was dried only to about 30 % of its weight before the crosslinking step. A drop of 1 M $MgSO_4$ was added for the crosslinking, and after about 15 min the electrode was equilibrated with aqueous 0.25 M $MgSO_4$ for at least 2 h. The PPy was grown on the polymer gel as described above. The unswelled PEDOT-PSS/PPy electrode was prepared by electropolymerizing pyrrole on an uncrosslinked PEDOT-PSS-coated electrode from acetonitrile solution containing 0.25 M pyrrole and 0.1 M $LiClO_4$ at a constant potential of 0.85 V vs. an Ag/AgCl electrode. The PPy-coated electrode was prepared by growing PPy on a gold electrode under the same conditions as in the case of PEDOT-PSS/PPy electrodes.

The electrochemical cell in the supercapacitor geometry for the cyclic voltammetric and the chrono-potentiometric studies was a two-electrode set-up, with two identical electrodes face to face and parallel, in aqueous 1 M Na_2SO_4. For the swelled-polymer electrodes, i.e., in the cases where high power-density was applied the electrodes were at a fixed separation of 1 mm, whereas in other cases, the distance was about 1 cm. The cells were in ambient atmospheric conditions. The chrono-potentiometric studies of galvanostatic charging–discharging were carried out in the potential range of 0 V to 0.8 V. For calculation of the energy and power densities, the first discharge curve after equilibration of the cell at 0.8 V was analyzed, and the dry mass of the polymeric material on a single electrode was considered. The mass of the PEDOT-PSS was determined from the weight of the dispersion of known concentration that was applied to the electrode. The mass of PPy was calculated from the coulomb of charge passed for its electropolymerization, assuming 2.25 electrons per pyrrole unit are needed for the polymerization of PPy at 25 % doping level.

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Polythiophene Nanowires**

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Devices based on conjugated polymers are becoming commercially available in the form of light emitting diodes,[1] proto-type electronic polymer circuits of conjugated polymers are presently being demonstrated to work[2] and lasers are being developed.[3] All these applications make use of the polymer samples as solution cast thin films. Since the electronic and optical properties of the films are inherently related to their local structure, it is vitally important, for the performance of the devices, to achieve a greater control of the self-assembly process that takes the polymers from a disordered state in solution into a semi-ordered solid state. The desire to make nanometer scale devices for future electronic applications further emphasizes the need for such nanoscale control.

Here we report on the formation of polythiophene nanowires. The work is a continuation of previously reported studies[4] of Langmuir-Blodgett (LB) films of amphiphilic polythiophenes which are substituted by alternating hydrophilic and hydrophobic side groups along the backbone (**1** see Fig. 1A). Langmuir films of **1** form readily, and isothermic compression (Fig. 1B) leads to densely packed monolayers in which the polythiophene backbones are π-stacked parallel to the water surface as indicated in Figure 1A. The stacking of the polymers is highly ordered. Adjacent polymers of **1** are displaced one thiophene unit along the backbone, thereby allowing the alkyl chain of one polymer to fill the void space between the alkyl chains on the adjacent polymer.[4] From X-ray diffraction data, the domain size of the highly ordered π-stacked polymer has been estimated to be 6 nm in the stacking direction.[4] The average length of the polymers is ≤ 40 nm (i.e. ≤ 50 repeat units).[4,5]

As described below, monolayers of **1** spontaneously fold into wire-like structures when compressed beyond the collapse point on the LB-trough. These wires are microns long

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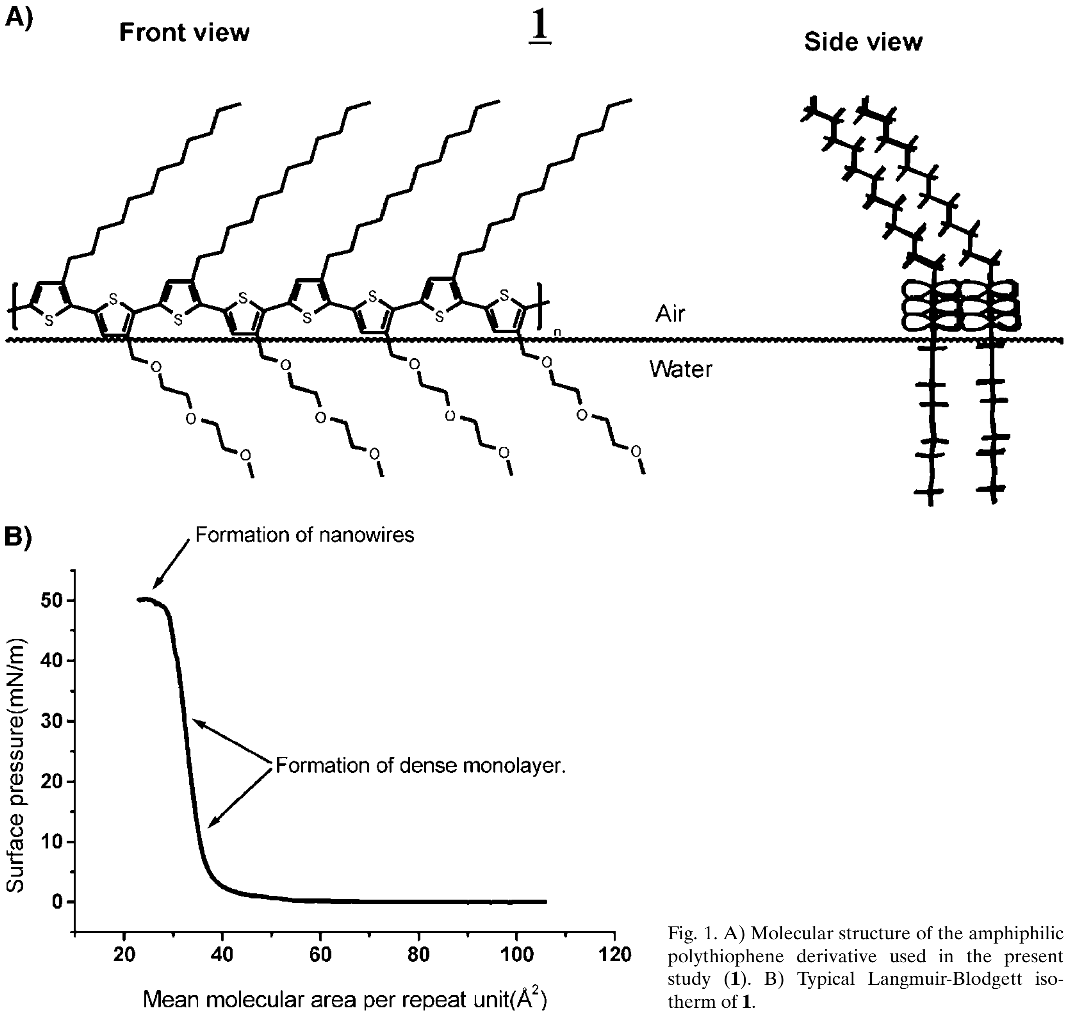

Fig. 1. A) Molecular structure of the amphiphilic polythiophene derivative used in the present study (**1**). B) Typical Langmuir-Blodgett isotherm of **1**.

with nano-scale cross sections. Bundles of the "nano-wires" can be manipulated to fill the gap between gold electrodes and they are shown to be highly conducting in the doped state at room temperature as well as at low temperatures (~ 50 K).

The photograph of the top view of the Langmuir trough shown in Figure 2A reveals the formation of visible threads running parallel to the barrier across the Langmuir trough. The threads form when the monolayer of **1**, for example, is compressed beyond the collapse point. These structures are readily transferred to solid substrates by horizontal dipping of the substrate into the surface covered by threads. Optical microscopy reveals considerable texture in these threads showing that they are formed by bundling of smaller structures (Fig. 2B). Viewed under crossed polarizers, it is evident that the polymer threads possess some structural orientation along the thread's long-axis as seen in Figure 2C; the bundles of wires lying parallel to the polarizer appear dark, whereas other bundles appear light. A dichroic ratio of 1.4 is typically measured by polarized UV-vis spectroscopy favoring a polymer backbone alignment along the direction of the thread. By transferring the threads to a mica surface it is possible to image them by atomic force microscopy. The AFM micrograph permits visualization of the size of the smallest structures in the threads as shown in Figure 2D. The AFM reveals the formation of wires which are microns long, exhibiting widths of only 60 nm and heights of 10–15 nm. In some cases, the wire can divide into two separate wires illustrating their soft liquid crystal-like nature (Fig. 2D).

Collapse of the monolayer is accompanied by some loss of local order, as observed by comparing the X-ray diffraction from an intact monolayer to the diffraction from the monolayer collapsed into wires.[5] When pressurized beyond the collapse point, the monolayer presumably folds into multilayer structures in which the crystalline domains forming the monolayer are almost randomly packed, with only a 40 % excess of domain alignment along the wire direction, as estimated from the dichroic ratio of 1.4. The height of the wire measured by atomic force microscopy (~10 nm, Fig. 2D) roughly corresponds to five stacked monolayers. The width measured to ~60 nm corresponds to the average polymer length. Taken together, these observations would suggest that the wires consist of disrupted elongated crystalline domains, with the polymer strands preferentially oriented along the long axis of the wire.

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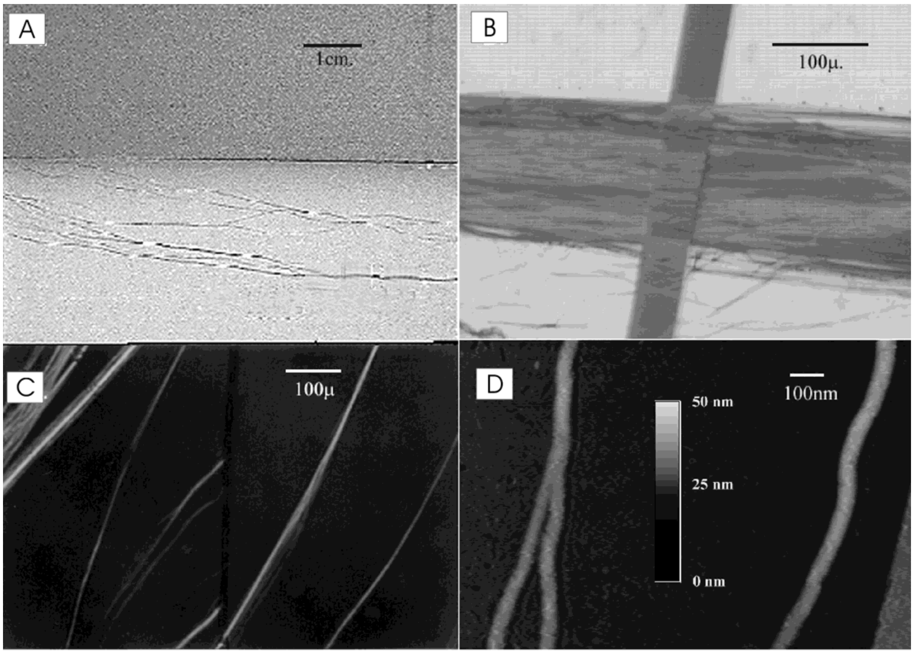

Fig. 2. A) Photograph of the top view of Langmuir trough with collapsed monolayer of **1**. B) Optical microscope picture of bundles of polythiophene wires crossing the gap (dark grey) between gold electrodes (light grey). C) Optical microscopy picture of bundles of polymer wires of **1** in crossed polarized light. D) Atomic force micrograph of single polymer nanowires of **1**. The threads are approx. 60 nm wide and 10–15 nm high.

The electrical resistance of bundles of wires placed between two gold electrodes (Fig. 3B) has been measured from room temperature down to 4.2 K. The room temperature conductivity of the undoped wires is less that 10^{-5} S/cm, in agreement with the expected semi-conducting/insulating nature of the neutral polymer. When the sample is exposed to vapor from an iodine crystal, the conductivity changes by more than six orders of magnitude, reaching a value of σ = 40 S/cm ($\rho \approx 2.5 \times 10^{-4}$ Ω). Interestingly, between room temperature and 250 K, the wires display a negative temperature dependence of conductivity. The apparent metallic behavior could be due to differences in iodine vapor pressure, at the temperatures in question. A more detailed investigation is, however, needed in order to determine the exact nature of the this behavior. Below 250 K, a weakly activated resistivity was observed (Fig. 3). The rather low activation energy (see below) results in a considerable residual conductivity at temperatures comparable to the critical temperature of high temperature superconductors (~100 K). In future studies, the wires will be combined with the high T_c superconductors in an effort to search for the organic polymer proximity effects.[6,7]

In order to compare the transport properties of the polymer wires with those of other conjugated polymers, the temperature dependence of the resistivity was analyzed further. In Figure 3, the resistivity versus temperature curves from cool-down and subsequent warm-up of the same sample are shown. Following the method recently reviewed in the *Handbook of Conducting Polymers*,[8] the conducting polymer wires were characterized with respect to the metal-insulator transition through the reduced activation energy *W* defined as follows.[8–10]

$$W = -\frac{\mathrm{d}\ln\rho}{\mathrm{d}\ln T} \tag{1}$$

In Figure 3 (inset), *W* is shown to be a decreasing function of temperature indicating that the nanowires are in the insulating regime close to the critical regime.[8] In the insulating regime the dominant type of conduction is the variable range hopping (VRH).[8,11–13] The solid line through the experimental data in Figure 3A has been fitted with the VRH model given by Equation 2.

$$\rho = \rho_0 \cdot \exp\left(\left(\frac{T_0}{T}\right)^{\alpha}\right) \tag{2}$$

The data of Figure 3 is found to fit nicely with Equation 2 using an α = 0.5. This value of α deviates from the α = 0.25 which is expected and observed for homogeneously doped polymer films in which conduction takes place by activated hopping between localized states.[11] The observed value of α = 0.5 is actually more typical for granular metals,[8,11] thus indicating that the conductivity of the wires has the same characteristics as that of "metallic islands" connected through insulating disordered regions.

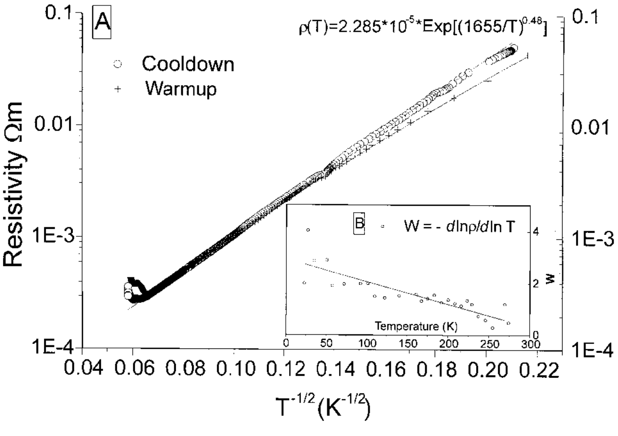

Fig. 3. A) Resistivity vs. temperature curves from cool-down and subsequent warm-up of a bundle of wires placed between gold electrodes, separated by a 50 µm gap. The line fitted to the data points is the theoretical curve given by Equation 2. B) The inset shows the reduced activation energy *W* as a function of temperature. Data points for every $\Delta\ln T \approx 1$ is plotted, to give a better overview, as suggested in [8].

In summary, we have prepared for the first time, nanometer size threads of a conjugated polymer by collapsing a monolayer of amphiphilic polythiophene on a LB trough. The wires exhibit a room temperature conductivity of 40 S/cm, which is higher than any previously reported conductivity from a single component LB-film derived sample.[14] X-ray diffraction experiments showed that the wires were less ordered than the monolayer from which they were formed and the conductivity of 40 S/cm can hence be regarded as being a lower estimate of the conductivity in the highly ordered local domains of the LB films of **1**. The intrinsic conductivity of these domains is presently under investigation.[15]

Experimental

Samples of polymer **1** were obtained from synthesis as described earlier [4]. A Lauda LB-trough was used to fabricate Langmuir films on a pure water subphase (Milli-Q filtered) [4]. Polarized optical microscopy pictures of the wires were obtained with a Nikon Optiphot microscope equipped with crossed polarizers. The dichroic ratio was derived from the absorption spectra obtained in a Perkin Elmer UV/VIS/NIR lambda 9 spectrometer equipped with polarizers. Images and cross-sections of the wires were recorded with a Nanoscope IIIa AFM from Digital Instruments working in contact mode. Analysis of the cross section of the wires including deconvolution of tip and thread structure using a tip radius of curvature of approximately 30 nm, show that the threads shown in Fig. 2D are approx. 60 nm wide and 10–15 nm high. The cross section of the bundles of wires used for conductivity measurements was obtained by analyzing the data from the AFM. The four probe technique was used for the D.C. conductivity measurements. The electrical contacts were fabricated on the substrate prior to nano-wire transfer, by evaporating gold on the substrate through a mask.

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Electroless Deposition of Conducting Polymers Using the Scanning Electrochemical Microscope**

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The unique electronic properties of conducting polymers such as polyaniline, polypyrrole, and polythiophene have attracted much attention. Possible applications including batteries, capacitors, transistors, Schottky diodes, photovoltaic cells, light emitting diodes, and sensors have already been reported.[1–3] Most of these, and future microelectronic devices, require high resolution patterning capabilities of the polymers. Nevertheless, conventional micro-photolithography techniques, which are widely employed in the microelectronics industry, are not suited for the micropatterning of organic substances such as conducting polymers.

On the other hand, novel scanning probe microscopy techniques have accomplished significant progress, especially in driving nanometer surface modifications.[4–6] However, while the nanochemistry carried out by techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM)[4,5] is usually a result of applying either mechanical forces or electrical fields, the scanning electrochemical microscope (SECM) enables surface modifications to be carried out using faradaic current.[6] The SECM approach is based on scanning an ultramicroelectrode (UME) close to a surface immersed in an electrolyte solution that also contains an electroactive species. The current measured at the UME originates from the electrochemical oxidation or reduction of this electroactive species and is strongly dependent on the distance from the surface and its electrochemical nature. Thus, scanning the UME at a constant height can provide lateral information of the surface properties.[7] On the other hand, micropatterns can be formed in the case where the electroactive species, electrogenerated at the UME, reacts with the surface.[6] The dimensions of the UME, using recent advanced approaches for UME fabrication, can be of the order of nanometers.[8]

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