# Self-Assembly of Regioregular, Amphiphilic Polythiophenes into Highly Ordered π-Stacked Conjugated Polymer Thin Films and Nanocircuits

Thomas Bjørnholm,*,† Daniel R. Greve,† Niels Reitzel,†
Tue Hassenkam,† Kristian Kjaer,‡ Paul B. Howes,‡
Niels B. Larsen,‡ Jesper Bøgelund,‡ Manikandan Jayaraman,§
Paul C. Ewbank,§ and Richard D. McCullough*,§

*CISMI, Department of Chemistry, University of Copenhagen
Fruebjergvej 3, DK-2100 Copenhagen, Denmark
Physics Department, RISØ National Laboratory
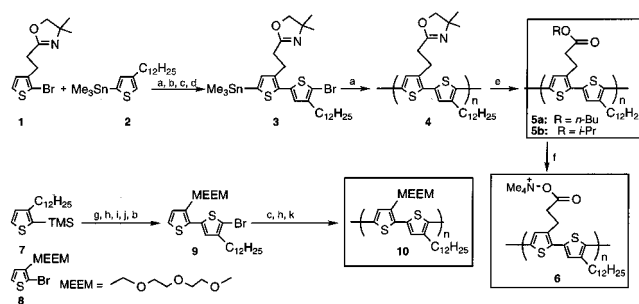DK-4000 Roskilde, Denmark
Department of Chemistry, Carnegie Mellon University
Pittsburgh, Pennsylvania 15213*

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Molecular self-assembly is rapidly becoming a method to optimize performance in materials and devices by directing the formation of supramolecular structure. In the area of conjugated (or conducting) organic polymers, self-assembly has been used to build layer by layer[1] polymer heterostructures[2] and polydiacetylene self-assembled monolayers (SAMs),[3] to generate polymers with high electrical conductivities,[4a] and to create water-based polymer chemoselective sensors[4b] and polymers that exhibit highly sensitive, solvent-induced chiral optical effects.[5]

The Langmuir−Blodgett technique[6,7] has been successfully used to prepare thin films of functional molecular surfactants[8] as well as nonamphiphilic polymers decorated with alkyl chains.[9] Here we present amphiphilic, regioregular polythiophenes that can be processed by the Langmuir−Blodgett technique into nanoscale structures. These amphiphilic polythiophenes self-assemble into π-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.[10] The key to the above results lies with the design and synthesis of

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* Corresponding authors (e-mail: tb@symbion.ki.ku.dk and rm5g@andrew.cmu.edu).
† University of Copenhagen.
‡ RISØ National Laboratory.
§ Carnegie Mellon University.

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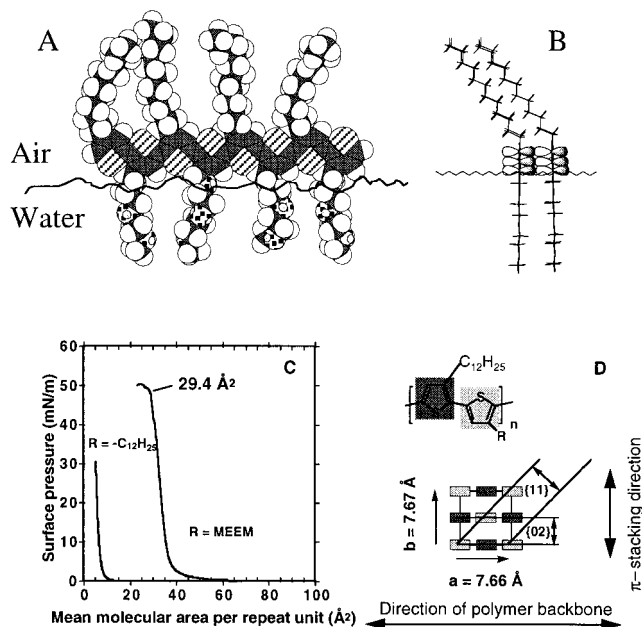
**Scheme 1**[a]



[a] Conditions: (a) $Pd_2(dba)_3$, $PPh_3$, CuO, DMF, 100 °C, 70%; (b) NBS, THF, RT, 80%; (c) LDA, THF, −78 °C; (d) $Me_3SnCl$, 80%; (e) ROH, $H_2O$, $H_2SO_4$, 100 °C, 90%; (f) $Me_4NOH$, THF, MeOH, 100%; (g) BuLi, THF, −78 °C; (h) $MgBr_2 \cdot OEt_2$; (i) **8**, $Ni(dppp)Cl_2$, 80%; (j) TBAF, THF, 100%; (k) $Ni(dppp)Cl_2$, 20%.

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.[4b,11−13] The synthesis of polythiophenes **4**, **5a**, **5b**, **6**, and **10** is shown in Scheme 1. Dimer **3** can be regiospecifically polymerized in excellent yield by a modified Stille coupling recently developed for the synthesis of regioregular, water-soluble carboxylate polymers of polythiophene[4b] (Scheme 1, top reaction sequence). Polymer **4** bears an oxazoline protecting group as a masked carboxylate and hence allows for the preparation of regioregular, amphiphilic polythiophenes, such as esters **5a** and **5b** and carboxylate **6**. We have also polymerized[12] dimer **9** to give amphiphilic **10**. From the routes shown in Scheme 1, a diverse array of amphiphilic polythiophenes can be prepared which have novel properties as described below.

Chloroform solutions of regioregular, amphiphilic **10** are readily spread onto the water surface of a Langmuir trough. Isothermic compression leads to a close-packed monolayer consisting of oriented polythiophene chains (Figure 1). The pressure−area isotherm for the Langmuir film of **10** shown in Figure 1C reveals a collapse of ∼29 Å$^2$ per polymer repeat unit. This collapse area agrees with the anticipated structure shown in Figure 1D in which efficient π-stacking of adjacent polymers is accomplished by displacing the polymers by one thiophene unit along the backbone, thereby allowing the alkyl chains on one polymer to fill the void space (Figure 1A) between the alkyl chains on the adjacent polymer. The collapse areas for polymers **4**, **5a**, **5b**, and **6** are found to be 30, 29, 30, and 29 Å$^2$, respectively, suggesting that all the regioregular, amphiphilic polythiophenes investigated here form monolayer arrangements roughly similar to that represented for **10**. It is important to note that nonamphiphilic poly(3-dodecylthiophene) (R = $C_{12}H_{25}$, Figure 1C) does not form a monolayer, emphasizing the importance of the amphiphilic nature of the polymer.

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(13) Polymers **4**, **5a**, **5b**, **6**, and **10** have molecular weights ($M_n$) of 11K with polydispersity indexes (PDI) of around 2. Preparative fractionation of these polymers can provide PDIs as low as 1.2. The structure and purity of all key intermediates were determined by ^{1}H and ^{13}C NMR, and elemental analysis. The polymers **5**, **10**, and **6** were characterized by ^{1}H NMR, GPC, and UV−vis. Details are found in the Supporting Information.

**Figure 1.** (A) Model of a segment of polymer **10** showing the void space between the alkyl chains present on the upper (hydrophobic) side of the polymer oriented at the air−water interface. (B) Side view of the $\pi$-stacked polymer indicating the presence of good electronic contacts from one polymer to the next. (C) Compression isotherm ($T = 20\ °C$) of amphiphilic and nonamphiphilic regioregular polythiophene. (D) Top view of unit cell obtained from X-ray diffraction from the self-assembled monolayer at the air−water interface. The $\pi$−$\pi$ stacking distance is 3.84 Å, and the projected area taken up by one repeat unit is 3.84 Å × 7.66 Å = 29.4 Å$^2$. This area is close to the collapse area of the monlayer depicted on the isotherm (C), indicating full monolayer coverage of the water surface.

The structure of the Langmuir monolayer of **10** ($M_n = 12\ 000$, PDI = 1.3) compressed to 30 mN/m pressure has been elucidated by diffraction and reflection of synchrotron X-rays.[8b,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 $\pi$-stacking of the polythiophenes along the water surface ($d = 3.84$ Å), and the broad peak corresponds to scattering from the alkyl chains in a disordered state. From detailed analysis[16] of the peak positions and widths these results show that the thiophene part of the polymers scatters from domains in which roughly 15 $\pi$-stacked polymers give rise to coherent scattering. The unit cell dimensions[16] 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**, **5b**, **6**, and **10** to a solid hydrophilic support (glass or silicon) by the Langmuir−Blodgett technique proceeds with a transfer ratio of $1.0 ± 0.1$. Magenta-colored Langmuir−Blodgett monolayer films form with an anisotropic orientation of the ordered domains as seen from a dichroic ratio of about 4 observed in the optical absorption spectrum of the films. The largest absorption is along the dipping direction, showing that the transferred films have the polymer backbones oriented along this direction. Within the domains the polymers are still highly conjugated as indicated by the solid state $\lambda_{max} = 544$ nm, approaching the highest $\lambda_{max}$ ob-

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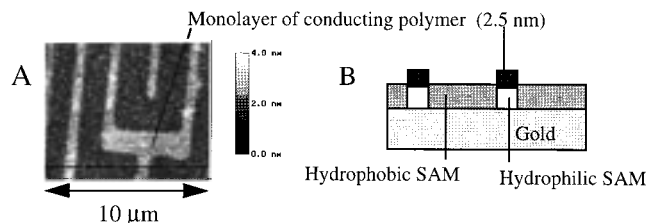(16) Reitzel, N., et al. Manuscript in preparation.



**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 hydrophobic and hydrophilic 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).

served for polythiophene thin films.[4a,17] 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 printing[10,18] 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.[4a]

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]

**Supporting Information Available:** Full experimental details for the synthesis of molecules and polymers **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, and **10**, ^{1}H 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.

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