens new fields of investigation and control for ICPs. Among the techniques used to obtain nanoscale materials, electrospinning has been seen as a method of choice to produce continuous nanofibers from a number of polymers. Alan MacDiarmid and coworkers were the first to report on the electrospinning of nanofibers containing ICPs¹. Following his work, a number of different ICP-based nanofibers have been produced by this method: polyaniline^{2,3}, polypyrrole^{4,5}, poly(p-phenylene vinylenes)^{6,7}, polythiophenes⁸⁻¹⁰ and polyfluorenes^{11,12}.

Poly(ethylenedioxythiophene) (PEDOT) is one of the most widely used ICP, due to its high conductivity and oxidative stability¹³. The highest conductivities for PEDOT ultrathin films have been obtained by using a vapour-phase polymerization technique and are above 10^3 S/cm¹⁴. PEDOT not being electrospinnable by itself, different strategies have been employed to overcome this problem, namely: the use of polymer precursors that can be converted into ICPs in a second step¹⁵ or the addition of a spinable polymer to assist the formation of fibers^{9,16}.

This study investigates the combination of electrospinning and base-inhibited vapour-phase polymerization (BI-VPP), to obtain highly conductive PEDOT nanofibers.

Experimental Section

Materials. 3,4-Ethylenedioxythiophene (EDOT) (Baytron M V2) and ferric tosylate (FeTos) solution in ethanol (Baytron CB40) were purchased from H.C. Starck. Polyethylene oxide (PEO, Mw = 600,000 g/mol) was obtained from Polyscience (USA, PA). Pyridine was obtained from Sigma-Aldrich and used without further purification.

Sample preparation. The electrospinning solutions were obtained by dissolving 1 wt% PEO in the Baytron CB40 solution. Pyridine (0.5 mole per mole of FeTos) was added to the solution as a base inhibitor. The solution was stirred at 70°C for at least 3 h to ensure perfect homogeneity.

Electrospinning. The sample solutions were filled into a glass syringe terminated by a stainless steel needle. The syringe was placed in an automatic pump (Harvard Apparatus PHD4400) and grounded. A stainless steel plate covered by the substrate was connected to a high voltage power supply (Gamma High Voltage Research Model ES75P-10W). For the electrical conductivity measurements, the nanofiber mats were electrospun on non-conductive polyimide (Thermalimide RCBS from Airtech) or PET (Mylar from Dupont) sheets, which served as rigid substrates easier to handle than the unsupported mats. For spectroscopic measurements, the substrate was a glass slide and for electrochemical studies a platinum grid. The use of a heatgun with controlled temperature and speed was necessary to prevent the solution from solidifying in the syringe and needle (cf. Fig. 1). The electrospinning experiments were carried at 22-23 °C and 15-20 % relative humidity.

BI-VPP. The substrates covered with the electrospun PEO/FeTos/pyridine fibers were inserted in a reaction chamber filled with argon and containing the EDOT monomer. The EDOT vapours were allowed to polymerize on the fibers for 80 min at 55°C. The samples were then taken out of the chamber, dried for 10 min in air, then thoroughly washed with methanol and dried under a nitrogen stream at ambient temperature.

Characterization. Optical Microscopy was carried out on a Dialux 20 microscope (Leitz Wetzlar, Germany). Scanning electron microscopy (SEM) was performed on a Hitachi S4700 microscope. Electrical conductivity measurements were carried out in ambient atmosphere by the four-point probe

method using a Bekktech conductivity cell and using a VMP3 multipotentiostat (Bio-Logic, France). Cyclic voltammetry was carried out in a three electrode configuration with an Ag/AgCl reference electrode and a platinum grid counter electrode, using the VMP3 multipotentiostat. UV-Vis-NIR spectra were obtained with a Perkin Elmer Lambda 950 spectrophotometer.

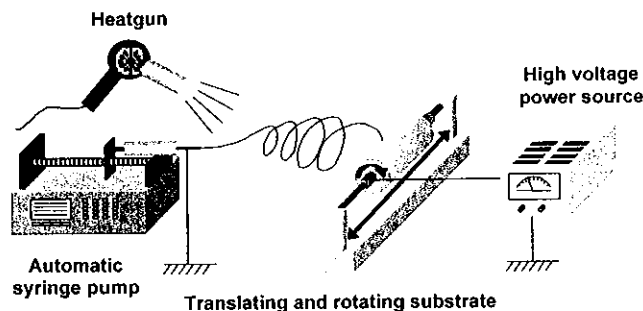


Figure 1. Schematic representation of IMI's electrospinning setup.

Results and discussion

The initial FeTos concentration in the Baytron CB40 was 40 wt%. During the electrospinning process, the solvent evaporated during the jet flight. The resulting fibers composition was then 91.3 wt% FeTos, 2.3 wt% PEO and 6.4 wt% pyridine. Surprisingly, nice fibers were reproducibly produced at a this very low polymer content. Without heatgun however, the viscosity was very high and chaotic electrospinning was observed. The hot air provided by the heatgun had to be precisely controlled in terms of temperature, air speed, angle and distance to the syringe to be able to produce fibers.

The fibers were characterized by optical microscopy (cf. Fig. 2a). They show the typical yellow color of the Baytron CB40 solution. Their diameter was 500 ± 200 nm. The fibers had a very low mechanical integrity because of the low polymer content. They were very sensitive to the ambient conditions and "liquefied" within a few hours if let in ambient conditions. It was not possible to observe them by SEM because of this instability issue.

Samples electrospun for further processing were transferred into the polymerization chamber directly after production to avoid any degradation. Fig. 2b shows an optical micrograph of the PEDOT nanofibers obtained after BI-VPP. Assuming that all the FeTos has reacted with EDOT and that the resulting PEDOT is doped with one tosylate anion every three monomer units, the fiber composition after evaporation of the solvents and the rinsing step can be calculated to be 75 wt% PEDOT-Tos_{0.33} and 25 wt% PEO. Their bright blue color is characteristic of PEDOT. The fibers seem to maintain their diameter after polymerization. Part of the nanofiber web was partially distorted at the surface, as can be observed on the SEM micrograph of Fig. 2c. It is possibly due to a partial softening of the fibers in the reaction chamber before the PEDOT polymerization provided enough mechanical strength to the fibers.

The UV-Vis-NIR spectrum of the nanofiber mat is presented in Fig. 3 and shows the typical absorption of a doped and conductive PEDOT¹⁴.

The electrical conductivity of the nanofiber mats was measured to be 200 ± 50 S/cm, which is the highest value ever reported to our knowledge for polymer nanofibrous materials. Conductivities found in the literature for PEDOT-containing fibers were always orders of magnitude lower than the ones obtained in the present study (the highest reported was 10 S/cm¹⁶). This difference in conductivity is believed to be due to the base-inhibited polymerization, known to produce very pure and conductive polymers¹⁷.

These values are lower than the values reported for spin-coated ultrathin films of BI-VPP PEDOT^{14,17}. It is important to note that the four-point probe technique provides volumic conductivities and is thus only suitable for bulk materials, not for highly porous materials like electrospun nanofiber mats. Hence, the electrical conductivity values obtained for the mats are only apparent conductivities, and do not apply to single fibers, which should present significantly higher conductivities.

Electroactivity of the nanofibers was investigated by cyclic voltammetry (cf. Fig. 4). The shape of the voltamogram is in good agreement with the ones reported in the literature for BI-VPP or electropolymerized PEDOTs^{18,19}.

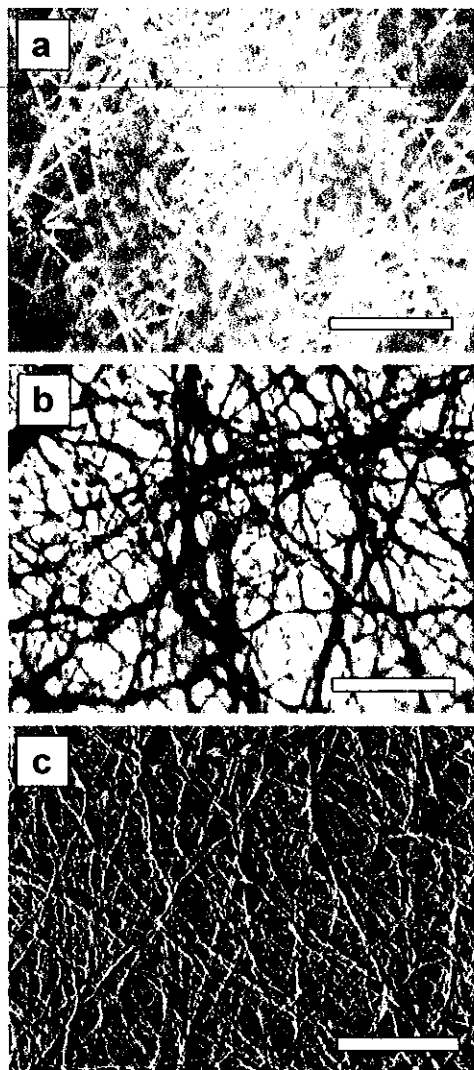


Figure 2. Optical micrographs of as-spun PEO/FeTos/pyridine (a, reflection mode) and BI-VPP PEDOT (b, transmission mode) fibers and SEM micrograph of BI-VPP PEDOT fibers (c). Scale bars represent 20 μm .

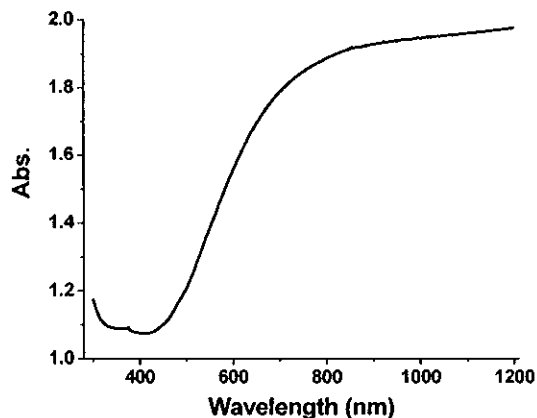


Figure 3. UV-Vis-NIR spectrum of a BI-VPP PEDOT nanofiber mat.

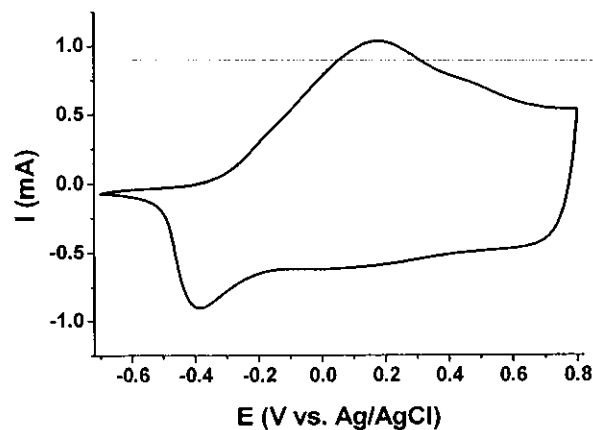


Figure 4. Cyclic voltammogram of BI-VPP PEDOT nanofibers deposited on a Pt grid. Electrolyte: tetrabutylammonium hexafluorophosphate 0.1M in acetonitrile. Scan rate 10 mV/s.

Conclusions

Highly conductive PEDOT nanofibers were obtained by combining electrospinning and base-inhibited vapour-phase polymerization. The nanofibers were composed of 75 wt% of doped PEDOT and 25 wt% PEO. The conductivity of the nanofiber mats was measured to be 200 ± 50 S/cm which is the highest value ever reported to our knowledge for conductive nanofibers. Potential applications of such nanofiber mats include conductive textiles, flexible organic electronics, energy storage and sensors.

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