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MORPHOLOGICAL CONTROL OF THE ELECTROPOLYMERIZATION OF 3-METHYLTHIOPHENE ON NUCLEPORE

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ABSTRACT

When 3-methylthiophene is electropolymerized on a Nuclepore covered electrode in a propylene carbonate solution containing tetrabutylammonium hexafluorophosphate, braided and helical fibrils are formed. When the electrodes are arranged horizontally with the working electrode on top, greater morphological control is achieved, and the resulting helical fibrils show increased crystallinity and a much higher conductivity than fibrils prepared in the normal manner with vertically arranged electrodes. The conductivity is temperature independent from 15 K to room temperature.

Keywords: electropolymerization, nucleopore, poly(3-methylthiophene), conductivity, morphological control

INTRODUCTION

Poly(3-methylthiophene), P3MT, has attracted attention because of claims of high conductivity, 2000 Scm^{-1}, in thin films[1] and high conductivity in comparison to polythiophene and poly(3-ethylthiophene)[2]. These highly conducting films were all doped with hexafluorophosphate. In order to improve orientation, we attempted to grow P3MT on Nuclepore, a polycarbonate or polyester thin film with 0.015 to 14.0 μm size pores drilled by a nuclear process. Indeed control of

the morphology of polypyrrole, PPy, and P3MT can be achieved[3] by electropolymerization on the porous substrate Nuclepore, allowing the pores to serve as nucleation sites for the growth of oriented fibrils to occur in the electrolyte solution. The PPy and P3MT fibrils are large enough to allow four probe conductivity measurements to be performed. Cai and Martin[4] performed similar work on these two electrically conducting polymers. They claim highly conducting fibrils are formed inside the pores of the Nuclepore, and, by indirect measurements, argue that the fibrils are highly conducting, although they are too small to be isolated.

In this work, the role of electrode geometry is explored. One may speculate that the helical form of the fibrils could be associated with hydrodynamic flow between the electrodes. One might expect that the spatial arrangement of the electrodes and associated gravitational effects would therefore play a role in determining the geometry and orientation of the fibrils. The electrodes for the polymerization were therefore placed horizontally into the cell with the working electrode placed above the counter electrode in an attempt to obtain more uniform fibrils.

EXPERIMENTAL

3-Methylthiopene was polymerized in a one compartment cell in a solution of propylene carbonate containing 0.03 M tetrabutylammonium hexafluorophosphate (Fluka) and 0.2 M 3-methylthiophene (Aldrich). The reaction was also performed with 0.03 M tetrabutylammonium perchlorate (Fluka) and 0.03 M tetrabutylammonium tetrafluoroborate (Fluka). All chemicals were used as received. A constant voltage of 10 volts was applied for 2 to 3 days. A polytetrafluroethylene, PTFE, case for the vitreous carbon working electrode held the 25.0 cm diameter Nuclepore film against the electrode by

contact around the edge. The reaction was performed with the electrodes arranged vertically and horizontally for comparison. In the horizontal arrangement, the encased vitreous carbon working electrode was on top of the platinum foil counter electrode. A PTFE electrode separator was employed so that electrodes could be kept parallel. A modified version of the PTFE working electrode holder described previously[3] fits snugly into the separator. Wires in PTFE spaghetti tubing connect the electrodes to alligator clips above the solution level so that the Nuclepore covered vitreous carbon and the platinum foil electrode surfaces are the only conducting surfaces exposed to the solution. The product was washed with anhydrous ethyl acetate and stored under vacuum.

Conductivity measurements were performed by the four probe method on individual fibrils as previously described[3]. Data were collected on a computer interfaced with a Lake Shore Cryogenics DRC-91C temperature controller, a Keithley 220 current source, a Keithley 181 nanovoltmeter, a Keithley 705 scanner, and a Hewlett Packard 59306A relay actuator. The samples were mounted on a custom built cold head attachment to a closed cycle cryogenic refrigerator.

A Phillips 501B scanning electron microscope, SEM, was used to determine the morphology of the fibrils and for measuring fibril dimensions.

X-ray diffraction patterns were taken on a Rigaku D/Max 2 diffractometer with Cu Kα radiation. The fibrils were ground with a mortar and pestle, and mounted on 3M Kapton tape # 92.

RESULTS AND DISCUSSION

P3MT doped with PF_6^- forms interesting braided and helical fibrils when grown on Nuclepore. Fibrils with this

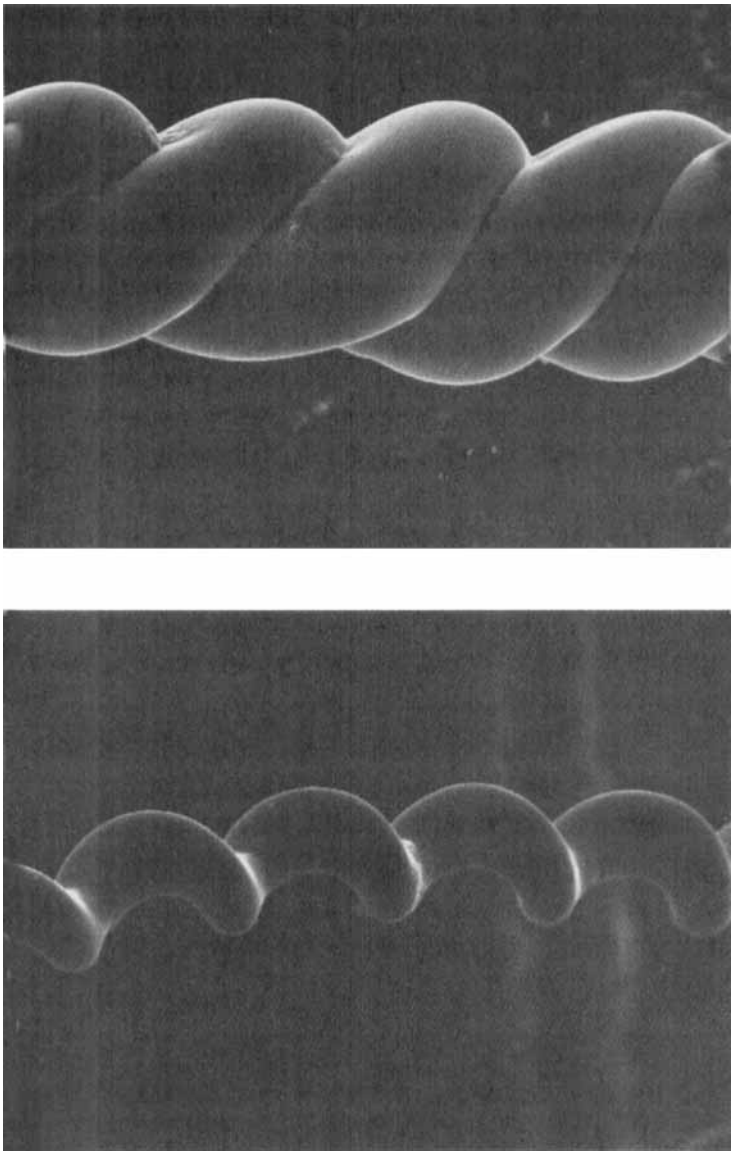

Figure 1 SEM micrographs at 320 times magnification of (a) braided P3MT fibril grown with the vertical electrode arrangement and (b) helical P3MT fibril grown with the horizontal electrode arrangement.

morphology are observed only with PF_6^- doped P3MT. Fibrils were observed with ClO_4^- and BF_4^- doped P3MT but without the interesting morphologies achieved with PF_6^- doped P3MT. With the electrodes arranged vertically, intertwined batches of braided and helical fibrils are formed. The fibrils start forming in the pores and continue growing downward over the lip of the PTFE electrode holder. Fibrils were grown in the horizontal electrode arrangement to achieve more uniform helical fibrils. Figure 1 shows SEM micrographs at 320 times magnification of (a) a braided fibril grown with the vertical electrode arrangement and (b) a helical fibril grown with the horizontal electrode arrangement. The braided fibril (Fig. 1a) is 70 μm wide, and the helical fibril is 22 μm wide. Helical P3MT and PPy have been observed on the microscopic

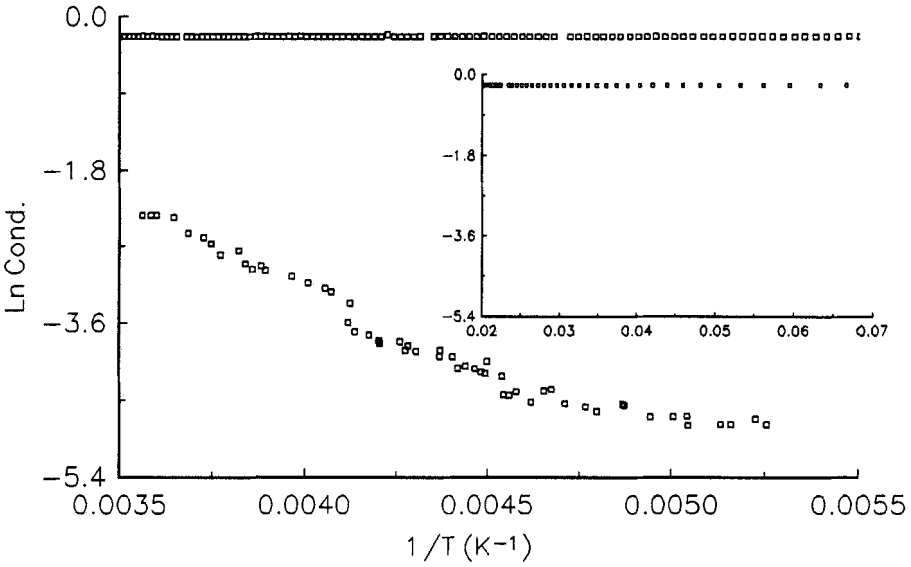

Figure 2 An Arrhenius plot of the temperature dependence of the conductivity for helical P3MT made with the electrodes arranged (top) horizontally and (bottom) vertically. Inset shows the low temperature region of the more oriented fibril.

level using scanning tunnelling microscopy[5]. The results reported here show helical formation on a more macroscopic level.

The room temperature conductivity of the P3MT fibrils made with the horizontal electrode arrangement, 0.90 Scm^{-1}, is two orders of magnitude greater than that of fibrils made with the vertical electrode arrangement, 1.0 x 10^{-2} Scm^{-1}. Figure 2 shows an Arrhenius plot of the temperature dependence of the conductivity for the two electrode arrangements. The more oriented helical fibril resulting from the horizontal electrode arrangement shows no temperature dependence from 15 K to room temperature, while the helical fibril from the vertical electrode arrangement shows a semiconducting temperature dependence.

A comparison of the x-ray diffraction, XRD, of helical

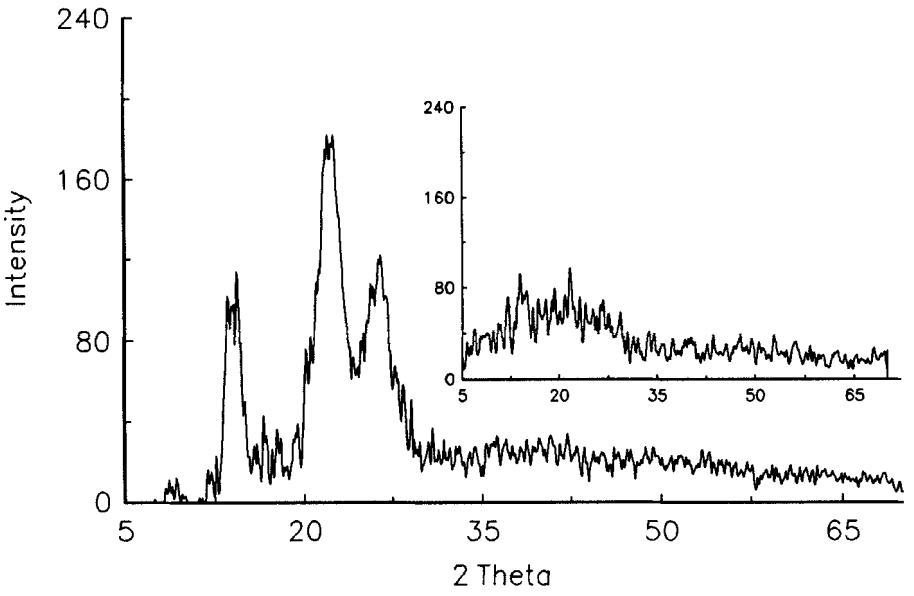

Figure 3 X-ray diffraction of helical P3MT fibrils made with the horizontal electrode arrangement. Inset shows fibrils made with the vertical arrangement.

fibrils to that of braided fibrils is shown in Figure 3. The diffraction pattern of the Kapton tape was subtracted from the fibril diffraction patterns, and the resulting spectrum smoothed. Scans were performed from 2θ of 2 to 120 degrees. Figure 2 shows the diffraction pattern from 5 to 70 degrees for helical fibrils and (inset) braided fibrils. The increased intensity and line sharpening is evident in the more oriented fibrils from the horizontal electrode arrangement. Garnier and co-workers[6] found that P3MT doped with 50 % $CF_3SO_3^-$ gives a diffraction with two broad peaks at 2θ from 13 to 20 and 27 to 32 degrees, different from what is presented here. They concluded from their x-ray data P3MT doped with 50 % $CF_3SO_3^-$ existed in a "coiled" structure. They did not find P3MT to exhibit this "coiled" structure on a macroscopic scale as is shown here. No low angle diffraction is seen here as is seen with stretch oriented poly(3-octylthiophene)[7].

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