

DOI: 10.1002/adma.200602651

High Carrier Mobility Polythiophene Thin Films: Structure Determination by Experiment and Theory**

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Polymer semiconductors such as the alkyl-substituted polythiophenes have long been recognized as solution-processable materials for device applications, but the carrier mobility of polymers is typically lower than insoluble organic small molecules such as pentacene. The lower mobility is generally attributed to less structural order; specifically the smaller and less-aligned crystals typical of polymer semiconductors should exhibit reduced intermolecular π -orbital overlap at grain boundaries.^[1] The more disordered nature of polymer semiconductors has made it challenging to determine the details of their thin-film crystal structure.^[2] Structure measurements are further complicated by the small volume of the thin, 20–50 nm, polymer semiconductor films used in organic field effect transistors.^[3,4] X-ray diffraction (XRD) usually provides only primary index peaks, most often the $\langle h00 \rangle$ and $\langle 010 \rangle$ series, that reveal crystal structure, orientation, and size, but exact atomic positions can rarely be determined. Moreover, it is clear that the thin-film crystal structure can differ from single crystal or powder structure.^[5]

Alkyl-substituted polythiophenes feature a backbone of sequentially bonded thiophene rings with linear alkane chains attached to their sides. In thin films, they self-assemble into lamellae; comparing typical unit-cell dimensions to molecular dimensions leads to a generally accepted layer-packing motif where planar backbones π stack in aromatic lamellae vertically segregated from lamellae of side chains.^[6–8] Two critical

but poorly characterized aspects of the crystal structure are the conjugated-plane tilt and the alkane side-chain configuration. In the lamellar motif, the conjugated planes must be roughly vertical (orthogonal to the lamella) so that they can π stack face-to-face within a quasi two-dimensional sheet. However, a variety of conjugated-plane tilts and a rich possibility of side-chain configurations—distinguished by varying tilt and degree of interdigitation—are consistent with this layer-packing motif and available diffraction data. Greater structural detail will support the development of new synthetic and processing strategies, because carrier transport critically depends on the intermolecular overlap of carrier band orbitals, which is controlled by the conjugated-plane spacing and tilt.

Recently, poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophenes) (pBTTT) have been reported to exhibit hole mobility comparable to that of many small molecule semiconductors^[9] and rivaling what is achievable in amorphous silicon. The structure of this material is indicated schematically in the insets of Figures 1 and 3a. The high performance of the pBTTTs was attributed to greater structural order than typical polymer semiconductors, and XRD indicated large and well-oriented crystals.^[9] Here we exploit this crystallinity to study structural detail within ca. 25 nm thick films of a pBTTT with tetradecyl side chains (pBTTT-C₁₄). From first-principles energy minimization using density functional theory (DFT), we predict that the conjugated planes of pBTTT polymers substantially tilt

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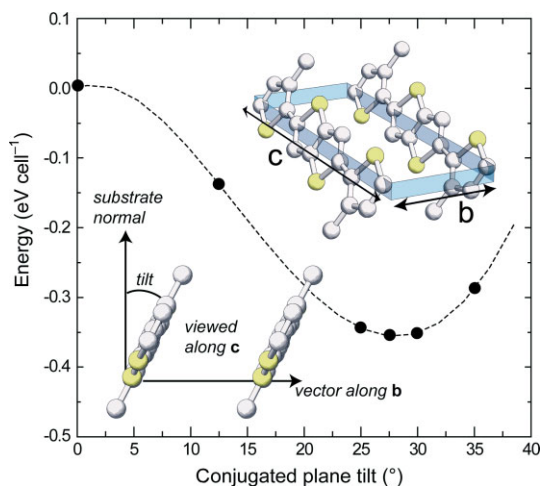


Figure 1. Energy variation with tilt. Insets show the pBTTT-C₁ two-dimensional unit cell and tilt definition.

within their crystalline lamellae. We confirm this prediction experimentally using a combination of polarized photon spectroscopies. Using the same techniques, we also find that the side chains of pBTTT-C₁₄ are tilted so as to require significant interdigitation within the side-chain lamellae.

pBTTT-C₁₄ synthesis using Stille copolymerization^[9] afforded a polymer with a number average molecular mass (M_n) of 28 kDa ($1 \text{ Da} \approx 1.66 \times 10^{-27} \text{ kg}$) and a polydispersity of ca. 2 measured by using gel-permeation chromatography against polystyrene standards. A typical polymer was therefore ca. 40 monomers in length. From differential scanning calorimetry results, pBTTT-C₁₄ is known to exhibit a phase transition to a mesophase at ca. 140 °C.^[9] Here we studied ca. 20 nm thick spin-cast pBTTT-C₁₄ films heated to this mesophase and then cooled to room temperature atop octyl-trichlorosilane-modified silicon oxide. This process increases crystallinity and hole mobility.^[9]

First-principles total energy calculations for two-dimensional sheets of the pBTTT backbone with methyl side groups demonstrated that tilting of the conjugated plane is energetically favorable. These calculations were carried out within the DFT as described elsewhere.^[1,10] The calculations employed first-principles pseudopotentials and a plane-wave basis having a cutoff energy of 40 Ry ($1 \text{ Ry} \approx 2.18 \times 10^{-18} \text{ J}$). A two-dimensional unit cell was employed and the optimum lattice constants in the lamellar plane were determined by energy minimization to be $b = 0.38 \text{ nm}$ and $c = 1.35 \text{ nm}$. The lattice vectors relative to the molecular structure are illustrated in the Figure 1 inset. We considered unit cells where horizontally adjacent backbones had relative translation, but energy minimization indicated that the optimal unit cell is rectangular.

The dependence of the total energy on the tilt of the conjugated plane is shown in Figure 1, where it is seen that the energy has a local maximum for a tilt of 0° and a minimum for a tilt of 27.5°. This prediction was obtained with CH₃ side groups, and it is likely that longer side chains may subtly shift the tilt landscape. The total binding energy of the sheets was obtained by expanding the b lattice constant from its optimum length, 0.38 nm, to a value sufficient to eliminate the interaction between the molecules. This resulted in a binding energy of $0.67 \text{ eV cell}^{-1}$ ($1 \text{ eV} \approx 1.602 \times 10^{-19} \text{ J}$), where each unit cell contained one monomer. The energy reduction arising from tilting the conjugated planes from 0° to 27.5° was $0.35 \text{ eV cell}^{-1}$. Thus, the conjugated-plane tilt strongly contributes to the energetic stability of the crystal structure.

Hole delocalization in the π - π stacking direction plays a crucial role in models of transport in polymers.^[1] It is therefore important to gauge the effect that the packing structure has on the electronic structure. Our calculations showed that the backbone tilt had a significant effect on the electronic structure of pBTTT, for both the electrons and the holes. The calculations indicated that the hole bandwidth in the π - π stacking direction was reduced by 30 % (from 0.72 eV to 0.50 eV) when the backbone was tilted from 0° to 27°. Backbone tilting reduced the corresponding electron band width from 0.96 eV to 0.20 eV, a reduction of 80 %. It is clear that

backbone tilting is an important structural feature that must be included when modeling both the optical and transport properties of pBTTT and similar polymers. Backbone tilting also appears to be a common phenomenon, as our calculations predicted a similar backbone tilt for the widely used polymer regioregular poly(3-hexylthiophene). Calculations performed with a head to tail arrangement of C₆H₁₃ alkyl side chains indicated an optimum conjugated-plane tilt of ca. 23° and an associated energy reduction of $0.31 \text{ eV cell}^{-1}$.

We have experimentally verified the predicted conjugated-plane tilt using a combination of polarized photon spectroscopies. Their interpretation critically depends on the film morphology, which was determined using atomic force microscopy (AFM), as shown in Figure 2. Terraces of ca. 2.2 nm height extended laterally several hundreds of nanometers. The terrace domain size was greater than reported previously for pBTTTs;^[9] the films here were thinner and exhibited greater structural order. The crystalline morphology of pBTTT-C₁₄ is different than that reported for other alkane-substituted polythiophenes. Most AFM microscopy images of polythiophene crystal geometry have revealed rods or needles, where the

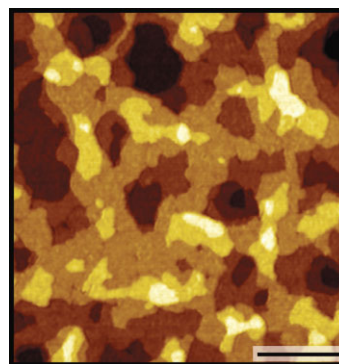


Figure 2. Tapping-mode AFM microscopy image of a 20 nm thick pBTTT-C₁₄ film. Vertical scale is 20 nm; scale bar is 500 nm.

conjugated-plane normal was nominally parallel to the rod long axis; these structures were usually only observed for polythiophenes with M_n less than 10 kDa.^[11–13] The terrace morphology observed in Figure 2 is a clear manifestation of the generally accepted layered-packing motif attributed to larger M_n alkane-substituted polythiophenes.^[8] These layers have not been observed by using AFM before and are typically inferred from XRD.

The flatness and ca. 2.2 nm height of the pBTTT-C₁₄ terraces suggested that the ca. 60 nm long polymer backbones lay within the film plane. The backbone long-axis orientation can be confirmed using spectroscopic ellipsometry (SE).^[14] The dielectric function $\epsilon = \epsilon' + i\epsilon''$ in the visible range was determined from multiple-angle measurements on duplicate films cast on both native oxide and 200 nm oxide substrates, and was adequately represented by a uniaxial model where the imaginary part was oriented within the film plane, as shown in Figure 3a. The imaginary part of ϵ arises from the

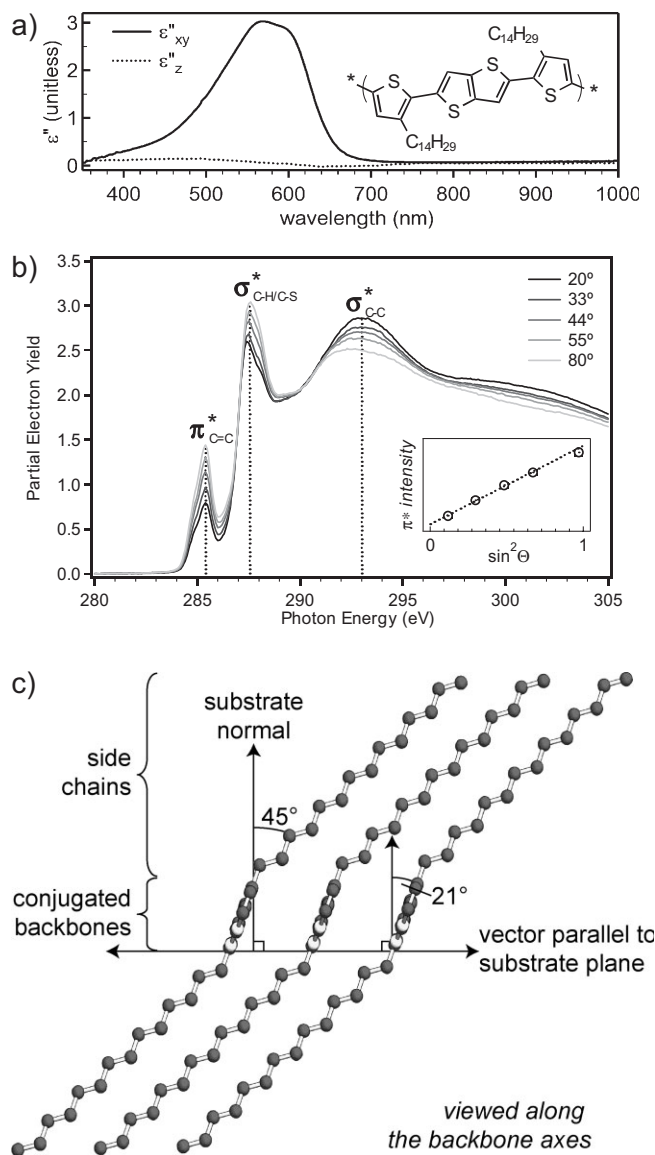


Figure 3. a) Imaginary dielectric functions from spectroscopic ellipsometry. The inset shows a pBTTT-C₁₄ chemical structure. b) Carbon K-edge NEXAFS spectra at five incident angles. The inset shows the fit used to determine tilt. The π^* intensity is of arbitrary units on a linear scale. c) Experimentally determined details of the pBTTT-C₁₄ packing geometry.

first singlet $\pi \rightarrow \pi^*$ transition of pBTTT-C₁₄ that is oriented along the polymer backbone axis. The backbone was therefore strongly oriented within the film plane. The peak absorption in solution occurred near 430 nm, whereas the peak in the thin film ϵ_{xy}'' was red shifted to 570 nm, indicating an increased conjugation length (less torsional disorder along the backbone) because of packing. The peak in ϵ_z'' occurred near 470 nm, suggesting that the out-of-plane absorption was caused by disordered material and not misoriented grains. We can estimate the crystalline fraction of the film, f , from a simple model of ϵ'' .

$$\epsilon'' = (1-f) \begin{pmatrix} \frac{\alpha}{3} & 0 & 0 \\ 0 & \frac{\alpha}{3} & 0 \\ 0 & 0 & \frac{\alpha}{3} \end{pmatrix} + f \begin{pmatrix} \frac{\alpha}{2} & 0 & 0 \\ 0 & \frac{\alpha}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (1)$$

where α is the imaginary part of the dielectric constant along the chain axis for a perfectly ordered (anisotropic in-plane) biaxial crystal, and the ratio of ϵ_z'' to ϵ_{xy}'' . Based on the integral of ϵ'' over the 400–700 nm range, we estimate f to be 93 %, which is consistent with the comprehensive crystallinity inferred from the terracing in AFM.

Conjugated-plane orientation was measured using near edge X-ray absorption fine structure (NEXAFS) spectroscopy at the National Synchrotron Light Source NIST (National Institute of Standards and Technology) beamline U7A. In NEXAFS spectroscopy, tunable and linearly polarized soft X-rays are absorbed into resonant excitations of core $1s$ electrons to unfilled molecular orbitals such as the π^* or σ^* .^[15] The carbon K-edge NEXAFS spectra of a pBTTT-C₁₄ film are shown in Figure 3b. NEXAFS partial electron yield (PEY) mode counts electrons emitted via Auger decay and represents a surface-weighted average that probes up to ca. 7 nm into a free surface. Prominent resonances were the carbon–carbon $1s \rightarrow \pi^*$ at 285.4 eV, the superimposed carbon–hydrogen and carbon–sulfur $1s \rightarrow \sigma^*$ at 287.5 eV, and the carbon–carbon $1s \rightarrow \sigma^*$ at 293 eV. The π^* resonance intensity is proportional to the squared dot product of the incident electric field vector and the spatial distribution of the final state relative to the atomic center of excitation, which is a vector that extends orthogonally from each double bond. If all backbone rings within the polymer are coplanar, as observed in single-crystal structures of model alkyl-substituted oligothiophenes,^[2] then these π^* vectors add to form a single vector normal to the conjugated plane of the backbone. We quantified the tilt of this π^* vector with a dichroic ratio, R , which is the difference between the extrapolated π^* intensities at 90° and 0° incidence, normalized by their sum.^[16] For the elliptical polarization of our beamline, R can vary from 0.7 for a fully edge-on plane to –1.0 for a fully flat plane. For the data presented in Figure 3b, the greatest π^* intensity was observed nearest normal incidence, where the electric-field vector was primarily within the film plane, indicating that the π^* vector was also preferentially oriented within the film plane, and the conjugated plane of the polymer was preferentially edge-on upon the substrate. The fit shown within the Figure 3b inset results in $R = 0.39 \pm 0.01$.

An additional measurement was required to determine whether the top-surface orientation is comprehensive throughout the film. We delaminated the film using a procedure recently employed on films of another alkyl-substituted polythiophene.^[17] In this procedure, a thin sheet of polydimethylsiloxane elastomer was laminated onto the top surface, and then carefully lifted off. The pBTTT-C₁₄ film adhered to and was supported by the elastomer; the exposed interface is

reported not to be disrupted or relaxed by this process.^[17] The supported pBTTT-C₁₄ film with exposed ex situ bottom interface could then be measured in NEXAFS PEY mode, with a similar result of $R=0.39\pm0.02$. The conjugated plane was therefore preferentially edge-on throughout the film thickness, though not as vertical as for some oligothiophenes ($R=0.5\text{--}0.6$)^[18] and pentacene ($R=0.6$).^[16]

Orientations determined by using NEXAFS or other polarized light spectroscopies are not often interpreted as explicit molecular orientations within crystals because they are the azimuthal averages of unknown orientation distributions. For pBTTT-C₁₄ films, however, the AFM microscopy image and SE dielectric function both indicated comprehensive crystallinity of a single type. It is then reasonable to assume a tight and monomodal orientation distribution of the conjugated planes. If we assume a single tilt angle from the surface normal θ with an isotropic azimuthal distribution, we can relate the figure of merit R to the tilt of the normal vector of the conjugated plane by expanding relationships for intensity at 90° and 0° incidence given in [15] and obtain

$$R = \frac{P(1 - 3 \langle \cos^2 \theta \rangle)}{2(1 - \langle \cos^2 \theta \rangle) + P(3 \langle \cos^2 \theta \rangle - 1)} \quad (2)$$

where P is the fractional polarization of the x-ray beam (ca. 0.85). For pBTTT-C₁₄, the normal vector of the conjugated plane tilted (68–70°) away from surface normal for (100–93 %) crystallinity. The conjugated-plane tilt of ca. 21° inferred from the NEXAFS data is in good agreement with that predicted by the DFT energy minimization.

The NEXAFS σ^*_{C-C} resonance reflects the side-chain orientation, but it includes some backbone contribution. The sign of R for σ^*_{C-C} is opposite to that of π^* , establishing that the side chains are closer to the surface normal than the magic angle (54.7°). IR absorption measurements provided additional insight into the side-chain structure; for the mesophase-heated film the methylene group antisymmetric stretch occurred at 2919.8 cm⁻¹, indicating a high degree of trans order.^[19] Assuming the side chains are all-trans, both NEXAFS^[20] and IR dichroism^[21] analyses indicate that they are tilted nominally 45° off normal. This tilt angle, combined with simple consideration of the length of the C₁₄ all-trans chain (ca. 1.8 nm allowing for the Van der Waals radius of the methyl), and the available interplane distance (2.2 nm), requires significant interdigitation of sidechains that belong to vertically adjacent lamellae.

The orientations from SE, NEXAFS, and IR support the illustration of pBTTT-C₁₄ packing detail that is shown in Figure 3c. The backbone axes are within the substrate plane, the conjugated planes are slightly tilted, and the side chains are substantially tilted. The displacement of the side chains from the conjugated plane in Figure 3c is speculative, but consistent with their known tilt. The slight “slip” of face-to-face π stacking exhibited by pBTTT-C₁₄ is also observed in small-molecule semiconductors where packing is redirected from a natu-

rally edge-to-face (herringbone) arrangement by the synthetic addition of large groups to the conjugated-plane edge.^[22,23] It is perhaps not surprising that pBTTT-C₁₄ exhibits this similarity, because unfunctionalized oligothiophenes also exhibit herringbone packing.^[24] Our DFT calculations indicate that tilt of the conjugated planes is a common feature in alkyl-functionalized thiophene polymers. The experimental verification of conjugated-plane tilt, made possible by the highly crystalline pBTTT-C₁₄, supports the validity of the calculations and indicates that π stacking slip is an important structural feature for this class of polymer semiconductors.

Experimental

Materials: The polymer semiconductor pBTTT-C₁₄ was synthesized by using Stille copolymerization as reported previously [25] Films were cast from pBTTT-C₁₄ solutions of 5 mg mL⁻¹ in 1,2-dichlorobenzene at 75 °C. Substrates were the native oxides of <100> silicon cleaned by ozone exposure for 10 min and then exposed to 0.002 M octyltrichlorosilane (Gelest) in anhydrous hexadecane (Aldrich) [26] for 16 h to result in a water contact angle of 105°. Films were spin-cast at 1500 rpm with 100 rpm s⁻¹ acceleration. After casting, films were heated to 180 °C for 10 min and then cooled at ca. 5 °C min⁻¹ to room temperature.

Characterization: AFM was performed on a Digital Instruments Nanoscope IV in tapping mode. NEXAFS spectroscopy was performed at NIST beamline U7A of the National Synchrotron Light Source. Carbon K-edge collection was performed in PEY mode with a grid bias of -50 V. Spectra collected at the five incident angles were normalized with respect to carbon concentration by their intensity at 330 eV. Spectroscopic ellipsometry was collected at three angles from the surface plane (45°, 27.5°, and 10°) with an M-2000 series ellipsometer (J. A. Woollam Co., Inc.) and analyzed using vendor-supplied software. Polarized, transmission Fourier transform IR (FTIR) spectroscopy was performed using a Magna 860 FTIR spectroscope (Thermo Nicolet) on films cast on double-side-polished Si substrates with the sample tilted at Brewster's angle of 16.3° with respect to the incident beam. Polarization was controlled by using a wire-grid polarizer. The data was analyzed following the procedures of Gurau et al. [27].

Received: November 20, 2006

Revised: January 8, 2006

Published online: February 16, 2007

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