Self-Assembly of Regioregular, Amphiphilic Polythiophenes into Highly Ordered \(\pi\)-Stacked Conjugated Polymer Thin Films and Nanocircuits


CISMI, Department of Chemistry, University of Copenhagen, Fruebjergvej 3, DK-2100 Copenhagen, Denmark

Physics Department, RISØ National Laboratory, DK-4000 Roskilde, Denmark

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Received March 31, 1998

Molecular self-assembly is rapidly becoming a method to optimize performance in materials and devices by directing the formation of supramolecular structures. In the area of conjugated (or conducting) organic polymers, self-assembly has been used to build layer by layer polymer heterostructures and to create water-based polymer chemoselective sensors and polymers that exhibit highly sensitive, solvent-induced chiral optical effects.

The Langmuir–Blodgett technique has been successfully used to prepare thin films of functional molecular surfactants as well as nonamphiphilic polymers decorated with alkyl chains. Here we present amphiphilic, regioregular polythiophenes that can be processed by the Langmuir–Blodgett technique into nanoscale structures. These amphiphilic polythiophenes self-assemble into \(\pi\)-stacked conjugated chains that form a very stable cell-membrane-like monomolecular layer with a local structure that is optimized for high electrical conductivity. These well-ordered polymer monolayers can be transferred to solid supports, forming highly conductive ultrathin films. They can also be micropatterned by chemical means as demonstrated by the fabrication of an electronic microchip replica. The fabrication of the chip structure, producing a pattern of 2.5 nm thick and 1000 nm wide conjugated polymer “wires,” is performed at ambient conditions by purely chemical self-assembly methods.

The key to the above results lies with the design and synthesis of new regioregular amphiphilic polythiophene copolymers where perfectly alternating hydrophobic and hydrophilic side groups form a rigid rod polymer that has a hydrophobic side and a hydrophilic side. Other studies on the formation and properties of LB films of conducting polymers have started with polymers containing many structural defects (or the polymer was not amphiphilic), rendering the polymer unable to form highly ordered systems.

Five new, amphiphilic, regioregular, alternating copolymers of polythiophene have been prepared using modifications of the methods previously developed by McCullough et al. The synthesis of polythiophenes has been prepared using modifications of the methods previously developed by McCullough et al. The synthesis of polythiophenes has been prepared using modifications of the methods previously developed by McCullough et al. The synthesis of polythiophenes has been prepared using modifications of the methods previously developed by McCullough et al. The synthesis of polythiophenes has been prepared using modifications of the methods previously developed by McCullough et al. The synthesis of polythiophenes has been prepared using modifications of the methods previously developed by McCullough et al.
The structure of the Langmuir monolayer of 10 (M_w = 12,000, PDL = 1.3) compressed to 30 mN/m pressure has been elucidated by diffraction and reflection of synchrotron X-rays.15,16 A plot of the X-ray intensity vs horizontal scattering angle reveals two narrow peaks and one broad peak. The dominant narrow peaks arise due to the π-π stacking of the polythiophenes along the water surface (d = 3.8 Å), and the broad peak corresponds to scattering from the alkyl chains in a disordered state. From detailed analysis16 of the peak positions and widths these results show that the thiophene part of the polymers scatters from domains in which roughly 15 π-stacked polymers give rise to coherent scattering. The unit cell dimensions16 depicted in Figure 1D are inferred from the positions of the observed narrow peaks (corresponding to the (02) and (11) reflections), combined with a polymer repeat unit (=a in Figure 1D) that is taken from crystallographic data on oligothiophenes. Further details of the X-ray experiments will be the subject of a manuscript in preparation.16

Transfer of monolayers of each of the polymers 4, 5a, 6, and 10 to a solid hydrophilic support (glass or silicon) by the LB technique. The amphiphilic polythiophene only sticks to the hydrophilic areas, resulting in a replication of the original electronic chip pattern now as 2.5 nm high and 1000 nm wide polythiophene “wires”. The whole process has been carried out under ambient conditions. (B) Schematic illustration of the cross section of the microchip structure along the solid line shown in (A).

Figure 2. (A) Contact mode AFM image of a polythiophene microchip structure. The image shows a gold-coated silicon wafer which has been patterned into hydrophilic and hydrophobic areas by micro contact printing and subsequently drawn out of a water subphase covered by a monolayer of amphiphilic polythiophene 10 by the LB technique. The amphiphilic polythiophene only sticks to the hydrophilic areas, resulting in a replication of the original electronic chip pattern now as 2.5 nm high and 1000 nm wide polythiophene “wires”. The whole process has been carried out under ambient conditions. (B) Schematic illustration of the cross section of the microchip structure along the solid line shown in (A). Stability over time of the films is very good; no bleaching or other signs of degradation were observed one month after preparation of the films. Attempts to bleach the films in intense UV light were unsuccessful.

Transfer of monolayers of 10 to a substrate which has been patterned into hydrophilic and hydrophobic areas of nearly equal heights results in the replication of the pattern. This has been demonstrated by printing the pattern of a microchip onto a gold-coated silicon wafer by microcontact printing10,18 using functionalized alkanethiols.4 After transfer of a monolayer to the patterned silicon wafer, imaging with atomic force microscopy reveals the same pattern now represented by 2.5 nm high lanes of polythiophene (Figure 2). This demonstrates that the “hydrophobic effect” readily used by nature to structure biomolecules can also be exploited to structure molecular electronic systems on solid supports.

Preliminary four-probe measurements of the electrical conductivity of a monolayer film of 10, performed by contacting four Pt wires to evaporated gold contacts on the film and subsequent exposure of the sample to iodine vapor, causing a transition to the highly conductive state, yield values in the range of 1–50 S/cm. For comparisons I_2-doped, 100 nm thick spin cast films of regioregular poly(3-dodecylthiophene) were measured. Conductivity values between 500 and 750 S/cm were found in agreement with previous reports.44

As demonstrated above, ultrathin films of amphiphilic polythiophene can be manipulated and processed on the nano- and micrometer scales by self-assembly methods, opening new possibilities for, e.g., fabrication of integrated circuit structures including nanoscale field effect transistors of polythiophene. Prototype field effect transistors with high carrier mobilities have recently been prepared from solution cast thin films of regioregular poly(3-alkylthiophene).19

Acknowledgment. This work was supported by NSF Grant CHE-9509959 (R.D.M.), NATO Grant CRG-941351 (R.D.M./T.B.), the Danish Research Councils, DanSync, MODECS, and the European Union through TMR for financial support of this work, and HASYLAB at DESY, Hamburg, for beam time at beamline BW1. We are also grateful to the Department of Chemistry at the University of Copenhagen for support of visiting positions at CISMI for R.D.M.

Supporting Information Available: Full experimental details for the synthesis of molecules and polymers 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10, 1H NMR spectra of molecules and polymers 3, 4, 5, 6, 9, and 10 (both full and expanded), and details of the microcontact printing (22 pages, print/PDF). Ordering information is given on any current masthead page. See any current masthead page for ordering information and Web access instructions.

JA981077E