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


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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 polymer heterostructures and to create water-based polymer chemoselective sensors. Here we present amphiphilic, regioregular polythiophenes that assemble into π-stacked conjugated chains that 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 4a, 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 (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 polymerized12 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 Å² per polymer repeat unit. This collapse area agrees with the anticipated structure shown in Figure 1D in which efficient π-interchain interaction is accomplished by displacing the polythiophene 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 4a, 5a, 5b, and 6 are found to be 30, 29, 30, and 29 Å², 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 = C₁₂H₂₅, Figure 1C) does not form a monolayer, emphasizing the importance of the amphiphilic nature of the polymer.

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* Conditions: (a) Pd(dba)₃, PPh₃, CuO, DMF, 100 °C, 70%; (b) NBS, THF, RT, 80%; (c) LDA, THF, −78 °C; (d) Me₃SnCl, 80%; (e) ROH, H₂O, H₂SO₄, 100 °C, 90%; (f) Me₃NOH, THF, MeOH, 100%; (g) BuLi, THF, −78 °C; (h) MgBr₂·EtMgCl; (i) Ni(C₆H₅)_₄Cl, 80%; (j) TBAF, THF, 100%; (k) Ni(dppe)Cl₂, 20%.
analysis of the peak positions and widths these results show from the alkyl chains in a disordered state. From detailed analyses arise due to the narrow peaks and one broad peak. The dominant narrow peaks \( P_{\text{DI}} \) polymer repeat unit (16) will be the subject of a manuscript in preparation.\(^\text{16}\) Theoretical data on oligothiophenes. Further details of the X-ray scattering. The unit cell dimensions \( a = 7.66 \, \text{Å} \) depicted in Figure 1D are seen from one polymer to the next. (C) Compression isotherm \( (T = 20 \, ^\circ\text{C}) \) 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 \, \text{Å}, and the projected area taken up by one repeat unit is 3.84 \, \text{Å} \times 7.66 \, \text{Å} = 29.4 \, \text{Å}^2\). This area is close to the collapse area of the monolayer depicted on the isotherm (C), indicating full monolayer coverage of the water surface.

The structure of the Langmuir monolayer of 10 \( (M_n = 12,000, \text{PDI} = 1.3) \) compressed to 30 mN/m pressure has been elucidated by diffraction and reflection of synchrotron X-rays.\(^\text{39,15,16}\) 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 \( \pi-\pi \) stacking of the polythiophenes along the water surface \( (d = 3.84 \, \text{Å}) \), and the broad peak corresponds to scattering from the alkyl chains in a disordered state. From detailed analysis\(^\text{16}\) of the peak positions and widths these results show that the thiophene part of the polymers scatters from domains in which roughly 15 \( \pi-\pi \) stacked polymers give rise to coherent scattering. The unit cell dimensions\(^\text{16}\) 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 \( (=a \text{ in Figure 1D}) \) that is taken from crystallographic data on oligothiophenes. Further details of the X-ray experiments will be the subject of a manuscript in preparation.\(^\text{16}\)

Transfer of monolayers of each of the polymers 4, 5a, 6, \( \text{and 10} \) to a solid hydrophilic support (glass or silicon) by the Langmuir–Blodgett technique proceeds with a transfer ratio of \( 1.0 \pm 0.1 \). 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 \( \lambda_{\text{max}} = 544 \, \text{nm}, \) approaching the highest \( \lambda_{\text{max}} \) ob-

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**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 \( \pi-\pi \)-stacked polymer indicating the presence of good electronic contacts from one polymer to the next. (C) Compression isotherm \( (T = 20 \, ^\circ\text{C}) \) 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 \, \text{Å}, and the projected area taken up by one repeat unit is 3.84 \, \text{Å} \times 7.66 \, \text{Å} = 29.4 \, \text{Å}^2\). This area is close to the collapse area of the monolayer depicted on the isotherm (C), indicating full monolayer coverage of the water surface.

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**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).

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


(18) See Supporting Information for experimental details.