Molecular Characterization of Organic Electronic Films


Organic electronics have emerged as a viable competitor to amorphous silicon for the active layer in low-cost electronics. The critical performance of organic electronic materials is closely related to their morphology and molecular packing. Unlike their inorganic counterparts, polymers combine complex repeat unit structure and crystalline disorder. This combination prevents any single technique from being able to uniquely solve the packing arrangement of the molecules. Here, a general methodology for combining multiple, complementary techniques that provide accurate unit cell dimensions and molecular orientation is described. The combination of measurements results in a nearly complete picture of the organic film morphology.

1. Introduction

Organic electronics provide an opportunity for low-cost, large-area electronics in diverse applications such as displays, sensors, solid-state lighting, and photovoltaic cells. [1–3] Polymers and small molecules are soluble in common solvents when properly substituted and can be deposited as an ink through any number of printing technologies. [6,7] Each of the active layers (insulators, conductors, and semiconductors) can be printed in a roll-to-roll fabrication line in an analogous fashion to red, green, and blue inks in a color newspaper production line. These printing technologies provide an opportunity to significantly reduce the cost of electronics manufacturing for applications with low-performance requirements. The charge-carrier mobility in organic electronic materials is orders of magnitude lower than that of the crystalline silicon used in computer microprocessors; however, their performance is adequate for use in applications that include thin-film transistors for driving pixels in displays, processing simple information in radiofrequency identification (RFID) tags, and controlling sensors. Although these applications do not require high performance, improved performance increases the number of potential applications. [8] Therefore, determining the physical properties that limit the performance and methods to improve performance is vital to the expansion of the field.

Unlike the nearly perfect crystals of inorganic semiconductors, the crystals of organic electronic materials are weakly bound by van der Waals forces. The extent of crystalline ordering and the density of crystalline defects vary considerably between small molecules and polymers. Small molecules, due to their consistent size and shape, usually form larger crystals with fewer defects than most polymers. Some small molecules can form millimeter-scale single crystals, while irregularly shaped small molecules can be completely amorphous. [9] Polymers, by definition, are much larger than small molecules and tend to form relatively small crystals with a large population of defects. The large size of the polymer molecules impedes their packing and limits their opportunities for rearrangement. This results in a large configurational entropy effect. Polymers also tend to have a large polydispersity, with molecular lengths often varying by up to a factor of two, which further impedes efficient packing and leads to defects. The typical microstructure for a semicrystalline semiconductor polymer would be nanoscale crystalline domains bounded by highly disordered “amorphous” regions with some molecules bridging neighboring ordered domains. [10] The details of the microstructure are important because the local packing of neighboring molecules determines the intramolecular electronic orbital overlap and the electronic structure of the polymer film, and because the connectivity of the domains determine the paths taken by charge carriers through the film. Additionally, the local packing of the molecules strongly affects larger-scale microstructural parameters such as the domain size and the connectivity between neighboring domains. All of these physical properties combine to determine the key electronic property that affects the performance of thin-film transistors: the charge carrier mobility of the polymer film.

2. Measurements of the Microstructure

There are multiple length scales of interest for the microstructure of organic electronic films. For this review, we will focus on the local-scale packing of neighboring molecules and how
that, in turn, relates to domain structure. We will further focus on a class of polymer semiconductors with rigid backbones and flexible side chains.\textsuperscript{[11,12]} This class of materials presents a unique challenge to the measurement of local packing. The rigid, π-conjugated core gives the molecule its semiconducting properties and a strong intermolecular attractive force. The flexible side chains hinder the intermolecular attraction sufficiently to render the molecules soluble and thus highly processable. The flexible side chains also help direct secondary crystallization, which is crucial to achieving long-range ordering of the molecules. Their flexibility also induces packing disorder in the crystal that limits the observable X-ray diffraction (XRD) to a handful of peaks and adds considerable complexity to the crystalline basis. The combination of the limited number of peaks and the large number of atoms in each repeat unit prevents XRD from directly solving the details of the molecular packing. Linear spectroscopies, on the other hand, can measure the average orientation of the constituents of the molecule. The limitation of these techniques is that no information on local packing is obtained and the average does not contain information on the distribution of orientations. The orientation distribution could be narrow, broad, or even a mixture of multiple narrow distributions and give the same average orientation. We overcome the limitations of individual techniques by combining complementary techniques and allowing several key assumptions to be made that simplify the interpretation of the measurements.\textsuperscript{[13]} In the subsequent sections we describe the important details of each of the measurement techniques that we use in our analysis. We then show two case studies where the results of each complementary technique can be combined to obtain detailed structural information that is not otherwise attainable.

We restrict the discussion primarily to two semiconducting polymers: poly-3-hexylthiophene (P3HT)\textsuperscript{[11]} and poly(2,5-bis(3-alkylthiophen-2-yl) thieno[3,2-b]thiophene) (pBTTT)\textsuperscript{[12]} (see Figure 1). Unless otherwise noted, the polymers are of moderate molecular weight (20 to 40 kDa). pBTTT exhibits a mesophase transition near 140 °C (varying with side chain length) and a second transition near 240 °C. P3HT exhibits a melting transition near 240 °C.

2.1. Atomic Force Microscopy

Atomic force microscopy (AFM) is a method that uses a sharp (typical radius of curvature =5 nm) tip to scan across the surface of a material to obtain a high-resolution topographical map.\textsuperscript{[14]} For organic electronic films it is most common to use a resonant mode, where the tip taps on the surface of a film at a few hundred kHz. Resonant modes reduce the lateral shear that occurs as the tip moves across the surface of the film. Resonant modes can provide additional information about the surface composition through phase imaging and harmonic analysis.\textsuperscript{[15]} The image obtained from AFM is a convolution of the shape of the tip with the shape of the sample.\textsuperscript{[16]} If the sample features are sharper than the tip, the image is merely an image of the tip. Extreme care must be taken to ensure that the tip is always sharper than the sample to avoid these tip artifacts. Since the silicon tip is substantially harder than the organic films, the tip does not dull through wear. The most frequent artifacts arise when the end of the tip is contaminated with small pieces of the sample. This is quite common in polymer films that are above their glass transition temperature and become “sticky” (e.g., having some significant adhesion to the tip). The resolution of the AFM image is also usually limited by the tip sharpness. A blunt, contaminated

![Figure 1. Schematic of a) P3HT and b) pBTTT.](wileyonlinelibrary.com)
In some cases, AFM images resolve single molecules. \cite{17} Most examples of molecular resolution for semiconducting polymers involve a partial monolayer of molecules deposited on highly oriented pyrolytic graphite (HOPG). \cite{18-20} These images show chain folding of a variety of forms. The molecular packing observed in these images do not correspond to the structure in the crystals seen in films on more traditional substrates. The graphite surface strongly interacts with the \( \pi \)-planes of the conjugated backbone and forces the molecules to lie face-down on the substrate. \cite{21} The polythiophenes used for thin-film transistors (TFTs), on the other hand, almost always pack edge-on (with side chains up and down and the backbone in the plane of the substrate) and weakly interact with the substrate. \cite{22,23} The strong interaction with the HOPG substrate forces the molecules to take conformations they might not otherwise assume.

Examples of AFM images of semiconducting polymers are shown in Figure 2. Figure 2a shows an as-cast pBTTT film. It consists of small nodules and is similar to that typically.

Figure 2. AFM images of pBTTT films as a function of substrate chemistry and heat treatment. Images are of a) an as-cast film on silicon oxide, films cast on b) silicon oxide and c) OTS that were heated to the mesophase (180 °C), and d) a film on silicon oxide heated to the isotropic phase (250 °C). The steps in (b–d) are molecular steps and correspond to the lamellar repeat distance. (b) and (c) adapted and reproduced with permission. \cite{28} Copyright 2007, AIP.
reported for P3HT films.[24,25] Figure 2b and c show a pBTTT film after heating to the mesophase on silicon oxide and octyl-trichlorosilane- (OTS) treated oxide, respectively. Figure 2d shows an AFM image of a pBTTT film that has been heated to the isotropic phase and recrystallized. The heated films clearly show molecular terraces with height differences that correspond to the (100) spacing measured by XRD (see below). After it is heated to its isotropic phase, the film exhibits a terraced ribbon structure that will be discussed in detail in a later section.[26] From these images, it would be tempting to conclude that Figure 2a is of an amorphous film, and Figure 2b, c, and d are of crystalline films, but this is in fact not the case. All of these films exhibit strong diffraction indicative of crystallinity. The annealed pBTTT films have highly oriented, large crystals, while the as-cast pBTTT film (and typically P3HT) has smaller, less-oriented crystals.[27] On the other hand, XRD of films on bare silicon oxide and OTS-treated silicon oxide are nominally similar, but the charge-carrier mobility is different by an order of magnitude.[28] The AFM images show that the apparent domain size is considerably larger on OTS than on bare oxide, providing insight into the mechanisms underlying the mobility dependence on substrate. AFM is a powerful measurement that is simple to implement, but is best used in combination with other measurements.

2.2. Grazing-Incidence X-ray Diffraction

Grazing-incidence X-ray diffraction (GIXD) is a method for characterizing the details of crystallographic structure and the microstructure in thin films.[29] GIXD is primarily performed at a synchrotron, but recently some GIXD measurements from lab sources have been reported for stronger scattering films.[30,31] The synchrotron source is optimal due to both the high flux and collimation of the photons. In the discussion below, we assume for simplicity that the thin-film samples are mounted horizontally (surface normal nearly vertical), although this is not a requirement. We also assume that the films are isotropically oriented in-plane (i.e., have fiber texture). Unlike conventional thin-film diffraction, GIXD requires high beam collimation primarily in the vertical direction to narrowly define the incidence angle (ϕ). For polymers the horizontal collimation usually does not need to be as high, since the diffraction peaks are broad as a result of the inherently broad diffraction for the sample and instrumental effects (see below). The physics of GIXD is similar to that of X-ray reflectivity.[12] The index of refraction (n) for solids at X-ray energies is less than one, with index of refraction becoming smaller as the electron density increases (Equation 1).

\[ n = 1 - \frac{\lambda^2 \varepsilon}{2 \pi m_e c^2} f \]  

(1)

\[ \alpha_c = \cos^{-1} \left( \frac{n_{\text{solid}}}{n_{\text{air}}} \right) \]  

(2)

where λ is the X-ray wavelength, ε is the electron charge, \( \rho_a \) is the atomic density, \( m_e \) is the electron mass, c is the speed of light, and f is the atomic scattering factor. For X-rays, Snell's law predicts that when going from a material of low electron density (often air with \( n = 1 \)) to one of higher electron density, total external reflection occurs below the critical angle, \( \alpha_c \) (Equation 2). Below the critical angle (typically \( \approx 0.2^\circ \) for 8 keV X-rays and an organic film), the X-rays travel as an evanescent plane wave along the sample surface. The penetration depth of the X-rays is determined by the incidence angle, allowing precise control of the X-ray intensity through the film depth. This property can be utilized in GIXD to separate diffraction in the near surface region of a film from that of the bulk of the film. It can also be used to reduce the intensity of scattering from a more electron-dense substrate by operating at an incidence angle above the critical angle for the film but below the critical angle for the substrate. This is the typical operating mode for organic electronics films. The scattering intensity is very sensitive to the incidence angle. Near the critical angle, small changes in the incidence angle result in a large change in the penetration depth and, thus, both the sampling volume and the scattering intensity. This sensitivity to millidegree changes in the incidence angle necessitates accurate control of the angle, a small beam divergence, and a flat sample to properly control the penetration depth.

As the X-ray plane wave travels through the film, some of the X-rays are diffracted by the film. The diffraction angle of the X-rays is related to the spacing of the crystallographic planes of the film through Bragg’s law, and the direction of the diffracted beam is related to orientation of the planes. There are two primary methods for measuring the scattering angle and scattered intensity of the diffracted X-rays: a point-detector and an area detector (see Figure 3). The two methods each have their advantages and disadvantages. In the point-detector configuration, a detector with collimating slits is positioned at one specific scattering angle and the collimating slits allow only X-rays with this specific scattering angle to hit the detector. The point detector provides both high accuracy and high resolution; these allow both accurate determination of the film reciprocal lattice vectors, and the diffraction peak width (related to defect densities). The primary limitation is that the measurement is slow because each scattering angle and direction must be separately measured. Due to time limitations and beam damage from the long exposure times, only a small fraction of the reciprocal space volume is measurable. The area-detector configuration, on the other hand, allows rapid collection of a large range of scattering angles at the expense of resolution and accuracy. The area detector is usually a charge-coupled detector (CCD) array, gas-proportional counter array, or an image plate. The collimated beam interacts with the sample film and the area detector “takes a picture” of the scattered X-rays. Since a large number of scattering angles are collected simultaneously, the area-detector configuration can provide rapid data from exposures that are often less than a minute long (depending on the detector, the source intensity, the film thickness, and crystalline quality). The quick measurements reduce the effects of beam damage and allow time-resolved measurements such as in situ heating. The resolution of the scattering angle is primarily determined by the size of the illuminated area of the sample relative to the distance between the sample and detector.[33] Illumination over a large area produces conditions where X-rays diffracted at different spots on the sample with the same scattering angle will
hit different pixels on the detector and X-rays diffracting from different spots on the sample with different scattering angles can hit the same pixel. This results in significant peak broadening and poor resolution.

Another significant limitation of the area-detector GIXD configuration arises from the fixed incidence angle and sample orientation. Specular scans, those solely along $Q_z$ with $Q_{xy} = 0$, are impossible in this geometry, and thus the method does not measure the diffraction of planes parallel to the substrate. The apparently out-of-plane data on the area detector (vertical section through the beam center) are not specular diffraction; the measured planes can deviate from a few, to up to ten degrees from perpendicular with the substrate. This deviation increases with increasing scattering angle and is approximately equal to half of the scattering angle (assuming incidence angles $\ll$ scanning angle). While this issue has been pointed out before,[30,34,35] it is often ignored in the literature. A similar problem occurs with the in-plane sample orientation for films with a high degree of in-plane orientation (such as single crystals or aligned films). However, this problem is irrelevant for films with isotropic in-plane orientation.

Diffraction measures the magnitude and direction of the reciprocal lattice vectors of crystals in the film.[36,37] The magnitude of the reciprocal lattice vector is related to the interplanar spacing (e.g., $d_{010}$). The reciprocal lattice vectors ($a^\ast$, $b^\ast$, and $c^\ast$) are perpendicular to the crystallographic planes and not necessarily parallel to the real space lattice vectors ($a$, $b$ and $c$). In the case of a non-orthorhombic unit cell, $b$ and $b^\ast$ are not parallel and $d_{010} \neq |b|$ (see Figure 4). This is apparent from Equation 3.

$$a^\ast = 2\pi \frac{b \times c}{a \cdot (b \times c)} \left| a^\ast \right| = \frac{2\pi}{d_{100}}$$

The unit cell angles are required to convert the reciprocal lattice vectors into the real space lattice constants. In cases, such as those commonly observed for polymer-based organic electronics, where there are not a sufficient number of peaks to uniquely solve the full unit cell, only the interplanar spacings can be reported. Since the direction of the reciprocal lattice vectors is defined by the crystallographic planes, the diffraction pattern reveals the orientation of the diffracting crystals. For a film with isotropic crystal orientation, the diffraction will result in a uniform ring on the detector (see Figure 5). For a film with a preferred out-of-plane orientation and isotropic in-plane orientation, the diffraction pattern will consist of spots for each crystallographic plane for a narrow orientation distribution and arcs for a broader orientation distribution. For a biaxially oriented film (e.g., having two distinct orientation axes and out-of-plane orientation with orientation in the plane), only a small number of diffraction spots (or none at all) will show up for a given sample rotation angle, because the sample must be rotated such that the Bragg condition is met.

The integrated intensity of a diffracted spot is proportional to the amount of crystalline material in the X-ray beam among other factors. In principle, this integrated intensity can be used
However, the relative crystallinity is more easily obtained.\[^{38}\] For such a determination, the diffraction of the chosen peak must be integrated over all orientations. For a line-scan measurement such as the typical specular scan done on a lab source with a point detector, an observed difference in peak intensity does not necessarily indicate that the crystallinity is different; this mistake is unfortunately often encountered in published work. The line scan only measures the scattering intensity for one specific scattering vector orientation (typically normal to the sample plane). Any difference in scattering intensity could also arise from a difference in the orientation distribution. A film in which the crystals shift from randomly oriented to highly aligned with respect to the surface normal would exhibit a substantial increase in the scattering intensity in a specular scan, even if the crystallinity remained the same. To definitively determine a change in crystallinity, a pole figure, or the orientation distribution function that measures the diffraction intensity of one specific diffraction peak as a function of all sample orientations, must be obtained.\[^{38,39}\] For absolute values of crystallinity, diffraction patterns of 100% crystalline and 100% amorphous are required, because even amorphous films scatter diffusely. These reference samples are typically difficult to create for the semicrystalline polymers used in organic electronics.

The most common structural characteristics extracted from GIXD for semiconducting polymers are crystal orientation, crystal plane spacings, and the relative crystallinity.\[^{21,27,35,40–43}\] The molecular packing is obtained less frequently. Figure 6 shows example 2D diffraction patterns from P3HT films that are plane-on ([010] oriented normal to substrate) or edge-on ([100] oriented normal to substrate). These P3HT films are uniaxially oriented with no preferred in-plane orientation. The diffraction appears as arcs, showing that the films are not highly oriented and have an orientation distribution of 20° to 30°. For the (100) oriented film, the (010) peak is oriented in-plane and for the (010) film, the (100) is oriented in-plane. This arrangement of the (100) and (010) peaks does not require the unit cell to be orthorhombic (γ, the angle between a and b, to be 90°). For the (100) orientation, a nonorthogonal γ would reduce the multiplicity in the diffraction pattern and shift the (H10) and (H10) peaks up or down. Since the film is isotropic (contains all in-plane orientations), the (H10) and (H10) peaks appear on both the right and left sides of the diffraction pattern and when γ is not 90°, the {H10} peaks split into the (H10) and (H00) peaks. For P3HT, no mixed-index peaks (e.g., (hk0) peaks with h and k both nonzero) are apparent in these diffraction patterns. This lack of mixed-index peaks (e.g., (H10)) is suggestive of poor interlayer registry between adjacent lamella and makes the determination of γ impossible. In general, several (HKL) peaks are needed to uniquely solve the unit cell (three lattice spacings and three angles) for the low symmetry structures often found in organic films.\[^{44}\] Since P3HT diffraction normally does not contain any (HKL) or (H01) peaks, it is usually not possible to determine a unique unit cell from GIXD data.

Figure 6 also shows 2D diffraction patterns for as-cast and mesophase-annealed pBTTF. Along the vertical slice, the as-cast film has arcs for the (H00) diffraction while the mesophase-annealed sample has ellipses for the (H00) peaks. These patterns indicate that the as-cast films have a distribution of orientations while the mesophase-annealed sample is very highly oriented. The same result can be revealed with specular scans and rocking curves. pBTTF also exhibits well-defined (H10) and (H03) series of peaks, indicating substantial 3D ordering in the film. The diffraction also includes several additional scattering features that are likely due to secondary crystallization.

For almost all semicrystalline polymer thin films, there are not enough resolved diffraction peaks to perform the usual X-ray
crystalllographic analysis to determine the molecular packing, even when assuming a known rigid molecule. Thus, another approach must be employed. For this, it can be useful to appeal to molecular modeling for help. By using the diffraction data to obtain a putative unit cell (lattice parameters and angles) as a starting point, molecular modeling approaches can be used to minimize the crystal energy. The resulting crystal structure can then be used to generate a diffraction pattern that can be compared to the diffraction data (e.g., Figure 6). If there is good agreement, then the modeled structure is likely close to the real structure. If not (as is often the case initially), then the differences between the diffraction patterns can be used to give a better starting point for the modeling. For instance, the unit cell (which is often not completely determined empirically) can be altered to agree with the data. Additionally, the orientation of specific moieties of the molecule can be measured to provide additional constraints on the modeling and, in some cases, allow structural insight without modeling. The following sections will describe how spectroscopic techniques can determine the orientation of various parts of the polymer molecule within the unit cell.

2.3. Near-Edge X-ray Absorption Fine Structure Spectroscopy

2.3.1. General Features of NEXAFS Spectroscopy

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has recently become a useful part of characterization strategies for organic electronics materials. NEXAFS spectroscopy measures the absorption of soft X-rays by core shell electrons, which are then promoted to unfilled molecular orbitals, typically of antibonding character. NEXAFS is elementally specific by the energy selection of the core shell accessed, and it provides molecular bonding information through the energy difference between the core shell and the final state, which gives rise to the spectral peaks. NEXAFS is especially useful in investigations of organic electronics materials because the C–C 1s → π* resonance is relatively strong and well-resolved, and, thus, it can be used to chemically measure differences in π-bonding character and to measure the orientation of conjugated molecules.

NEXAFS spectroscopy of light element K edges (e.g., boron to fluorine) requires monochromatic vacuum ultraviolet light in the energy range of ≈100 to ≈1000 eV, which is best provided by a synchrotron light source. The technique is typically practiced in ultrahigh vacuum for those elements and solid samples must be of low volatility. Because the technique produces photoelectrons, sample charging can occur, which must be eliminated using a grounded conducting substrate or another compensation method. The beam spot is <1 mm for most beamlines and solid samples should be large enough to provide (ideally) multiple measurement regions. Aside from these considerations, NEXAFS spectroscopy has few sample constraints; it can be practiced on films, powders, or even gases.

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NEXAFS spectra can be measured in many modes. The simplest measurement mode is total electron yield (TEY), which measures the charge compensation current through the grounding path. While TEY mode is experimentally straightforward, its interpretation can be ambiguous, especially when attempting to quantify the depth within the sample from which the signal originates. Other electron-yield modes typically measure electrons ejected from the sample surface using an electron detector. With an appropriate high-pass kinetic energy
filter (shown as a grid in Figure 7), the electron-yield signal can be adjusted to include only unscattered Auger electrons (AEY), or to include some Auger electrons that have been inelastically scattered from deeper within the sample (PEY). AEY and PEY modes are unambiguous with respect to sampled depth; furthermore, the PEY mode permits a near-surface depth profiling capability with adjustment of the energy filter bias. While all of the NEXAFS electron yield modes are surface-sensitive, it is also possible to measure a bulk-sensitive fluorescence yield (FY). FY experiments, however, can be experimentally complex because scattered incident light must be separated from the fluorescence signal.

2.3.2. NEXAFS for Chemistry and Composition Measurements

NEXAFS is a very sensitive probe of the chemical structure of organic compounds. The elemental composition can be measured through the post-edge intensity when collected at the orientation-insensitive “magic” incidence angle of 54.7°, and the specific bonds present can be measured in spectral peaks. Notably, the C–C π* and C–O π* have strong peaks in NEXAFS spectra; we have used these peaks to follow the chemical changes in thermally convertible oligothiophenes for organic electronics applications.[46] Composition in blends can also be determined by directly fitting a combination of reference spectra to the blend spectrum.[47] This approach has proven useful for determining the composition at interfaces of organic photovoltaic blends.[48] Because this approach combines aspects of elemental analysis (by post-edge intensity) and bond detection (by near-edge peaks), this type of composition analysis typically has far lower uncertainty than the typical sample-to-sample variation for blend systems employed in organic electronics.

For composition measurements, NEXAFS spectroscopy is sometimes compared to X-ray photoelectron spectroscopy (XPS) because both techniques provide chemical information, require an X-ray source, and are typically detected via electrons. The physical mechanisms of NEXAFS and XPS are quite different, however, and each technique has specific strengths. XPS requires a fixed energy, monochromatic X-ray source, enabling its placement in many laboratory environments, whereas NEXAFS requires a high-intensity, tunable X-ray source, limiting its placement to large light source facilities. XPS has a broad atomic number range for elemental detection because there is a relatively narrow distribution of binding energies for valence electrons across the elements. NEXAFS has a more limited atomic number range because core shells are very widely distributed in energy across the elements, and accessing several core shells with high-resolution monochromatic X-rays is constrained by monochromator design limitations. In practice most NEXAFS beamlines that are appropriate for organic materials are tuned to access the K edges of elements from boron (N = 3) to fluorine (N = 9), including the carbon, nitrogen, and oxygen K edges. In a carbon K edge NEXAFS spectrum, peaks specific to different carbon chemistries (e.g., sp² vs. sp³, what element is bonded to carbon, etc.) are typically well-separated in energy, making molecular structure determination more straightforward than for XPS because little to no peak deconvolution is necessary. Finally, a key strength of NEXAFS is its ability to determine molecular orientation.

2.3.3. NEXAFS for Orientation Measurements

The X-ray wavelength at the carbon K edge, ~10 nm, is sufficiently large that the dipole approximation is still nominally valid and each core–valence transition will have a characteristic transition dipole direction determined by the final-state orbital. The intrinsically polarized nature of synchrotron light enables the study of each transition dipole direction. Since organic semiconductors are relatively rigid molecules, the orientation of specific NEXAFS excitations is often sufficient to identify molecular orientation, or at least place specific constraints on possible orientation distributions. Molecular orientation is important because it affects the nature of π-overlap within an organic semiconducting film. In films with a single, highly oriented crystal type, NEXAFS can be used to determine the orientation of molecules or molecular subunits within the unit cell. In films that are less crystalline, NEXAFS can be used to determine or place constraints on the crystallinity or crystal orientation because it is sensitive to all molecules within a sample. For example, if only a single type of well-oriented crystal is known to be present, then the NEXAFS molecular orientation can be assumed to be the sum of orientations from those crystals (extracted from a packing model) plus a contribution from amorphous domains (assuming amorphous domains to be isotropic). The measured orientation then can be used to mathematically estimate the crystalline fraction.

NEXAFS orientation analysis has been used to study a wide variety of organic semiconductors. For example, we used NEXAFS to determine the sensitivity of the P3HT conjugated plane orientation to the drying rate during casting, with the finding that P3HT can adopt a thermodynamically preferred “edge-on” orientation for slow drying or a kinetically preferred “plane-on” orientation for fast drying.[49] Others have subsequently used P3HT NEXAFS to investigate the effects of solvent quality on interface orientation.[50] For P3HT, as for other organic semiconductors, the C–C 1s → π* transition is typically used to determine the orientation of the thiophene core because it occurs before the edge jump associated with atomic carbon concentration, and therefore has little convolution with other spectral
features. Like P3HT, most organic semiconductors have extended conjugation such that the lowest energy conformation is for all sp² bonds to fall within a single conjugated plane. The π resonance intensity has therefore been a focus of NEXAFS studies applied to a wide variety of organic semiconductors including phthalocyanines,[51,52] oligofluorenes,[33,34] oligobenzocenes,[55–60] oligophenylenes,[61] oligothiophenes,[62] and perylene.[63]

The molecular orientation can be determined from NEXAFS spectra collected at several incident angles, such as those in Figure 8 for P3HT. Because spectra are usually collected at different points on a sample, compositional heterogeneity can be mistaken for orientation if few spectra are taken, and it is therefore best practice to use at least five incident angles in any orientation determination. The spectra in Figure 8 have been normalized with respect to overall carbon content (e.g., post-edge intensity) to account for the changing spot size as the incident angle is changed. The angular variations in peak intensity of the normalized spectra indicate an oriented resonance. The \( 1 \text{s} \rightarrow \pi^* \) transition exhibits the greatest orientation, evidenced by its systematic variation with incident angle. The sample measured in Figure 8 shows the greatest π* intensity near normal incidence, where the incident electric field vector is close to parallel with the substrate. This trend indicates that the \( \pi^* \) vector is preferentially oriented parallel to the substrate plane. Since this vector extends perpendicular to the conjugated plane of P3HT, it indicates that the P3HT conjugated plane is preferentially oriented “edge-on” upon the substrate.

The orientation of the \( \pi^* \) can be quantified using a dichroic ratio, \( R \), defined as \( R = (I(90°) - I(0°))/(I(90°) + I(0°)) \) where \( I(\Theta) \) indicates the intensity at an angle of incidence with respect to the surface plane of \( \Theta \) (as illustrated in Figure 7). For an azimuthally symmetric system, with the transition dipole tilted from the surface normal by an angle \( \theta \),

\[
R = \frac{P(1 - 3 \cos^2 \theta)}{2(1 - <\cos^2 \theta>)} = \frac{P(1 - 3 \cos^2 \theta)}{P(1 - 3 \cos^2 \theta)} ,
\]

where \( P \) is the polarization purity of the beam line, \( \approx 0.83 \). \( R \) can vary from 0.7, for a perfectly edge-on conjugated plane (for which no naturally occurring examples exist to our knowledge) to \( -1 \) for a perfectly plane-on system (such as highly oriented pyrolytic graphite). An \( R \) of 0 is either consistent with a disordered transition orientation or a fixed magic-angle orientation of \( 54.7° \) away from surface normal \( <\cos^2 \theta_o> = 1/3 \). For well-ordered, nominally edge-on P3HT films (as confirmed by GIXD), we typically observe a maximum \( R \) for the \( \pi^* \) transition of 0.25 to 0.30. If these films were completely crystalline, with a single crystal orientation, this tilt could be interpreted as a conjugated plane tilt of \( \approx 27° \) away from the perfect edge-on condition.

2.3.4. Delamination

NEXAFS measurements in all electron-yield modes are intrinsically surface-sensitive. With a relatively low grid bias of \( \approx 50 \text{ V} \) in PEY yield for example, \( \approx 50\% \) of the signal originates within the top 2 nm of a film, and \( \approx 75\% \) within the top 4 nm. In typical organic semiconductor films, the measurement only represents the top of the film. For bottom-gated transistors, however, the most relevant measurement is the bottom-most \( \approx 6 \text{ nm} \), where the mobile charge carriers travel.[2] To access the bottom interface, we apply delamination methods to remove organic semiconductor films from their substrates. Our typical method is to apply a flexible support material to the top side of the film, and then mechanically remove it from its substrate.

In our work, we have considered several flexible support materials for delamination. Poly(dimethylsiloxane) (PDMS) stamps have previously been used to delaminate polymer semiconductor films.[64] The experiment revealed that mechanical removal did not significantly alter the electronic properties of the film’s bottom interface. We have used PDMS stamps to delaminate films for NEXAFS experiments. One disadvantage of PDMS is that it continually degasses in a vacuum environment, producing species (presumably chemical analogues to methylsilane) that can alter the appearance of NEXAFS spectra. Artifacts from PDMS can be mitigated, but not eliminated, by using PDMS that has been formulated for low-degassing applications (e.g., “space-grade” PDMS). An alternative support material is vacuum-deposited parylene C, which does not significantly degas in vacuum. However, it is less mechanically rigid than PDMS because it can only be applied in relatively thin films (10 to 100 \( \mu \text{m} \)).

Once the flexible support is applied, the films are removed from their substrates. On hydrophobic surfaces, toward which organic semiconductor films typically exhibit little adhesion, the films can simply be mechanically removed from their substrates. On hydrophobic surfaces, liquid water is used to hydrate the substrate interface and permit delamination. The effect of water on composition and orientation is typically checked in control samples, via top-surface measurements, to ensure that it has no effect.

An important aspect of delamination experiments is to ensure that the films adhesively fail at the substrate interface,
and not within the organic semiconductor layer. The delamination can be checked by using NEXAFS to measure the former substrate and ensure that no organic semiconductor remains. Because NEXAFS is sensitive to the sub-monolayer presence of organic species, this is an effective means to ensure that the delamination was successful. Typically, some amount of adventitious hydrocarbon is observed on inorganic substrates after delamination. For organically modified hydrophobic substrates, the hydrophobic monolayer is typically observed.

2.3.5. Quantifying the Orientation of the $\sigma^*$ Resonance

The C–C $\pi^*$ resonance is well-resolved from the carbon edge, but the $\sigma^*$ resonance suffers from significant background effects that must be subtracted from the spectrum during quantitative analysis. The manner in which the absorption edge is modeled, especially its position, height, and decay, can significantly affect the measured intensity of the C–C $\sigma^*$ resonance, which can in turn affect the measured orientation. The challenge presented by the absorption edge is highlighted in the NEXAFS measurement of orientation in arachidate monolayers formed by the Langmuir–Blodgett technique.\[65–67\] In the earliest manuscripts,\[66,66\] the variation of C–C $\sigma^*$ intensity with electric field vector orientation was shown to support a C–C $\sigma^*$ transition dipole moment with a significant component that was oriented off the long axis of an all-anti-conformation alkane chain. In a later manuscript,\[67\] the variation of C–C $\sigma^*$ intensity was shown to be inconsistent with off-axis contributions, and could only be explained by a single transition dipole moment vector that was parallel to the alkane long axis. These contrasting results were supported by different strategies for modeling the absorption edge.

In practice, we have found that unique simultaneous fits for the absorption edge and C–C $\sigma^*$ peaks are nearly impossible to achieve, because the decay of the absorption edge and the asymmetry in the Gaussian C–C $\sigma^*$ peaks have similar impacts on the modeled spectral shape, even if the peak shapes are determined from difference spectra. With constraints on modeled absorption edge location, height, and decay, $\sigma^*$ intensities can be determined and orientations can be calculated, but these quantities are best used for relative comparisons, or to determine whether a proposed $\sigma^*$ orientation is consistent with the NEXAFS measurement. For example, the orientation of the P3HT side chains is indicated by the variation in $1s \rightarrow \sigma^*$ intensity with incident angle in Figure 8a. The general trend in intensity is opposite that of the $\pi^*$, indicating a transition that is preferentially oriented perpendicular to the surface. In our work with high-performance polythiophene semiconductors, we used a fixed post-edge height, location, and decay to find that a NEXAFS-determined side chain orientation was consistent with measurements from FTIR. In general, however, determinations of absolute bond orientation from C–C $\sigma^*$ peak intensity are likely to be inaccurate, or at least not unique solutions of the raw data, for complex molecules.

2.4. Polarized Photon Optical and IR Spectroscopies

Optical (UV to NIR) and IR spectroscopies benefit from the very mature state of detectors (many approaching single photon sensitivity) and physical models. The techniques in general are inexpensive, precise, and amenable to both in situ and on-line measurements. Additionally, they can be adapted to microscopic measurements, limited by diffraction to a resolution on the order of the wavelength employed. They are rich in contrast, but, unlike the X-ray-based techniques, the intrinsic cross sections are difficult to calculate and thus require additional standards and/or models. The most common measurements on thin films are simple transmission and reflection and ellipsometry. In a standard ellipsometry measurement, the incident and reflected beams are assumed to be completely polarized and the ratio $\rho$ of the field reflection coefficients, $r$, for $p$ (electric field in the plane of incidence) or $s$ (electric field perpendicular to the plane of incidence) is determined by

$$\rho = \rho_1 + i \rho_2 = \frac{r_p}{r_s} = \tan[\Psi]e^{\Delta}$$

(5)

where the magnitude and phase of $\rho$ is often described in terms of the angles $\Psi$ and $\Delta$. In a reflection measurement, the intensity of the detected beam, $I_p$, is recorded. Because it is a ratiometric technique, ellipsometry is very precise. Commercial instruments are available to span the wavelength range, $\lambda = 190$ to 1700 nm, of atmospheric transparency that is accessible to photomultiplier tubes and Si- and InGaAs-based solid-state detectors. Extensions of standard ellipsometry include generalized ellipsometry,\[68,69\] where the off-diagonal elements of the Jones reflectivity matrix, $r_{pp}/r_{ss}$, $r_{ps}/r_{sp}$, $r_{vp}/r_{sv}$, are recorded and full Mueller measurements\[70,71\] where the 16 elements of the Mueller matrix describing the sample are recorded.

While precise, ellipsometric parameters are often not transparently related to the physical properties of the sample. Fortunately, very accurate (and elaborate) computer codes have been created to model ellipsometric data. In general, models begin with the assumption that the sample is composed of a series of planar layers, with defined thickness and dielectric constant, on a similarly well-defined substrate. Perturbations to the ideal model, in terms of interface mixing, surface roughness, and layer inhomogeneities can be introduced.

The simplest model is that of an abrupt, isotropic substrate, ambient interface. In the case of a known ambient environment (air or vacuum), there are two unknowns: the real and imaginary parts of the relative dielectric constant of the substrate, $\varepsilon = \varepsilon' + i \varepsilon'' = (N + n + ik)^2$. In principle, the two components of $\varepsilon$ can be inverted to determine the substrate $\varepsilon$. For a simple, single thin film on a known substrate, the problem is nominally underdetermined, as one must determine the layer thickness, $d$, along with the complex $\varepsilon(\lambda)$. If the absorption coefficient is known to be negligible in a spectral region, then $\varepsilon''$ is 0 and one can determine $\varepsilon'$ and $d$. Similarly, if $\varepsilon(\lambda)$ must obey the Kramers–Kronig (K–K) relations one can often determine $\varepsilon(\lambda)$ and $d$ independently if a large wavelength range is measured and one either assumes a flexible, causal model for $\varepsilon(\lambda)$, or computes this numerically in a K–K consistent fashion.

When performed on an oriented single crystal, generalized ellipsometry can, in principle, completely determine the full dielectric tensor of even a low-symmetry, triclinic sample.\[72\] In the case of thin films, even if polycrystalline, the symmetry of the system is usually higher than that of the underlying crystal due to averaging. Thus, the effective dielectric function in the
lab is typically either isotropic (symmetric crystal or unoriented system), uniaxial (symmetric in-plane, typical for spin-cast or vapor-deposited films) with ε-axis along the surface normal, or biaxial (symmetric in-plane, for aligned films formed by either deposition on asymmetric substrates, mechanical buffing, etc.)

The focus of this work is on spin-coated, uniaxial films. In this case, ε is diagonal and ε_{xx} = ε_{yy}. For thin films, it is often very difficult to uniquely determine ε_{zz} ≠ ε_{xx}. In high-index materials, due to Snell’s law, the internal electromagnetic wave propagates close to the lab z-axis, and thus the electric field has little projection along the z-axis. The limited sensitivity results in strong correlations in the fit parameters. These limitations can often be overcome by either measuring multiple samples of varying film thickness,\(^{[73,74]}\) measuring samples on different substrates,\(^{[75]}\) combining ellipsometry data with transmission data,\(^{[76]}\) or by measuring films on “special” substrates.\(^{[77]}\) As the film microstructure can vary with deposition conditions (thickness), we use the multiple sample approach, typically recording three angles of incidence for identical films deposited on two samples: a native oxide layer on a Si wafer and an ~200 nm thermal oxide (typical gate dielectric) on a Si wafer.

Schemes for the optical models for the two samples are shown in Figure 9. The optical constants for Si and the oxides are taken from the literature,\(^{[74]}\) and the oxide thicknesses are determined from measurements on references. The dielectric functions for the two sample films are assumed to be the same, but their thickness is independently fit to allow for processing variation. The film ε_{il} can either be fit wavelength-by-wavelength (λ-by-λ), or parameterized by a sum of K–K consistent line-shape functions. In general, the multiple sample approach is sufficiently robust that we extract λ-by-λ fits that maximally preserve the spectral resolution of the data, but also are most strongly affected by limited statistics (noise).

Shown in Figure 10 is ε for two thin regioregular P3HT films that display the typical range of dielectric behavior exhibited by that polymer. Film a was deposited from a 4 mg mL\(^{-1}\) solution in CHCl\(_3\) at 500 \(\pm 2\) rad min\(^{-1}\) (500 rpm) with a resultant ~50 nm film thickness. Film b was deposited from a 2 mg mL\(^{-1}\) solution at 2000 \(\pm 2\) rad min\(^{-1}\) (2000 rpm) and then annealed above the melting temperature with a resultant ~19 nm film thickness.\(^{[78]}\) Both films exhibit pronounced anisotropy, with ε_{zz} < ε_{xx}. The fine structure observable in the spectrum is attributed to Franck–Condon coupling between the electronically excited state and vibrations (C = C stretch) of the polymer. Qualitatively, pronounced fine structure is reflective of well-ordered (little inhomogeneous broadening) systems. Quantitatively, the relative strength of the 0–0 and 0–1 features has recently been related to the strength of the intermolecular coupling.\(^{[79]}\) For film a, the ε_{xx} and ε_{yy} spectra look similar, suggesting that the microstructure giving rise to the transitions is similar. In this case, we can adopt a simple, linear, effective medium model for the dielectric constant:

$$\varepsilon = \begin{bmatrix} \varepsilon_{xx} & 0 & 0 \\ 0 & \varepsilon_{yy} & 0 \\ 0 & 0 & \varepsilon_{zz} \end{bmatrix}$$

$$= \int R_{il}(\theta, \Psi, \phi) R_{ilm}(\theta, \Psi, \phi)$$

$$\times \varepsilon_{lm}^{\text{micro}} f(\theta, \Psi, \phi) \sin \theta d\theta d\Psi d\phi;$$

where the microscopic dielectric function \(\varepsilon_{lm}^{\text{micro}}\) is averaged over the orientation distribution function, \(f\), for the three Euler angles, \(\theta\), \(\Psi\), and \(\phi\), using the rotation matrices \(R_{il}\). For spin-cast films, it is assumed that \(f\) is independent of \(\phi\). Either semi-empirical or ab initio quantum chemical calculations can be performed to assess the orientation of the transition dipole, \(\mu\), with respect to the molecular axes. When \(\mu\) is along the chain axis (c), a simple cylindrical \(\varepsilon_{mc}^{\text{micro}}\) can be developed:

$$\begin{bmatrix} \varepsilon_{c} & 0 & 0 \\ 0 & \varepsilon_{c} & 0 \\ 0 & 0 & \varepsilon_{l} + i\varepsilon_{ln} \end{bmatrix}.$$
This is essentially equivalent to the result of McBranch et al.\textsuperscript{[80]} More sophisticated effective-medium models have been developed,\textsuperscript{[81]} and they represent less than a 10% correction to the simple model for this system. In the case of P3HT, quantum chemical calculations using the INDO1/s formalism indicate the single, strong, singlet transition of the π-system is essentially oriented along the long chain axis.\textsuperscript{[82,83]} For film a in Figure 10, where $\varepsilon''/\varepsilon''_x = 0.44$, $<\cos^2\theta> = 0.18$.

Film b, which was annealed above the melting point, exhibits a significantly higher degree of in-plane order, as desired for a good TFT. The spectrum for $\varepsilon''_x$ no longer resembles that of $\varepsilon''_y$, the Franck–Condon structure is suppressed and the peak absorbance is blue-shifted (from 558 nm in $x$ to 481 nm in $z$). This suggests the out-of-plane absorption arises from regions of different, more disordered structure. In this case we can use the ellipsometry to attempt to define the volume fraction, $f$, of the film that is highly ordered from a simple model of $\varepsilon''$ representing a mixture of perfectly in-plane oriented regions and isotropic, amorphous regions:

$$\varepsilon'' = (1-f) \begin{bmatrix} 3/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2/3 \end{bmatrix} + f \begin{bmatrix} 3/2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2/3 \end{bmatrix}.$$  

(8)

Simple algebra results in:

$$\frac{\varepsilon''_y}{\varepsilon''_x} = \frac{2(1-f)}{3f}.$$  

(9)

This analysis presumes that the oscillator strength for the disordered (isotropic) state is the same as that for the ordered state. Simple exciton models\textsuperscript{[84]} and oligimer calculations indicate that the absorption ($\mu I^2$) per monomer is nominally constant for moderate conjugation lengths. Based on the integral of $\varepsilon''$ over the 400 to 640 nm range, we can estimate $f$ to be 82%. We note in passing that the nominal conservation of total oscillator strength in Figure 10 between the two films. The increase in $\varepsilon''_x$ in the more-ordered film comes at the expense of $\varepsilon''_y$, as required by either Equation 7 or 9. Often, normal incidence transmission spectra are used to characterize film absorbance and increases in absorption upon film processing are attributed to intrinsic changes in the transition dipole strength. For anisotropic films this is problematic, as only $\varepsilon''_x$ is sampled in the measurement.

The utility of visible ellipsometry in the study of many systems is limited by the number of observable transitions. This is a particular problem for the polythiophenes, which are dominated by a single optical transition. The resultant cylindrical $\varepsilon''$ implies that only the orientation distribution function for $\theta$ can be characterized. Ellipsometry for these systems is, thus, highly synergistic with NEXAFS, which accurately characterizes the orthogonal 1 $s$–$\pi^*$ transition dipole.

Relative to UV-vis spectroscopy, IR spectroscopy has the advantage of a much richer spectrum. In many cases, three independent and mutually orthogonal transition dipole observables for each major functional group or molecular fragment, allowing more detailed orientation analysis. Conceptually, vibrational spectroscopy of thin films can be treated in an identical fashion to that in the visible, and IR ellipsometers are commercially available to characterize the full dielectric function. However, weak bench-top IR sources (heated silicon carbide rods known as “globars”) combined with the limited sensitivity of deuterated triglycine sulfate (DTGS)IR detectors and/or the nonlinearity of mercury cadmium telluride (MCT) detectors makes IR ellipsometry of thin (<100 nm) films very difficult. Additional complications arise for reflection on IR transparent substrates, such as Si, because the intensity of the signal is significantly diminished. Therefore, we choose to record the p- and s-polarized Brewster angle transmission spectra of the films and obtain orientation information by forward simulating the figure of merit: $A_{p}/A_{s}$ where $A$ is the peak absorbance ($-\log_{10}(T/T_0)$) in the spirit of Equation 7. This is similar to the approach of Harder et al.\textsuperscript{[85]}

Shown in Figure 11 are the polarized Brewster angle transmission spectra of thin (20 nm) P3HT films spin-coated onto an hexamethyldisilazane-pretreated, native oxide-coated double side polished Si wafer and heated above the melting point (as in Figure 10, film b). The principle features are assigned in Table 1. The broad features near 1100 and 1300 cm$^{-1}$ in the isotropic pressed KBr pellet are due to oxidative doping and are absent in the freshly deposited films. The features at 1106 and 1250 cm$^{-1}$ in the p-polarized spectrum are artifacts due to incomplete normalization of the substrate oxide.

The vibrational spectroscopy of alkane chains is quite mature. In the spectral region from 1140 to 1400 cm$^{-1}$, characteristic of CH deformations, specific features have been associated with specific defects.\textsuperscript{[86]} For example, features near 1368 cm$^{-1}$ arise from GTG (gauche, trans, gauche) structures, while 1354 cm$^{-1}$ is attributed to GGT sequences and 1344 cm$^{-1}$ to terminal gauche defects. Unfortunately, these features are very weak in the thin-film spectra and not typically amenable to quantitative analysis. However, a strong qualitative correlation exists between the CH$_2$ asymmetric stretch, $\nu_{asym}$ frequency and the general level of order of the alkane chain: crystalline, all-anti chains are characterized by frequencies\textsuperscript{[87]} near

![Figure 11](image-url)
The standard deviation for the FTRIR position is ±0.7 cm⁻¹, based on the pooled variance of multiple spectra (two to three) for most samples. [b] The standard deviation for the A_p/A_s ratio is ±0.05, based on the pooled variance of multiple spectra (two to three) for most samples.

Table 1. IR mode assignments for P3HT.

<table>
<thead>
<tr>
<th>Frequency[a] [cm⁻¹], A_p/A_s[b]</th>
<th>Mode</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>3055</td>
<td>C = C-H stretch</td>
<td>x perp to alkane chain z</td>
</tr>
<tr>
<td>2956</td>
<td>CH₂ sym stretch</td>
<td>y perp to alkane chain z</td>
</tr>
<tr>
<td>2928, 0.51</td>
<td>CH₂ asy stretch</td>
<td>x perp to main chain (c)</td>
</tr>
<tr>
<td>2857, 0.47</td>
<td>CH₃ sym stretch</td>
<td>y perp to main chain (a)</td>
</tr>
<tr>
<td>1510, 0.19</td>
<td>C = C asy stretch</td>
<td>perp to main chain (a)</td>
</tr>
<tr>
<td>1465</td>
<td>CH₂ scissor</td>
<td>perp to main chain (a)</td>
</tr>
<tr>
<td>1378</td>
<td>CH₃ umbrella</td>
<td>perp to main chain (a)</td>
</tr>
<tr>
<td>820</td>
<td>C = C-H o.p. wag</td>
<td>Along π⁺</td>
</tr>
</tbody>
</table>

Figure 12. Computed figure of merit for analysis of polarized IR transmission data.

3. Example of Complementary Analysis

3.1. Isotropic In-Plane Oriented Films (Uniaxial Orientation)

pBTTh has emerged as a polymer material with superior TFT performance: mobilities of 0.3 to 0.4 cm² V⁻¹ s⁻¹ can be routinely achieved[90] and mobilities as high as 1 cm² V⁻¹ s⁻¹ have been reported.[91] Critical to the achievement of this high performance is thermal processing above a mesophase transition at ~140 °C. We have extensively characterized the structure of this polymer with the techniques described in this contribution[13,28,92-94] and highlight some of the results. Here we restrict our discussion to pBTTh-C₁₄ (C₁₄H₂₉ side chains) although the behaviors of analogous members of the series from C₁₀ to C₁₈ are similar. Initial as-cast films of pBTTh exhibit an AFM morphology (Figure 2) and GIXD pattern (Figure 6) similar to that of regio-regular P3HT and produce TFTs with mobilities of about 0.05 to 0.1 cm² V⁻¹ s⁻¹, slightly higher than what is typically achieved with P3HT.[23] After annealing into the mesophase, the degree of order in the film qualitatively changes: the AFM is characterized by almost micrometer scale terraces with step heights of ~2.2 nm and the GIXD displays a rich array of distinct diffraction peaks. From the (H00) series of in-plane peaks, one can determine a d₃₀₀ spacing in good agreement with the AFM step heights, indicating that the film consists of highly uniform, flat lamella. This was confirmed with high-resolution X-ray rocking scans.

Shown in Figure 13 are the dielectric functions derived from SE of an as-cast and annealed pBTTh-C₁₄ film prepared similarly to that of Figure 6. The calculated film thickness is ~20 nm. Both the as-cast and annealed films exhibit extremely high in-plane order, consistent with the GIXD and AFM. As with the earlier P3HT example, the ε″ₓ spectrum is distinctly blue shifted with respect to that of ε″ₓ suggesting it arises from minor
regions of disorder. Applying Equation 9 to the ratio of the integrals of $\varepsilon''$ and $\varepsilon'$ between 400 and 700 nm, we estimate that 93% of the film is in the highly ordered state. Unlike P3HT, there is no evidence for pronounced Franck-Condon coupling. However there is a slight red-shift and development of a long-wavelength shoulder upon annealing, suggestive of improved torsional order (longer conjugation length) after annealing.

Figure 14 shows the NEXAFS results for the annealed pBTTT film. There is a clear variation with incident angle of both the C–C π* and C–C σ* transitions. As for P3HT, there are opposing trends: the C–C π* is strongest for nearly normal incidence beams (indicating the relevant transition dipole is oriented near to the surface plane) while the C–C σ* is strongest for grazing incidence beams (indicating the transition dipole is oriented near the surface normal). As discussed, the C–C π* transition dipole is well-defined and oriented strictly perpendicular to the conjugated main chain plane. Given the extreme uniformity of the AFM, the strong diffraction in GIXD, and the high-anisotropy/uniformity of the SE, we treat the orientation distribution functions that determine SE, NEXAFS, and IR as narrow distributions, reflective of crystalline grains of lamella with the main chain axis in the surface plane with random in-plane orientation. In this case, we can interpret the $R$ factor from NEXAFS in terms of a single tilt angle of the π* director from the surface normal of 68°, such that the short axis of the conjugated plane is tilted 22° from surface normal (see Figure 16). We note that, as NEXAFS only determines $<\cos^2\theta>$, we cannot a priori exclude the possibility of an alternating, herringbone configuration of $+/-22^\circ$ tilts. However, such a configuration would lead to a doubling of the unit cell, which would contain two chains and would lead to extra, unobserved diffraction peaks in GIXD. Similarly, such a configuration would be expected to lead to a factor group splitting of the C-H wagging modes near 800 nm, as is observed in sexithiophene oligomers (where a herringbone structure is adopted). This factor group splitting is not seen and thus we propose a homogeneous tilt. This slipped structure is consistent with first-principles quantum chemistry calculations.
that predict a homogenous tilt of $27^\circ$.[13,96] The tilted structure can be viewed as arising from frustration of the natural, herringbone packing motif of large aromatic oligomers (acenes and thiophenes) by the side chains. This slipped packing is predicted to be present in the analogous P3HT and poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene)] (PQT). While P3HT does not develop as homogeneously ordered films as pBTTT does (see Figure 2, Figure 6, Figure 8), the NEXAFS results ($R = 0.25$) for our best ordered films (slow cooling after heating above the melting temperature[79]) are consistent with a $\pi^*$ director tilt of $\approx 27^\circ$ degrees, close to that predicted by theory.

Figure 15 shows polarized IR spectra in the CH stretch region of a meso-phase-annealed pBTTT-C14 film. The $CH_2\nu_{asy}$ frequency is $2920$ cm$^{-1}$, representative of a well-ordered, nearly all-anti chain. From the observed $A_s//A_p$ ratios of $CH_2\nu_{asy}$ (0.35) and $CH_2\nu_{sym}$ (0.42) and the assumption of a narrow distribution in angle, a chain tilt angle of $46^\circ$ from the surface normal can be estimated from Figure 12. An average side-chain director closer to the surface normal is consistent with the sign of the C-C $\sigma^*R$ observed by NEXAFS. As discussed earlier, quantitative interpretation of the $\sigma^*$ is complicated both by uncertainty in the background correction and in the proper determination of the relative contributions of the side chain versus the main chain. If we fit the $\approx 293$ eV resonance with an asymmetric Gaussian lineshape and then model an exponentially decaying step edge, the side-chain orientation can be quantified with a $R = -0.15$. If we subtract an in-plane contribution to this resonance from the pBTTT backbone (assuming the contribution is proportional to the number of single bonds), we arrive at $R = -0.30$, which corresponds to a C-C single bond tilt of $\approx 45^\circ$. Although this result is strongly consistent with the IR analysis, we do not recommend relying exclusively on the NEXAFS $\sigma^*$ resonance for determination of side-chain orientation in poly-thiophene semiconductors, not only because of the challenges in background subtraction, but also because the information is ambiguous if the side-chain conformation or orientation distribution are not known.

If we combine the observed main-chain and side-chain tilt with the lamella $d_{100}$ from GIXD, we can develop the combined structural schematic shown in Figure 16. The specific azimuthal arrangement of the plane of the side-chain tilt with respect to the main-chain plane is unknown, and shown only schematically. A key aspect of the structure is the significant interdigitation of the side chains, as revealed by knowledge of the side-chain order (all-anti), chain tilt ($\approx 45^\circ$), and $d_{100}$. Recently, molecular dynamics simulations have been combined with the high detail of the GIXD patterns for pBTTT in an attempt to derive the best “fit” unit cell structure. The key aspects of Figure 16, the main-chain tilt and side-chain interdigitation, are confirmed. A similar treatment of P3HT, where the side chains are disordered in with nearly random chain orientations, results in the conclusion that the side chains are not interdigitated. This is consistent with simple packing arguments and the attachment density of the the side chains along the backbone.[94]

The ability to form an interdigitated structure has been suggested to be an enabling feature for the development of the highly ordered polymer films necessary for good electrical performance. Interdigitation is found to be a common feature of many high-performance polymers such as PQT, pBTTT, and PATBT.[12,97]

3.2. In-Plane Oriented Films (Biaxial Orientation)

Our first example covered films that were isotropically oriented in-plane and could be modeled assuming average azimuthal tilts. For single crystals, films with very large domain size, and films with a preferred in-plane orientation, the data analysis is more complicated, but can potentially provide additional structural information. A recent example from our lab is pBTTT-C14 films that were aligned using a flow coating method.[96] AFM images of these films are shown in Figure 2. The terraced ribbons are nominally 60 nm wide, extend across the entire film, and are oriented perpendicular to the flow direction. Similarly to what was discussed for the spin-coated films, the ribbons exhibit terraces with a step height corresponding to the $\approx 2.2$ nm lamellar spacing measured by X-ray diffraction. Although AFM cannot prove that the films are biaxially oriented, it suggests that this is the case. 2D-GIXD images of a flow-coated film are shown in Figure 17. The two images are taken with the film nominally oriented with the flow direction parallel and perpendicular to the incident X-ray beam. The parallel and perpendicular images show different sets of in-plane peaks, proving that the films do have in-plane orientation. Note that the orientation of the normal of the diffraction planes is the difference between the incident and diffracted beam wave vectors (see Figure 3).

For small scattering angles, the normal of the diffraction planes is approximately perpendicular to the incident beam. For larger angles, the normal to the diffraction planes will differ by half of the scattering angle from incident beam normal. Thus, the 2D-GIXD experiment cannot measure parallel planes with a fixed sample orientation; the orientation of the measured diffraction planes deviates further from the horizontal normal of the incident beam as $Q_{xy}$ increases. This can be seen by the fact that the intensities of the peaks at $\pm Q_{xy}$ are different than those at $-Q_{xy}$. Because of this, 2D-GIXD is of limited utility for examining
birefringent lamellae. For the case of pBTTT, the in-plane angle is close to $90^\circ$ thus requires knowledge of a full and explicit molecular conformation. Knowledge of the in-plane angles greatly simplifies the determination of the complete unit cell of the thin film. If accurate measurements of the intensities of enough peaks are obtained, structural refinement on the molecular packing is possible, but generally assumes the molecules are rigid and thus requires knowledge of a full and explicit molecular conformation. For the case of pBTTT, the in-plane angle is close to $\alpha = 90^\circ$. Combining the AFM and GIXD data reveals a structure where the polymer molecules are oriented with their backbones perpendicular to the long direction of the ribbons ([010] $\pi$ peak is oriented along the ribbon long axis and the [003] backbone peak is oriented along the ribbon short axis). The width of the ribbons is comparable to the length for molecules of their molecular weight, so the chains are fully extended within the ribbons.

Spectroscopic ellipsometry of biaxially oriented films requires separation of the dielectric constants into their $x$-, $y$-, and $z$-components. This is facilitated by acquiring generalized ellipsometric data. We have modeled the flow-coated films as a diagonal (appropriate to orthorhombic symmetry or higher) biaxial layer. Data were acquired using the multiple sample approach on duplicate flow-coated films. In addition to multiple angles of incidence, multiple azimuthal angles were acquired. The total data suite was then fit in a \textit{\lambda}-by-\textit{\lambda} fashion. Figure 18 shows the $x$-, $y$-, and $z$-components of the derived real and imaginary parts of the dielectric constant for a flow-coated pBTTT-C14 film. As the prominent absorption peak results from the $\pi$–$\pi^*$ transition, whose dipole is oriented along the polymer backbone long axis, it is clear that the long axis is oriented in the flow direction ($x$), consistent with the picture developed from the GIXD measurement. Comparison with Figure 13 (pBTTT) confirms the nominal conservation of oscillator strength, as $\varepsilon_x''$ is twice as large as in the spin-coat case. As with the spin-coat films, $\varepsilon_z$ is blue-shifted with respect to $\varepsilon_x$, suggesting that the minimal out-of-plane absorption is due to minority disordered regions in the film. It is interesting to note that $\varepsilon_y$ exhibits nominally the same spectrum as $\varepsilon_x$ indicating that the in-plane disorder reflects the net orientation of locally well-ordered chains, and is not due to in-plane hairpin defects. The ratio of the integral of $\varepsilon_x''$ from 400 to 700 nm to that of $\varepsilon_y''$ is 7:1. The level of in-plane order is similar to that found for polyfluorene films aligned on mechanically buffered surfaces.$^{[98]}$

NEXAFS of biaxially oriented films can be used to evaluate the in-plane orientation of the $\pi$-planes and the side chains. Figure 19 shows the results of NEXAFS analysis of flow-coated pBTTT-C14 films. In configurations where the in-plane projection of the incident light electric field vector is parallel to the flow direction, the $\pi^*$ intensity is extremely attenuated. However, in configurations where the electric field vector is perpendicular to the flow direction, the $\pi^*$ intensity is greater. This result is consistent with the ellipsometry results because the $\pi^*$ orbital extends perpendicular to the polymer backbone. The surface-relative orientation of the conjugated plane is similar to that observed in the terraced morphology; the magnitude of incident angle dependence here is greater because the molecules are no longer azimuthally isotropic. NEXAFS has been applied in a similar manner to examine in-plane orientation of of sexipheny$^{[91]}$ and pentacene$^{[90]}$ crystals, as well as polymer semiconductors such as the polyfluorenes$^{[100,101]}$ and

Figure 17. 2D-GIXD of oriented films of pBTTT. Films are oriented with scattering vector nominally a) perpendicular to the flow direction and b) parallel to the flow direction. The circled peak is nominally oriented in the same direction as the $\pi$-stacking direction and is likely due to some structure within the unit cell basis. Note that the orientation distribution of the films ($\approx 20^\circ$) is broader than the change in orientation the scattering vector due to the fixed incident beam.

Figure 18. Elements of the biaxial dielectric function from spectroscopic ellipsometry of flow-coated films. The typical 90% confidence limit from the least squares analysis is indicated.
fluorene–thiophene copolymers,[102] although the extent of orientation we observe for pBTTT appears significantly greater.

One aspect of the measurements of interdigitated side chains shown in the uniaxial section is that we were unable to determine the in-plane angle between the backbone and the side chain. In some cases, polarized IR can measure the preferred orientation of the side chains in the films. We did not observe any ‘significant’ CH in-plane anisotropy in the flow-coated films. In the NEXAFS results shown above in Figure 19c, there is a clear insensitivity of the first $\sigma^*$ transition at 293 eV, which is dominated by the alkane side chains, to the rotation angle $\phi$. This result indicates that the in-plane projections of the side chains are either oriented close to 45° from the backbones, or have no preferred in-plane orientation relative to the backbone. We can exclude the possibilities of tight side chain orientations parallel to the backbone or perpendicular to the backbone.

4. Conclusions

We have shown a general methodology for combining the complementary measurements of AFM, GIXD, NEXAFS, VASE, and polarized IR to obtain a more complete picture of the molecular...
packing of semiconducting polymer films than what is attainable with any single technique. We have focused on pBTTT and showed that the interdigitation of the side chains is a critical driving force for improved molecular packing. This general methodology is applicable to a variety of semiconducting polymers and can be applied in situ during some processing steps (e.g., during heat treatments).

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