Unconventional Face-On Texture and Exceptional In-Plane Order of a High Mobility n-Type Polymer

Applications such as light emitting displays, smart sensors and circuits based on organic thin film transistors, and efficient low cost photovoltaics continue to drive the field of organic electronics.[1] Much of the advancement in device performance so far has been attributed to a better understanding of the ordering and orientation of new polymeric and small molecule materials and how they can more efficiently conduct charge. Unlike silicon technology, where complementary circuits can be made by doping the intrinsic material in such a way as to make it electron or hole conducting, organics molecules are intrinsically doped, and are synthesized so as to make them p-type (hole conducting) or n-type (electron conducting). The molecular packing and microstructure in organic thin films greatly affects the semiconducting performance of these films and has been extensively studied in p-type organic semiconductors. These studies, many conducted at SSRL, have elucidated the connection between chemistry or film processing, and performance.[5-7] It is generally believed that the best transport in thiophene-based polymers is attained when there is a high degree of π-stacking of the thiophene core in the substrate plane. Here the direction along which the cores are stacked is known as the π-stacking direction and when this stacking is parallel to the substrate this facilitates two-dimensional (2D) transport along the substrate.[7-9] Unfortunately, similar structure-property studies are not as well established in n-type polymers due to the dearth of high performing materials. We have made progress in this direction by investigating the molecular packing and structure for the high-performance n-type polymer P(NDI2OD-T2), Figure 1.

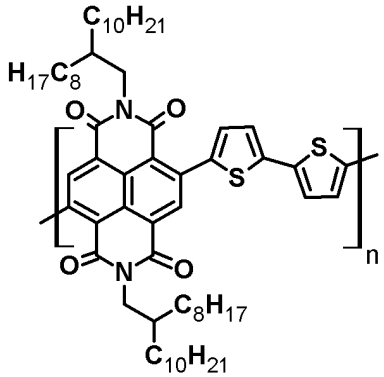

Figure 1. Chemical formula of the semiconducting material used, P(NDI2OD-T2).

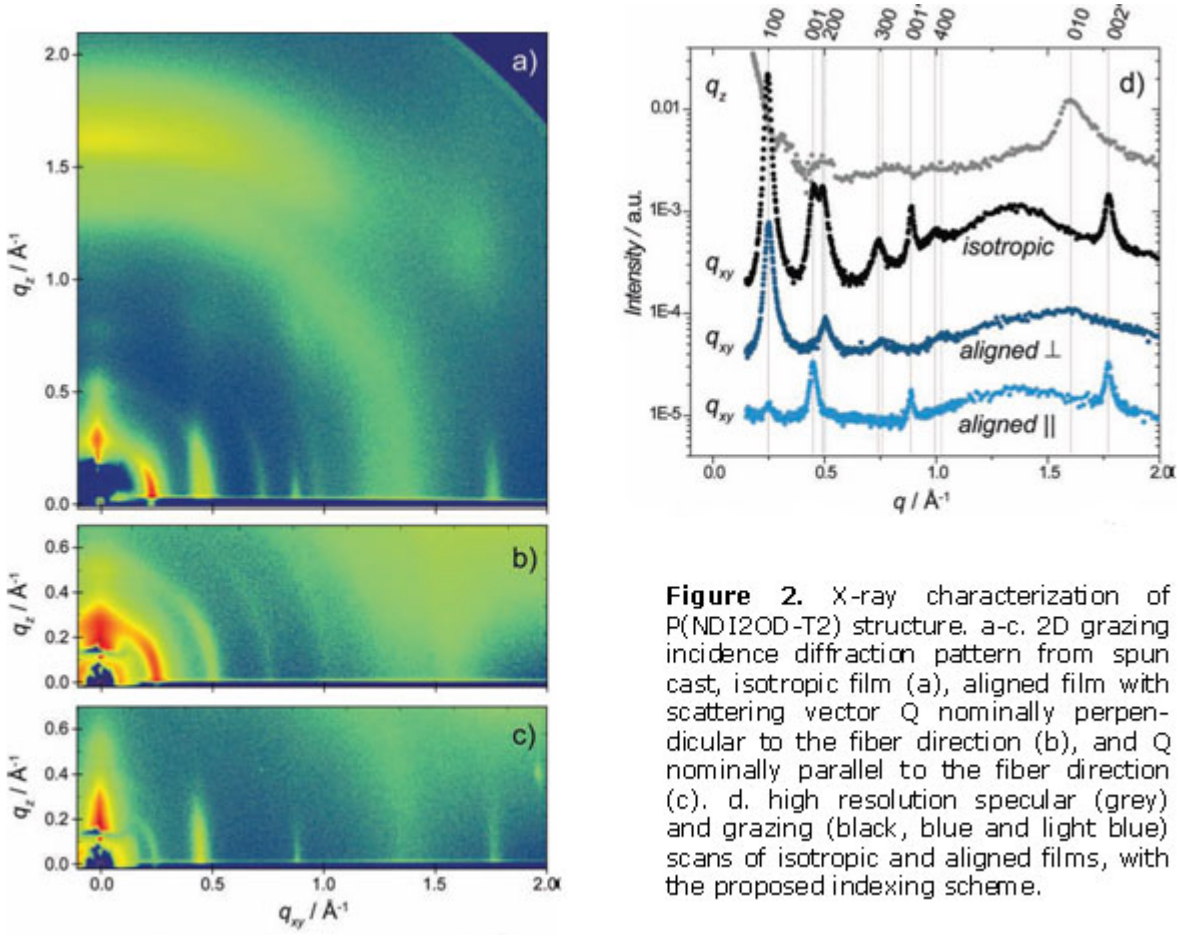

Figure 2. X-ray characterization of P(NDI2OD-T2) structure. a-c. 2D grazing incidence diffraction pattern from spun cast, isotropic film (a), aligned film with scattering vector Q nominally perpendicular to the fiber direction (b), and Q nominally parallel to the fiber direction (c). d. high resolution specular (grey) and grazing (black, blue and light blue) scans of isotropic and aligned films, with the proposed indexing scheme.

It was previously suggested that this polymer lacked significant long range crystalline order, and was potentially amorphous or at most highly disordered,[4,10] because of the lack of observed diffraction peaks (limited to specular X-ray scattering) and the weak dependence of mobility on molecular weight and polydispersity. However, we have shown that this conclusion was erroneous by using grazing incidence x-ray scattering at SSRL beam line 11-3 and high-resolution scattering in the grazing and specular geometries at beam lines 7-2 and 2-1. We used these beam lines to determine the structure of a high mobility P(NDI2OD-T2) film (mobility of 0.2 cm^2/Vs). The diffraction experiments (Figure 2) reveal a largely out-of-plane π-stacking as shown by the broad peak near $q_z \approx 1.6$ $Å^{-1}$. We also find significant diffracted intensity in-plane (near the q_{xy} axis), where multiple diffraction orders of the lamellar (h00) and chain backbone (00l) peaks are observed. Thus, the polymer packs in a so-called 'face-on' orientation. In addition, using aligned films of P(NDI2OD-T2), we are able to separate the in-plane diffraction features, index the observed pattern, and suggest an approximate packing motif and grain structure as shown in Figure 3. Such an organic film microstructure, with the π-stacking direction ([0k0]) normal to the substrate, had previously been thought to hinder high thin film transistor (TFT) mobility. We postulate that the film shows a high mobility despite this packing due to extensive inter-grain connectivity, where one polymer chain is connected to multiple crystalline grains. Additionally, the out-of-plane π-stacking may allow for an alternate electron transport pathway around a transport barrier at the polymer-dielectric interface.

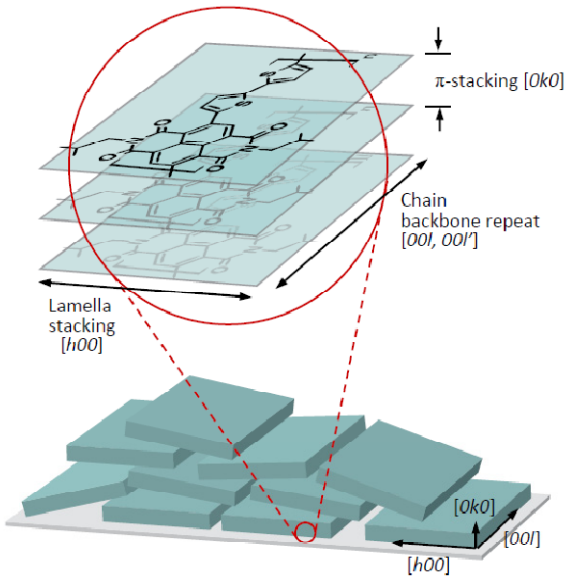

Figure 3. Schematic of face-on molecular packing of P(NDI2OD-T2) inferred from X-ray data (top). Proposed microstructural arrangement of the crystallites (bottom) indicating slight disorder in the π-stacking and lamella stacking directions of the flat, platelet-like crystallites and alignment of the chain backbone direction with the substrate.

The implications of our observation of a high performance polymer with face-on packing is important for the further development of related n-type and ambipolar materials. The out of plane π-stacking suggests that P(NDI2OD-T2) will have an enhanced diode mobility (i.e., measured perpendicular to the substrate), which was indeed recently observed.[11] Overall, this observation of high electron mobility out-of-plane, as well as the already observed high in-plane mobility, highlight the importance of structural understanding of these materials for both transistor and photovoltaic applications.

Primary Citation

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