Notes

Monolayer Behavior of Poly(*p*-pheneyleneethynylene) End-Capped with Thioacetate Groups

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The functionalization of chain ends of conjugated oligomers and polymers is critical to the design and synthesis of active molecules for nanometer-scale devices in which contacts between conjugated molecules and electrodes are critical to device performance.[1−3] Recently, the photoresponse and transistor behavior of rigid-rod poly(phenyleneethynylene)s (PPEs) with thioacetate end groups in nanoelectronic devices were reported.[4] The thioacetate groups were converted into thiol groups in a basic solution and were self-assembled onto metal electrodes to form metal−thiolate covalent bonds.[3] Carriers were injected through the metal−thiol bonds and transported by π-electrons.[1,2] The devices worked well as a nanometer-scale photoswitch and as a p-type transistor,[4] but little study on the molecular organization of the polymers in the active regions of the devices was carried out.

Molecular processing using the Langmuir−Blodgett (LB) technique is a powerful method to prepare well-organized thin films of conjugated polymers and allows the investigation of their aggregation behavior.[5−9] In particular, the formation of a π-stacked morphology in the LB film, and subsequent transfer of the π-stacked film to a substrate, offers the possibility of improving carrier mobility in thin film transistors, for example.[6−9] Previous LB studies of rigid-rod polymers showed that the film-forming properties of conjugated polymers at the air−water interface are related to the structure of polymers, particularly the nature of side chains. Kim and co-workers reported that the nature of the side chains could give rise to three different molecular orientations (face-on, edge-on, and zipper structures) of PPEs at the air−water interface.[5] In this work, we report the first observations demonstrating that the end groups of polymer chains may determine the molecular organization of LB films of conjugated polymers at the air−water interface. In particular, LB films of a nonyl-substituted PPE with thioacetate terminal groups (PPE-SAc) have an edge-on molecular orientation, whereas LB films of PPEs with iodo terminal groups (PPE-I) have a face-on morphology.

Figure 1 shows the synthetic route for PPE-I and PPE-SAc. The Pd-catalyzed coupling of diiodoarene (**1**) and bis(alkynyl)arene (**3**) in a THF/amine solvent is known to yield PPEs with very reactive iodo terminal groups (PPE-I).[10] The two monomers (**1** and **3**, 1 mmol) were dissolved in THF (15 mL) and triethylamine (20 mL), and the solution was degassed three times. After $Pd(PPh_3)_4$ (0.10 mmol) and CuI (0.20 mmol) were added, the reaction mixture was stirred at 60 °C for 24 h. Half of the reaction mixture was poured into methanol to give PPE-I. To the other half of the mixture, excess *S*-4-ethynylphenyl ethanethioate (**4**), an end-capping agent, was added. After another 24 h, the latter mixture was poured into methanol to yield brown PPE-SAc (see Supporting Information).

The chemical structures of PPE-I and PPE-SAc were confirmed with NMR and IR spectra shown in Figures S2 and S3 of the Supporting Information. In the NMR spectrum of PPE-I, two peaks at 7.65 and 7.27 ppm were assigned to the aromatic protons on the terminal iodobenzene groups of PPE-I. In the NMR spectrum of PPE-SAc, new peaks appeared at 7.55 and 2.41 ppm, which were assigned to the aromatic and methyl protons, respectively, of the terminal phenyl thioacetate groups of PPE-SAc. A carbonyl band at 1715 cm^{-1} present in the IR spectrum of PPE-SAc, but absent in the spectrum of PPE-I, is further evidence for the presence of thioacetate groups. The peaks due to the aromatic protons of the terminal iodobenzene groups were not present in the NMR spectrum of PPE-SAc, implying that both polymer chain ends of PPE-I were functionalized with the thioacetate groups in PPE-SAc.

The molecular weight of PPE-SAc was determined from both an end-group analysis of the NMR spectra and gel permeation chromatography (GPC). In the NMR spectrum of PPE-SAc, the relative area ratio of aromatic protons of the PPE backbone at 7.10 ppm to methyl protons of the thioacetate groups at 2.41 ppm provided a degree of polymerization (DP) and a number-averaged molecular weight (M_n), of 42 and 20 100, respectively. GPC with polystyrene standards gave a somewhat higher M_n of 25 700 and a polydispersity of 1.5. The use of the polystyrene standards tends to overestimate the molecular weight for rigid-rod polymers. Under the assumption that PPE-SAc has a linear, rigid-rod structure, the average molecular length was calculated to be ca. 29 nm (0.7 nm, the length of a repeating unit, times 42, the degree of polymerization). The DP of PPE-I, determined by the relative area ratio of the aromatic proton peak at 7.10 ppm to the area of the peaks assigned to the aromatic protons of the terminal iodobenzene groups at 7.65 ppm, was 37. The UV−vis spectra of the PPE derivatives in $CHCl_3$ exhibited a single absorption around 397 nm for the $\pi-\pi^*$ transition, regardless of the terminal groups, indicating that the end groups have little effect on the electronic structure of the polymers, as expected (Figure 2).

PPE-I and PPE-SAc showed different behavior in Langmuir−Blodgett (LB) film-forming experiments. When a chloroform solution of PPE-I (5 mL, 0.6 mg/mL) was dropped onto the water surface of the LB trough, the florescence (from irradiance

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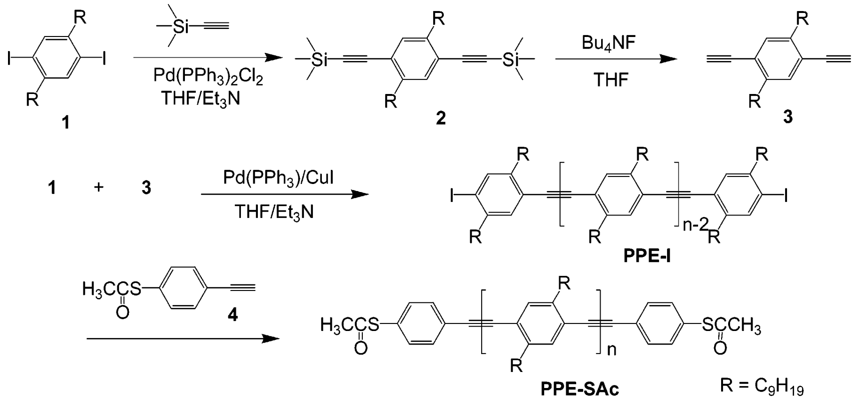

Figure 1. Synthesis of PPE-I and PPE-SAc (R = nonyl).

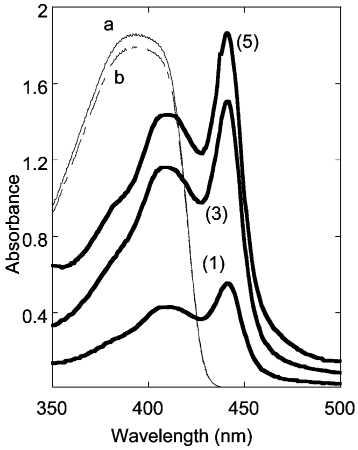

Figure 2. UV−vis spectra of (a) PPE-I and (b) PPE-SAc in $CHCl_3$ solution and PPE-SAc LB films, nominally 1, 3, and 5 monolayers thick (see text).

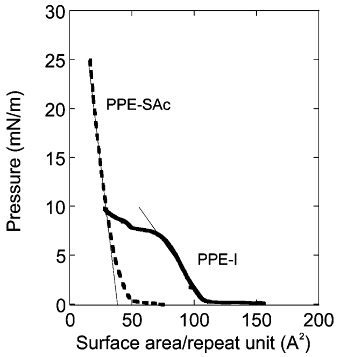

Figure 3. Pressure−area isotherms of PPE-I and PPE-SAc.

by a UV lamp, $\lambda \sim 254$ nm) of the film remaining after evaporation of the solvent showed that PPE-I was uniformly spread at the air−water interface. Isothermic compression led to a monolayer in which the area occupied by the repeat unit (mean monomer area) was ~105 Å^2 (Figure 3). Based on the fact that the length of the repeat unit is ca. 7 Å, PPE-I must lie face-on with respect to the water surface; i.e., the main polymer chains are parallel to the air−water interface with benzene rings lying flat on the water surface.[6] The films formed by PPE-I at the air−water interface were very sensitive to the amount and concentration of solutions. Larger amounts (10 or 15 mL) of the 0.6 mg/mL solution or higher concentration (1.2 mg/mL) provided domains of multilayers, as evidenced by nonuniform fluorescence intensity. Also, these results are consistent with the area calculated for the repeat unit in the film: 5 mL of 0.6 mg/mL solutions provides 1.4×10^{16} repeat units for a total monolayer area of ca. 75 cm^2, just less than the total area of the LB trough, 100 cm^2. Larger amounts of polymer give monolayers whose areas exceed the surface area of the LB trough, leading to multilayer formation.

On the other hand, using the same amounts of PPE-SAc (5, 10, or 15 mL of 0.6 mg/mL solution) gave uniform films that were uniformly spread at the air−water interface. As shown in Figure 3, the extrapolated area in the pressure−area isotherms of films of PPE-SAc was ~35 Å^2, implying that PPE-SAc is organized with the plane of its π system perpendicular to the air−water interface.[5] Using a value of 35 Å^2 for the area of a repeat unit, the calculated area of a monolayer produced by 15 mL of the polymer solution is only 75 cm^2, i.e., less than the area of the trough. The smaller area of the identical repeat unit in PPE-SAc vs PPE-I must be related to interactions between thioacetate groups and water, which affects the organization of polymer chains at the air−water interface. PPE-SAc tolerates a higher pressure and shows a steeper slope in the pressure−area isotherm, observations that are consistent with an edge-on configuration of the polymer molecules in the LB film.[5] In the face-on configuration of the PPE-I film, the alkyl side chains are flexible and, hence, compressible, but the conjugated cores in the edge-on structure of the PPE-SAc film are less so. Given that the length of the repeat unit is about 7 Å, the interlayer spacing in PPE-SAc must be ~5 Å, a value larger than the typical π−π stacking distance of ~3.8 Å in LB films of the amphiphilic polymers.[8,9] The increased distance is attributed to disorder of side chains. Xu and co-workers determined the conformation of side chains in the LB films of regioregular poly(3-hexylthiophene) by reflectance infrared spectroscopy and showed that gauche conformation defects were present in the side chains in the LB films.[6]

The Langmuir film (monolayer) of PPE-SAc was transferred with vertical strokes at a constant lateral pressure of 15 mN/m onto cover slides or onto SiO_2/Si substrates that were previously treated with HMDS. The films were observed to deposit only on a downward stroke with quantitative transfer ratio (>95%) over three layers. In the fourth layer, the transfer ratio was decreased to ~55%, indicating the monolayer was not well deposited, and no deposition occurred from the sixth downstroke on. Interestingly, the deposited layers were peeled off on an upward stoke. In general, a hydrophilic surface is required to best deposit a monolayer of an amphiphilic molecules on the upward stroke, considering the meniscus of the air−water interface on the substrate.[5c] However, the hydrophobic property of alkyl side chains is not favorable for the deposition on the upward stroke, and the peeling off of the deposited layers implies that the interaction between thioacetate groups and water is significant.

The transferred films were studied with UV−vis spectra, shown in Figure 2. The solution UV−vis spectra exhibited a single absorption around 397 nm for the $\pi-\pi^*$ transition. The spectra of the films are red-shifted and have two peaks at 410 and 442 nm that are also observed in UV−vis spectra of well-ordered, crystalline PPE films. The red shift is due to the planarization of the conjugated cores, and the peak at 442 nm is related to the aggregation of conjugated cores.[5,11] No dichroic behavior under polarized light was observed for the deposited films. This may be due to the formation of microdomains, each of which has different molecular orientation.[6] The different molecular orientation in each domain yields an average, isotropic absorption spectrum on a macro scale.

Attempts were made to build thin-film transistors by evaporating Au with shadow mask (top contacts) onto LB films of PPE-SAc that had been transferred onto HMDS-treated SiO_2/Si, but no field effect was observed. Similarly, spin-coated or drop-cast films of PPE-I or PPE-SAc showed no field effect even after annealing at 200 °C. The lack of an observable field effect is attributed to the low carrier mobility in these films, measured for PPE-I by the space charge limited current (SCLC) method to be $=10^{-11}$ $cm^2/(V\ s)$.

In summary, a Pd-catalyzed coupling reaction yielded PPE-I with reactive iodo terminal groups, and subsequent reaction between PPE-I and an end-capping reagent produced PPE-SAc with thioacetate groups at the chain ends. The terminal groups affect molecular organization at the air−water interface. PPE-SAc, with polar end groups, showed an edge-on LB film structure, whereas PPE-I showed a face-on molecular orientation.

Supporting Information Available: Experimental details and NMR and IR spectra of PPE-I and PPE-SAc. This material is available free of charge via the Internet at http://pubs.acs.org.

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