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Large Scale Crystallinity in Kinetically Stable Polythiophene-Based Langmuir−Blodgett Films

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Abstract: The first direct observation of large scale molecular level ordering in a complex poly(3-alkylthiophene)-based thin film is reported. The fabrication and characterization of highly ordered thin films made from the regioregular, amphiphilic polythiophene derivative poly(3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene) (PTHPUDT) are described. PTHPUDT affords kinetically stable, high optical quality films deposited layer-by-layer using the Langmuir−Blodgett (LB) method. X-ray diffraction studies confirm the deposition of a film with long-range order normal to the surface, characterized by bilayer separations of ~30 Å. The films display in-plane anisotropy, associated with the preferential alignment of the polymer main chain in the dipping direction. Molecular resolution atomic force microscopy shows the presence of highly ordered crystalline domains within the plane, consistent with an ordered array of parallel, closed-packed, polythiophene chains. Polarized optical microscopy confirms the formation of large scale domains that display uniform optical retardation across macroscopic length scales. $FeCl_3$-doped films yield anisotropic conduction behavior, suggesting higher rates of transport perpendicular to the main chain direction. The kinetic stability of these films is distinct from films of other polythiophenes, other deposition methods, and simpler amphiphiles, all of which tend toward their bulk, thermodynamically stable structures. This stability and long-range order are attributed to the amphiphilic nature of the polymer and the dimensional restrictions of the polymer's main chain, which limits the extent of structural defect-based reorganization, and the limited number of local structures of the alkyl chains. The degree and nature of the ordering in these semicrystalline films make them an ideal model system in which to elucidate the connection between morphology and physical property in complex π-conjugated polymers.

Introduction

The ability to control the morphologies of complex π-conjugated polymers represents a significant challenge in materials chemistry. With the recognition that the attractive aspects of polymer processability and polymer electronic structure could be combined advantageously in applications ranging from optoelectronics to organic light emitting diodes (OLEDs), field effect transistors (FETs), and organic photovoltaic devices has come the desire to optimize their electronic and photonic characteristics.[1] It is now generally accepted that the physical properties of these conducting polymers are greatly affected by their structure, orientation, and local environments.[2−4] A great deal of effort has been spent in trying to improve and control the crystallinity of these polymer systems with the promise of charge conduction efficiencies that rival their inorganic counterparts. However, in most cases, the direct connection between polymer morphology and physical property that would be expected from large scale polymer crystallinity is precluded by a large distribution of polymer morphologies. Even in systems containing significant degrees of crystallinity, a large distribution of sizes and orientations of the crystalline domains, as well as the complex nature of the regions separating them, prevent such a direct correlation. Here, we describe the first direct observation of large scale molecular level crystallinity in a thin film fabricated from a complex polythiophene polymer.

Previous efforts to affect the structure of conjugated polymer systems have included synthetic strategies to convey regiochemical control, producing regioregular (RR) polymers with near perfect *head-to-tail* couplings of monomer units. These materials are able to pack with a higher degree of crystallinity in the solid state than their regioirregular analogs, giving rise to smaller band gaps and higher carrier mobilities.[2,5−10] Kim and Swager[11] have used mechanical forces to induce reversible conformational changes in designed surfactant Langmuir films

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and linked the intrinsic optical response of the conjugated polymer to chain conformation. Reitzel et al. have described conjugated polymer self-assembly at the air water interface. Films of amphiphilic, *bithiophene*-based, regioregular polymers have been shown to form ordered polycrystalline domains, distinct from the dramatically lower degree of crystallinity evidenced in less regioregularly coupled polymers.[12] These films are characterized by crystalline domains of the polymer backbone of order 40 Å, with the polymer backbones separated by the softer, crystallographically disordered, alkyl chains.

One interesting example of a πCP with attractive properties is poly(3-(11-(2-tetrahydropyranyloxy)undecyl)thiophene) (PTHPUDT), which demonstrates the ability to be patterned in response to photoacid generation.[13] This material is both RR and amphiphilic, and thus, an excellent candidate to try to unravel the connection between polymer conformation and physical property using both synthetic and mechanical techniques to impart order. We have previously described some of the properties of these PTHPUDT-based LB films which indicate that they are highly ordered and anisotropic in the film plane.[14,15] Here, we demonstrate that it is possible to tailor the degree of molecular order in these films through the intermolecular interactions within the film, as well as from those forces inherent to the interface and from those under external (mechanical) control of the Langmuir–Blodgett (LB) trough, to afford crystalline packing of the polymer. We have examined the detailed structural properties of the polymer films via optical microscopy, X-ray diffraction (XRD), and molecular resolution atomic force microscopy (AFM). The resulting films show large scale crystallinity at the molecular level and represent a valuable model system in which to investigate πCP electronic properties, where large scale morphological inhomogeneity is limited.

Experimental Section

The synthesis of PTHPUDT has been discussed in detail previously.[13] PTHPUDT was synthesized from its corresponding brominated monomer using the Grignard cross coupling reaction according to the general method described by McCullough et al.[16] This polymer is RR, possessing >95% *head-to-tail* coupling, as determined by NMR spectroscopy. The weight average molecular weight is 22 100 Da with a polydispersity (PDI) of 1.56.

Polymer solutions of the amphiphilic molecules were prepared by dissolving 5 mg of polymer in 5 mL of spectroscopic grade chloroform ($CHCl_3$). LB films were made by adding 75 μL of polymer solution drop-by-drop, evenly across a fresh and clean Milli-pore water subphase (18.2 MΩ-cm resistivity) in a computer-controlled, Nima 600 series LB trough with a Wilhelmy plate pressure sensor. The solvent was allowed to evaporate for 5 min prior to film compression at a rate of 10 cm^2/min. Surface pressure–area isotherms were used to infer the structural transitions of the polymer. Polymer films were deposited onto hydrophobic substrates.

Substrates were made hydrophobic via the LB deposition of one monolayer of arachidic acid from a 1×10^{-4} M $Cd(NO_3)_2{\bullet}4H_2O$ subphase onto clean glass substrates (or freshly cleaved mica) at a surface pressure of 35 mN/m. Prior to deposition, the glass substrates were thoroughly cleaned by immersion into a fresh “piranha bath” consisting of a 3:1 volume ratio of 95% sulphuric acid and 30% hydrogen peroxide followed by repeated washing with Millipore water.

The Langmuir film was held for 5 min at the target pressure before dipping was commenced. The polymer film was then transferred onto the hydrophobic substrate under pressure control at a surface pressure of 17.5 mN/m. The films were deposited at a dipping rate of 10 mm/min using the vertical dipping mechanism of the trough. Y-type films with a *head-to-head* and *tail-to-tail* repeating architecture were deposited onto the substrates. The efficiency of polymer transfer onto the substrate was inferred by their transfer ratios which were typically 1.0 ± 0.1.

Mono- and multilayer films fabricated at variable temperatures employed a RM6 Lauda recirculating water bath attached to the trough to control the temperature of the water subphase. UV–visible absorption spectra of the resulting films were obtained from a Cary 3E (Varian) spectrophotometer. Polarized light microscopy images were acquired using an Olympus BX60 microscope with crossed polarizers. Low angle XRD experiments were carried out using a RAPID (Rigaku) X-ray diffractometer with a copper target ($\lambda_{K\alpha} = 1.542$ Å) and an image plate detector. Intermolecular distances and van der Waals radii calculations from space-filling models were performed with the program Molecular Modeling Basic Revision 2.38 published by ChemSW Software Inc. Optical second harmonic generation studies have been described in detail elsewhere.[14,17] Briefly, a small portion of the regeneratively amplified output (Positive Light, Spitfire) of a ti:sapphire oscillator (Spectra-Physics, Tsunami) pumped by a cw Nd:YVO_4 laser (Coherent, Verdi V-6) is directed toward a film of PTHPUDT in an external reflection geometry. The polarized second harmonic response of the film resulting from s- and p-polarized fundamental excitation, is recorded as a function of the film’s azimuthal rotation angle. AFM studies were carried out using a Thermomicroscopes Explorer scanning probe microscope system with an 8 μm Z-linearized dry scanner and a 2 μm tube scanner. AFM measurements were taken to assess the overall quality of the films, to determine film thickness and to obtain molecular resolution contact mode images in order to investigate film crystallinity. A NanoManipulator DP-100(3rdTech) was used in conjunction with the AFM to ensure that the contact mode scanning conditions did not damage or remove the LB film and to investigate the conditions necessary for sample removal.

Results and Discussion

Langmuir–Blodgett Isotherms. Langmuir films of PTHPUDT were formed at the air–water interface of the LB trough by the addition of a 1.0 mg/mL solution of PTHPUDT in $CHCl_3$. The resulting surface pressure–area isotherms (Figure 1) were reproducible and subject to only subtle changes with temperature. The isotherm shows an initial increase in surface pressure at a molecular area (here considered as an area per repeat unit of the polymer) corresponding to ~20 Å^2. The surface pressure rises at a moderate rate with decreasing area until a surface pressure of 30 mN/m is attained, at which point, the rate of increase in surface pressure with barrier compression decreases dramatically. This plateau region of the isotherm continues until a surface pressure ~42 mN/m is reached. Further barrier compression leads to a much faster rate of surface pressure increase until evidence of film collapse appears beyond surface pressures >45 mN/m.

Analysis of the first increase in surface pressure shows that the area per repeat unit when extrapolated to zero pressure corresponds to ~22 Å^2, consistent with the thiophene plane parallel to the water surface with hydrophilic THP moieties

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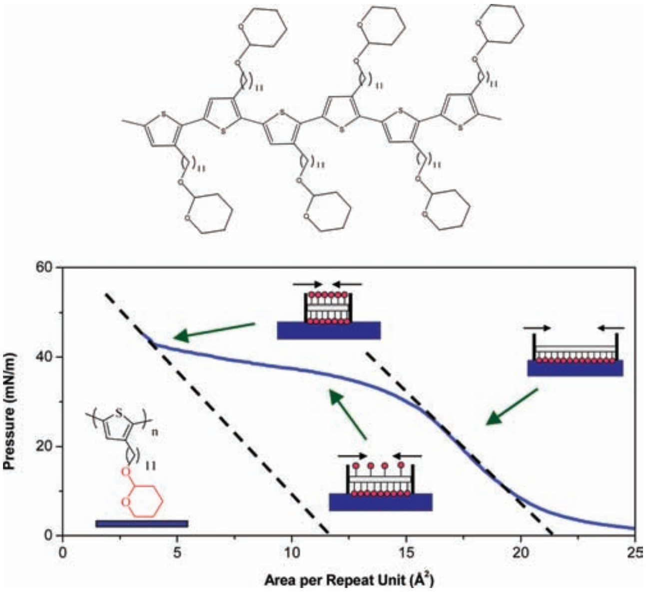

Figure 1. (Top) Molecular structure of regioregular PTHPUDT. (Bottom) Surface pressure vs area isotherm for PTHPUDT (blue line) obtained at 23 °C. (Insets) Orientation of the polymer under investigation at three different surface pressures indicated by the arrows. Dashed lines indicate the extrapolated area per repeat unit for the face-on (~22 Å^2) and edge-on (~11.5 Å^2) PTHPUDT orientations.

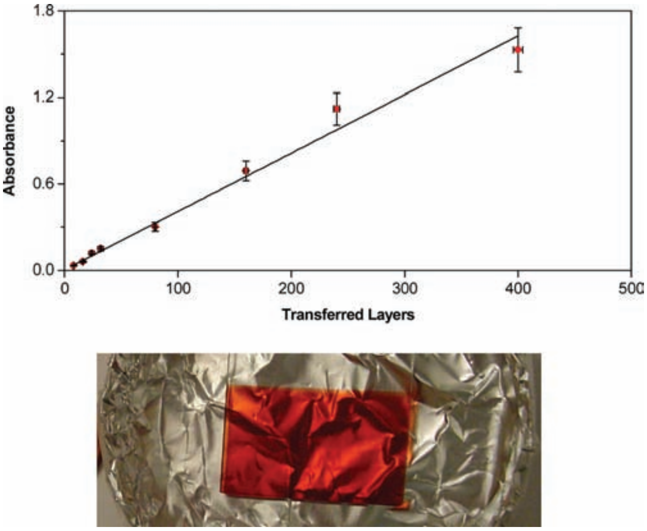

Figure 2. (Top) PTHPUDT film absorbance vs number of transferred layers. (Bottom) Image of a 100-layer film of PTHPUDT deposited onto a hydrophobic glass microscope slide. The slide is sitting in an aluminum foil-covered container.

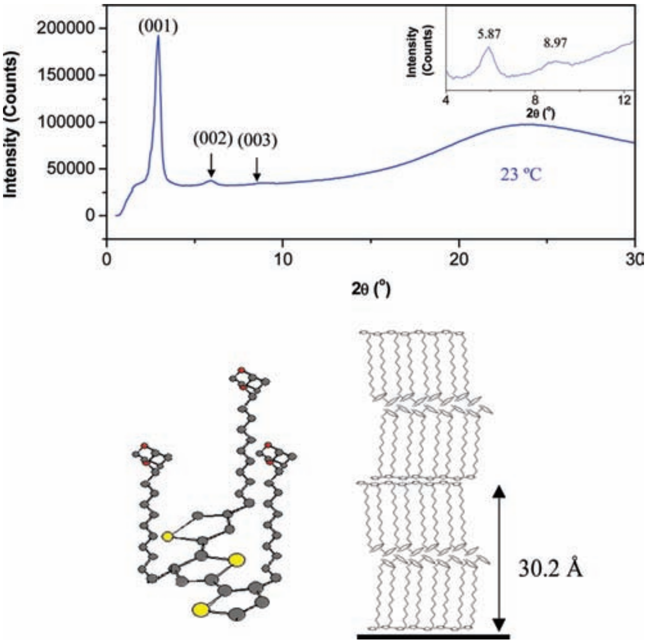

Figure 3. (Top) XRD pattern from a 100-layer LB film of PTHPUDT. The inset shows a magnified image of the (002) and (003) diffraction peaks. (Bottom) Architecture of a Y-type LB film of PTHPUDT on a hydrophobic substrate.

anchored into the water subphase with freedom to rotate. Analysis of the second rise in surface pressure shows an area per repeat unit of ~11.5 Å^2 when extrapolated to zero pressure, roughly half of that corresponding to the first increase and consistent with a polymer geometry that undergoes a transition from an orientation where the thiophene backbone lies face-on to the water surface to one in which the plane of the polymer backbone lies perpendicular (edge-on) to the water surface with every second THP group anchored into the subphase. Indeed, as others have reported, variations of angle between the thiophene ring plane and the water surface are responsible for variations in the area per repeat unit of this magnitude.[18] Attempts to deposit mono- and multilayer films at a surface pressure of ~42 mN/m were unsuccessful, consistent with such an end-on conformation in which the monolayers lose their amphiphilic nature.

Deposition. Attempts to transfer monolayers onto hydrophilic substrates met with limited success. Deposition (transfer) ratios for multilayer films showed inconsistent transfer. Leclerc et al.[19] reported similar findings on poly(3-alkylthiophene) (P3AT) derivatives with a perfluorinated group attached directly to the thiophene ring. The ineffective deposition was explained in terms of the strong hydrophobic nature of the material, which caused the polymer to peel from the substrate upon immersion into the water subphase.

In contrast, PTHPUDT was readily transferred via the vertical dipping mechanism of the trough onto hydrophobic substrates at surface pressures of 17.5 mN/m. Deposition was monitored by noting the advancing and receding water contact angles as the substrate passed through the monolayer-covered water surface and by the creation of a reddish film on the previously clear substrate. Multilayer fabrication of PTHPUDT was characterized by transfer ratios of 1.0 ± 0.1. Confirmation of layer-by-layer deposition was obtained by monitoring the optical absorbance of films of various thicknesses. The maximum absorbance of each film as a function of the number of transferred layers shows a linear correlation (Figure 2), consistent with the near unity transfer ratios observed for both the up- and down-strokes. The resulting film is of high optical-quality.

X-Ray Diffraction. The results of X-ray analysis of a 100-layer LB film of PTHPUDT deposited on a hydrophobic glass substrate are shown in Figure 3. The XRD pattern shows three peaks appearing at 2.93, 5.87, and 8.97° and are assigned to the first-, second-, and third-order peaks of the repeating interlayer spacing. Assuming an *all trans*, fully extended side

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chain with adjacent thiophenes possessing coplanar conformations, the theoretical interlayer spacing of PTHPUDT is computed to be 42 Å.[13] This is considerably larger than the observed experimental interlayer spacing of ~30 Å. Interdigitation of the THP containing side chains would be unexpected due to the 5.1 Å diameter of the THP moiety. Rather, the interlayer *d*-spacing in the LB film is more likely a reflection of the bilayer repeat distance and is consistent with the interlayer spacing obtained from ball-and-stick models where each thiophene unit has its THP containing side chain oriented in the same direction, while the thiophene backbone remains planar and parallel to the substrate (Figure 3).

Previous work on RR, amphiphilic PTs has shown *edge-on* conformation of the thiophene chains with respect to the surface. However, these studies have focused on bithiophene-based polymers with a hydrophilic and hydrophobic pendant group on each subunit.[12] Under these circumstances, it is not surprising that films such as these would yield edge-on architectures. Edge-on architectures in the case of PTHPUDT, however, would provide hydrophilic THP moieties oriented both toward and away from the water surface. Such an orientation of the polymer chain would tend to preclude deposition in the "*head-to-head* and *tail-to-tail*" fashion, which produces the Y-type LB film structure observed here.

Molecular-Resolution Atomic Force Microscopy. Freshly cleaved mica was employed as the substrate for AFM studies. It was also used as a standard to check the force constant of the cantilever, the condition of the silicon nitride tip, as well as to calibrate the operating condition of the AFM and to determine the resolution capabilities of the instrument (see Supporting Information). Mica is known to be hexagonal and to possess a lattice spacing of 5.2 Å.[20] The molecular resolution image of mica and its 2D FFT display a hexagonally packed arrangement with an experimentally determined lattice spacing of 5.31 ± 0.18 Å, consistent with previously published values.

As described, deposition of the PTHPUDT film onto hydrophobic substrates afforded high quality film transfer. Prior to deposition of PTHPUDT, the substrate was rendered hydrophobic by the deposition of eleven monolayers of cadmium arachidate (CdA). This 11-layer buffer film was selected based upon earlier studies of CdA, in which Viswanathan et al.[21] have shown the strained layer van der Waals epitaxial growth of CdA, and its tendency toward the bulk packing (thermodynamic) limit with the deposition of multiple bilayers. Under the same contact mode AFM scanning conditions used to obtain molecular resolution images of the mica surface, images of the 11-layer cadmium arachidate film yielded high quality molecular resolution images and an experimentally determined centered rectangular lattice spacing of 4.83 Å × 7.67 Å, consistent with previously published values.[22]

To determine the conditions necessary to modify the sample and to verify that the conditions employed here would not perturb the film, a NanoManipulator visualization system (3rdTech) for scanning probe microscopy was used in conjunction with a diamond-coated tip to examine the 11-layer cadmium arachidate film. Scanning small areas under different tip sample interaction (set point) conditions followed by viewing large area images under mild imaging conditions enabled us to establish the threshold conditions for sample damage. Sample removal required a diamond-coated tip and severe force-sample interactions. Under the circumstances employed to investigate the CdA and PTHPUDT films described in this manuscript, no evidence of sample modification was detected.

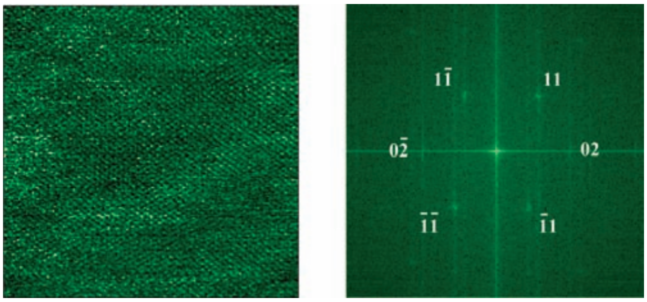

Figure 4. (Left) Unprocessed AFM contact mode internal sensor image (300 Å × 300 Å) of a 20-layer-thick film of PTHPUDT, LB-deposited onto a freshly cleaved sheet of mica, onto which 11 layers of cadmium arachidate had been deposited. (Right) Corresponding 2D FFT indicating a two-dimensional oblique (parallelogramic) unit cell. The diffraction spots appearing in the FFT are labeled with their two-dimensional unit cell directions.

AFM studies were subsequently conducted on 20-layer-thick films of PTHPUDT, deposited onto 11-layer, hydrophobic, buffer films of CdA. Figures 4 and 5 display the unprocessed AFM images of the polymer film. Figure 4 displays the 300 × 300 Å image of the PTHPUDT film and its two-dimensional FFT image. The image shows clearly the texture and repeat structure associated with in-plane ordering of the PTHPUDT polymer film. The corresponding 2D FFT data indicate a parallelogrammic (oblique) unit cell arrangement. The diffraction spots are labeled by the appropriate 2D reciprocal lattice directions.[23] Clearly visible in the FFT image are the horizontal offset of the $1\bar{1}$ and $\bar{1}\bar{1}$ spots and the same offset of the 11 and $\bar{1}1$ spots, behavior consistent with a 2D oblique lattice.

Figure 5a shows the 100 Å × 100 Å unprocessed image of the PTHPUDT LB film. Again, the signatures of crystalline packing of the film are evident. Shown in Figure 5b is a one-dimensional cross section taken along the [01] lattice direction of the two-dimensional self-correlation function. The cross section indicates a high degree of positional order over the dimension of the image. Figure 5c shows the oblique lattice in real space overlaid on an appropriately scaled model of segments of the thiophene main chains. Molecular modeling methods were employed to describe the thiophene main chain dimensions and next-nearest-neighbor distances between polymer chains. As Figure 5c demonstrates, there exists a strong correspondence between the observed oblique lattice structure and the distance between the 3-substituted positions of adjacent thiophene rings, consistent with an ordered array of parallel close packed polythiophene chains. Figure 5d shows the oblique lattice in real space with the experimentally determined dimensions labeled (filled circles). The lattice dimensions were determined by averaging the dimensions obtained from 5 independent images, three of which were 300 × 300 Å images and two 100 × 100 Å images. The unit cell contains two repeat units, and the area per repeat unit corresponds to one-half of the area of the parallelogram. The area per repeat unit derived from the AFM images corresponds

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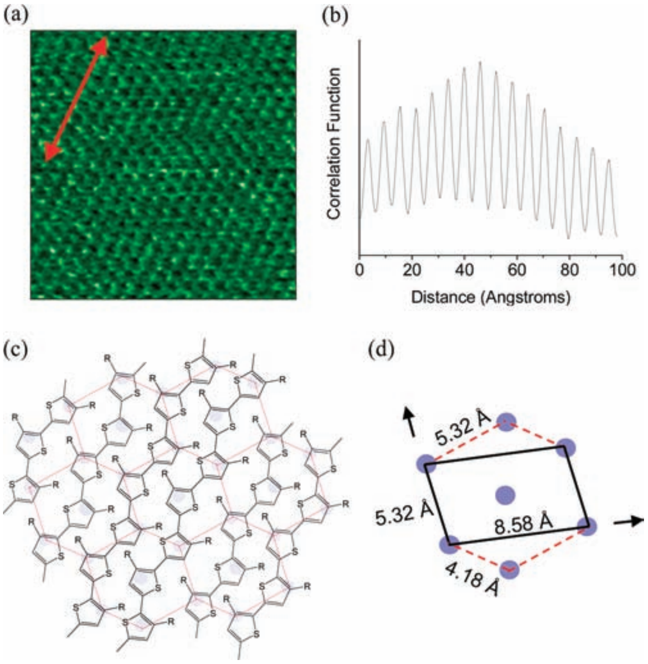

Figure 5. (a) A 100 Å × 100 Å internal sensor image of the 20-layer PTHPUDT LB film. The double ended red arrow indicates the LB dipping direction which has been correlated with the direction of the polymer main chain. (b) Cross section of the corresponding two-dimensional self-correlation function along the [01] lattice direction indicating a high degree of positional order. (c) Array of parallel, close-packed chains of 3-substituted polythiophenes with an interchain distance of 4.18 Å. A repeat representation of the oblique unit cell extracted from the AFM images (red lines) is overlaid on the array of polythiophene chains. The unit cell dimensions are consistent with the separation between 3-substituted positions on adjacent thiophene units of the same chain (5.32 Å) and the distance between 3-substituted positions on adjacent chains (4.18 Å). (d) Oblique unit cell of PTHPUDT extracted from the AFM images. Unit cell dimensions are the averaged cell parameters obtained from three 300 Å × 300 Å and two 100 Å × 100 Å images.

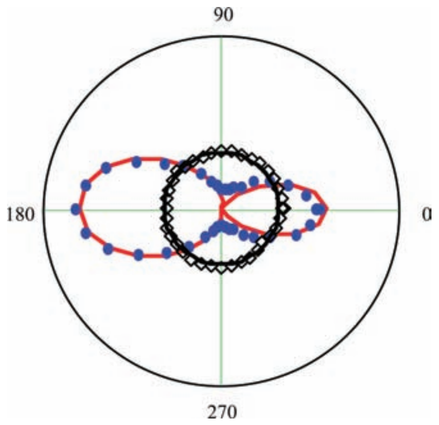

Figure 6. Polar plot of the optical second harmonic generation response detected at 400 nm with incident fundamental light at 800 nm obtained as a function of azimuthal rotation angle for a 100 layer thick LB-deposited film of PTHPUDT (blue circles) and a spin-cast film of malachite green (MG) (black diamonds). The response from the PTHPUDT film is obtained in a p-polarized input/p-polarized output configuration. The MG response was obtained in an s-polarized input/p-polarized output configuration. The solid lines are fits to the experimental data (ref 14) and show the anisotropic distribution of polythiophene chains in the plane of the PTHPUDT film, in contrast to the isotropic distribution of MG molecules in the plane of the MG film. The LB dipping direction of the PTHPUDT film is defined by the horizontal axis in the polar plot.

to ~24 Å^2, in good agreement with the critical area obtained from the LB isotherm data (~22 Å^2/repeat unit). It should be recognized that the area per repeat unit obtained from the Langmuir isotherm corresponds to a situation in which the hydrophilic THP groups of the polymer are interacting directly with the water subphase, while that obtained from AFM reflect film dimensions following transfer to a solid support.

By dividing the weight-averaged molecular weight of the polymer by the molecular weight of the repeat unit, the number of thiophene subunits in a typical thiophene chain can be approximated. For our sample of PTHPUDT, there are, on average, ~65 thiophene subunits in a polymer chain. In this and previous studies of the LB deposition of polythiophenes, two-dimensional film anisotropy has been observed.[14,24] The p-polarized second harmonic intensity generated by p-polarized incident radiation at 800 nm, from a PTHPUDT film as the film and substrate are rotated about their azimuth is displayed in Figure 6. Also shown in the figure is the corresponding response from a spin-cast chromophore distributed isotropically about the azimuth. The observed anisotropy indicates a preferential ordering of the polymer's transition dipole direction, known to lie along the main chain axis. This anisotropy has been linked with a preferential deposition of the polymer main chain in an orientation parallel to the LB dipping direction, an effect thought to be driven by hydrodynamic forces.[14,24] Since the orientation of the substrate was known and controlled when examined via AFM, such orientational anisotropy makes it possible to deduce the direction of the thiophene backbones in the AFM contact mode images. The dipping direction (i.e., the polythiophene main chain direction) is labeled by a double-headed arrow in Figure 5a and is consistent with the alignment of chains displayed in Figure 5c.

LB films deposited onto mica substrates have been shown to possess bulk-like properties including long-range positional order and grain boundaries. Crystallinity in LB deposited films has previously been observed by molecular resolution AFM in films formed from the salts of fatty acid molecules.[21–23,25,26] Specifically, these films are formed from straight chain fatty acids deposited from subphases containing divalent metal cations such as barium, calcium, magnesium, and cadmium. It is now well established that these films are able to possess domains containing different lattice structures and to show transformations between them.[22] This conversion is thought to proceed via local positional exchange of the amphiphilic anionic chains and the metal ions in the film. It has also been demonstrated that LB film deposition proceeds via an epitaxial-type growth mechanism, proceeding ultimately to the bulk, thermodynamically stable structure as film thickness is increased.[21] These observations suggest that the long-range positional and structural order within these films depend on several factors including the pH of the subphase, and on the nature of the particular metal ion present, which determines the strength of both intralayer, and interlayer interactions.

The observed lattice spacing in these fatty acid salt films, result from a combination of the attractive forces from the packing of the alkyl chains and from the repulsion of the head groups, which accounts for the observed distances between terminal methyl groups. In some cases, this competition between the packing of the head and tail groups in fatty acids necessitates

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structural defects to ensure the proper long-range ordering.[26] These defects can range from pinholes to large-scale reorganizations of the layers. These defects are possible, in part, because of the ability of individual molecules to locally exchange positions and orientations with one another.

The nature of the packing in the PTHPUDT polymer films described here is distinct from that found in the fatty acid salt-based films. The order normal to the substrate is dictated by the amphiphilic nature of the polymer and the layer-by-layer deposition of the LB technique. The structural constraints of the polymer result in stable films in which the alkyl chains terminated by the hydrophilic THP moieties interact with those in adjacent layers. This kinetically stable packing motif is distinct from the crystallinity observed in annealed PTHPUDT films deposited by conventional spin and drop cast methods, in which the thiophene's pendant alkyl chains are oriented on either side of the polymer main chain in a planar structure.[13] Evidently, the PTHPUDT LB films described here are formed in a kinetically stable structure, distinct from the LB films of fatty acid salts which tend to their bulk, thermodynamically stable soap structures even within a few monolayers from their underlying substrates, and from annealed spin and drop cast thiophene films.

Likewise, the in-plane ordering of these films is distinct from the behavior observed from films of fatty acid salt composition. While the distance between nearest neighbors in both cases represents a balance between the stabilizing van der Waals influences of the alkyl chains and repulsion of the hydrophilic head groups, in the case of PTHPUDT, the observed in-plane order also reflects the packing of the thiophene subunits in adjacent polymer chains. As the thiophene subunits of a given polymer chain are directly connected to each other via covalent bonds, they lack the freedom of individual amphiphiles and are unable to undergo positional exchange. In this polymer system, the in-plane order and domain size observed in the AFM images result from the dimensional restrictions of the polymer's main chain, limiting lattice expansion and the extent of structural defect-based reorganization. Thus, while structural incompatibility between local packing and long-range order can necessitate structural defects and reorganization to ensure proper global ordering in some cases, the additional connectivity of amphiphiles via the polymer's main chain and the restrictions that this connectivity imposes in the case of PTHPUDT, limit the number of different arrangements and local structures of the alkyl chains, and in turn, may limit the number of possible domain types. Nevertheless, based upon the correspondence of the observed lattice dimensions and the packing predicted by molecular modeling, it would appear that the in-plane order in the case of PTHPUDT is dictated primarily by the packing of the thiophene subunits and necessarily, their pendant alkyl chains.

Previous attempts to obtain molecular resolution AFM images of crystallinity in amphiphilic polythiophene films[12] were unsuccessful and attributed to the disordered state of the polymer's alkyl chains. Grazing angle incidence X-ray diffraction methods were used to approximate the size of in-plane microscopic domains of the *edge-on* bithiophenes, and were estimated to be on the order of ∼40 Å.

The contact mode AFM images of PTHPUDT indicate that the terminal thiophene groups are ordered and form larger scale crystalline domains. While it is difficult to estimate the size of these domains on the basis of finite dimension atomic force microscopy images, images obtained at many points over the film surface showed similar signatures of crystalline packing. One method typically employed to characterize domain structure and film uniformity employs polarized light microscopy. Images obtained under various magnifications indicate that these films exhibit uniform optical retardation across the entire field of view. Imaging of other areas of the film under the same magnification conditions, or at lower magnification, shows uniform optical retardation over the entire film surface. This discussion is not to imply that the PTHPUDT films are perfectly crystalline and free of defects. Rather, it seems unreasonable that a film of long polymer chains could adopt such a structure. However, an assembly of long parallel chains in a "hardwood floor" motif may present a somewhat forgiving structure with respect to packing defects. The high degree of regioregularity of the polymer combined with its large aspect ratio would limit the number of possible domain orientations and may concentrate defects at the termina of the polymer chains. Adjacent chains in the vicinity of such a defect may have sufficient flexibility to limit defect growth and provide a simple mechanism to heal the defects, and maintain long-range film order (Figure 7).

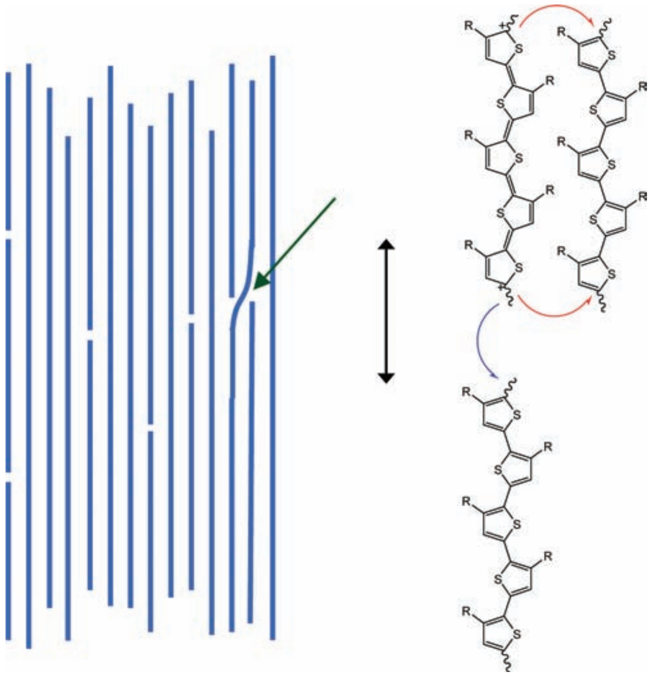

Figure 7. (Left) Cartoon arrangement of parallel, close-packed chains of PTHPUDT in a "hardwood floor" motif. Packing defects (green arrow) in such a structure may be concentrated at the termina of PTHPUDT main chains. Chain flexibility and the high aspect ratios associated with the polymer could provide a simple mechanism for healing these defects and maintaining long-range order. (Right) Segments of parallel 3-substituted polythiophene chains indicating charge transport along the main chain direction at a chain terminus (blue arrow) and interchain transport between parallel chains (red arrows). Conductivity measurements indicate transport perpendicular to the main chain is ∼20% greater than transport in the direction of the main chain. The double ended arrow indicates the LB dipping direction.

Preliminary investigations of the film conductivity via 4-point probe methods indicate that there is in-plane anisotropy in the film conductivity. Measurements show that the conductivity of $FeCl_3$-doped PTHPUDT LB films display conductivities in the direction parallel to the polymer main chain direction that are roughly 20% smaller than those observed for directions perpendicular to it (Figure 7). While these observations are preliminary, the effects of $FeCl_3$ doping on the film structure have yet to be characterized, and the 4-point probe method provides conductivity measurements that cannot readily be separated into purely parallel and perpendicular components, the measurements suggest that the conductivity along the polymer main chain is distinct and smaller than the interchain conductivity measured perpendicular to it. Further investigations of the effects of doping, conductivity, and charge transport mechanisms in these films are necessary to provide a more thorough understanding of the intrachain and interchain contributions to the film conductivity.

Conclusions

We have employed Langmuir–Blodgett methods to deposit multilayer films of a regioregular, amphiphilic polythiophene-based polymer and investigated their degree of order. The films undergo layer-by-layer deposition to form a kinetically stable structure in which bilayers defined by close contacts between the hydrophobic polythiophene chains and hydrophilic THP groups of adjacent layers lead to a face-on polymer morphology with bilayer separations of ∼30 Å.

We have examined the in-plane order of 20-layer PTHPUDT LB films via AFM and obtained molecular resolution images. The images display an oblique (parallelogrammic) two-dimensional lattice structure, consistent with the ordered packing of the thiophene subunits in adjacent, parallel, polymer chains. The films show a high degree of positional correlation over large length scales. PTHPUDT films are also of high optical-quality. Polarized light microscopy indicates uniform optical retardation over the entire film, consistent with a film characterized by significant long-range order. This order results, in part, from the dimensionality of the polymer main chain which limits the number of different arrangements and local structures of the polymer's pendant alkyl chains, as well as the degree of regioregularity and large aspect ratio of the polymer main chain which may mitigate defect density and growth.

The kinetically stable PTHPUDT LB films reported here show behavior that is distinct from that of polythiophenes deposited by conventional solution casting methods which yield thermodynamically stable structures, and from that of fatty acid salt-based LB films, whose surface lattices of sequentially thicker films evolves toward the bulk thermodynamically stable structure while retaining the substrate alignment. This behavior has been attributed to the weak intralayer interactions characteristic of these amphiphiles. In contrast, films characterized by strong intralayer interactions but weak, non specific interlayer interactions display van der Waals epitaxy[21] in which the adsorbed layer is oriented with respect to the underlying substrate and has long-range positional and orientational order while maintaining its bulk lattice constants. The PTHPUDT films described here represent an interesting middle ground in which the adsorbed layer is characterized by strong intralayer interactions in one dimension and weak intralayer interactions in the other. While it has been noted that film orientation in these circumstances may be dictated by external hydrodynamic forces, these effects are currently under further investigation. The resulting film orientation gives rise to differential film conductivity parallel and perpendicular to the polymer's main chain direction. Beyond the implications of providing a greater understanding of the charge transport properties in highly ordered conjugated polymers for device applications, the films described here represent an ideal model system in which to investigate the direct connection between polymer morphology and physical property more generally, including the prospects for investigating thermal chemistry, photochemistry, and solvation properties in highly ordered environments.

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Supporting Information Available: Full experimental details and molecular resolution atomic force microscopy calibration data and analysis methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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