

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

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Recent developments in materials design for both electron (n-type) and hole (p-type) transporting organic semiconductors have led to dramatic advances in performance for solution-processed and printed organic thin film transistors and complementary circuits.^[1,2] Hole mobilities in the range of 0.1–1 cm² V⁻¹ s⁻¹ have been demonstrated for p-type materials such as thiophene-based polymers,^[3–9] and these high mobilities have recently been matched by n-type polymeric materials—a major step towards the realization of polymer-based circuits based on complementary logic. Large electron mobilities up to 0.85 cm² V⁻¹ s⁻¹ have been achieved with a highly soluble, air stable, n-type polymer, poly{[N,N9-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene)}, (P(NDI2OD-T2), Polyera ActivInk N2200) in a staggered top gate configuration.^[9]

The importance of molecular packing and microstructure on the performance of p-type, thiophene based semiconductors is widely appreciated and has been extensively studied.^[4,8,10–14] It is generally believed that the best transport properties are attained when there is a high degree of in-plane π -stacking of the thiophene rings, facilitating two-dimensional (2D) transport in the plane of the substrate.^[12,15,16] Unfortunately, similar structure-property studies are not as well established in n-type polymers due to the dearth of high performing materials. In this paper, we investigate the molecular packing and structure for the high-performance n-type polymer P(NDI2OD-T2). X-ray scattering experiments reveal that this polymer exhibits an exceptional degree of in-plane ordering and adopts a largely face-on packing (π -stacking direction normal to the substrate),

which is an uncommon crystallographic texture for high field-effect mobility semiconducting polymers. We employ X-ray scattering from aligned films as well as atomic force microscopy (AFM) characterization of the top and bottom interfaces to support these findings, and discuss the implications of this unexpected crystalline texture for charge transport.

P(NDI2OD-T2) field effect transistor (FET) transport properties in both bottom-gate^[3] and top-gate^[9] configurations were carried out previously, however, limited structural characterization has been performed. Owing to the lack of significant diffracted intensity in specular X-ray scattering and the weak dependence of mobility on both polydispersity and molecular weight, it was suggested that this polymer lacked significant long range crystalline order, and was potentially amorphous.^[9] However, the nodular/fibrillar morphology evident by AFM, together with the melting-like differential scanning calorimetry (DSC) transition (Ref.^[9]) suggest the presence of a crystalline phase. Diffraction from similar rylene-based co-polymers revealed only weak scattering from a lamellar-like reflection, which is suggestive of only short range order.^[17] In both reports,^[9,17] diffraction data were collected in a specular geometry, probing the out-of-plane order of the thin films, with low intensity CuK α radiation. While the crystalline structure of similar polymers has been briefly investigated in extruded, fiber form,^[18] an extensive microstructural study of thin films of this class of high performance n-type polymers has not been performed.

Isotropic P(NDI2OD-T2) films were prepared for X-ray, AFM, and device fabrication as described in the Experimental section. A mobility of 0.18 \pm 0.04 cm² V⁻¹ s⁻¹ (for 5 devices) is measured when tested in the staggered top-gate geometry using Polyera D2200 gate dielectric, (Figure 1). This mobility is well within the high performance range reported previously^[9] for top-gated P(NDI2OD-T2) devices, assuring that films in this study are representative of the high-performance material.

To determine the molecular packing, a series of grazing incidence and specular diffraction scans were performed to probe both the in-plane and out-of-plane structure (Figure 2). A 2D grazing incidence X-ray scattering (GIXS) pattern of a spun cast film (Figure 2a), reveals only a broad, weak peak along the vertical axis (nominally q_z) at $q = 1.6 \text{ \AA}^{-1}$, corresponding to an expanded (3.93 \AA) π -stacking reflection. There are also remnants of diffraction at lower q in the specular geometry, but these features are weak and ill-defined. The majority of the diffracted intensity is found at the horizon of the 2D-GIXS patterns, corresponding to $q_z \sim 0$, or in-plane order. Because the unit cell of this polymer is not known, indexing of these peaks is challenging. Aligning the polymer backbones in the plane of the film reduces the symmetry of the microstructure and provides

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DOI: 10.1002/adma.201001202

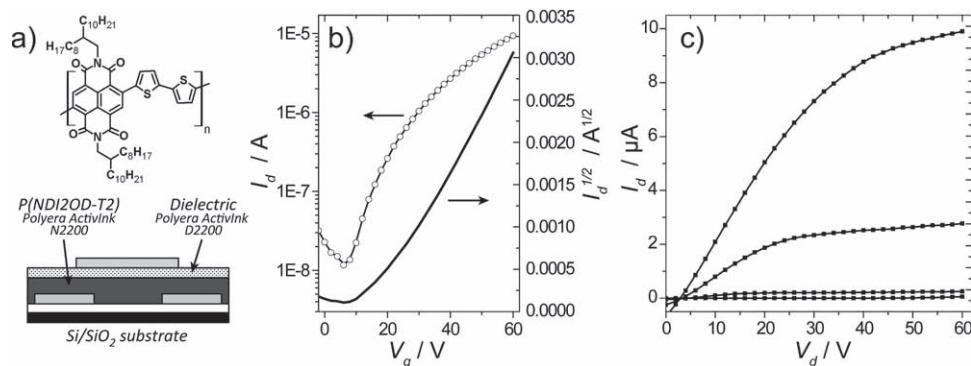


Figure 1. Electrical characteristics of a top-gated device. a) Chemical structure of P(NDI2OD-T2) (top), and staggered top-gate device structure (bottom). b) Transfer and c) output characteristics for a P(NDI2OD-T2) device with an electron mobility of $0.20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($W/L = 10$).

means to successfully index the diffraction peaks through knowledge of the macromolecular directions. Alignment of polymer films has been used to improve device performance,^[13,19] study inter-grain transport,^[20] and help elucidate crystalline packing motifs,^[13,21,22] as is the case here. Dip-coated AFM images of the P(NDI2OD-T2) films revealed an aligned, fibrillar morphology (Supplementary Figure 1), and are found to be highly anisotropic by X-ray analysis. Two-dimensional grazing incidence diffraction patterns (with the beam orientation parallel and perpendicular to the alignment direction) reveal that two families of reflections are present in the isotropic films, with the scattering vector near perpendicular and near parallel to the fibers, shown in Figure 2b,c, respectively. High resolution grazing incidence diffraction (Figure 2d) of the isotropic and aligned films with q perpendicular to the alignment direction reveals up to four orders of a lamellar stacking peak with the lowest order, (100), at $q_{xy} = 0.25 \text{ \AA}^{-1}$ ($d_{100} = 25.5 \text{ \AA}$). The data collected from both the isotropic films and with q parallel to the alignment direction show three peaks related to the chain backbone repeat. Due to the positions and breadths of peaks, it appears there are likely two polymorphs associated with the chain backbone, with the lowest orders (001) and (001') (exhibiting 2 orders) at $q_{xy} = 0.45 \text{ \AA}^{-1}$ ($d_{001} = 13.9 \text{ \AA}$) and $q_{xy} = 0.89 \text{ \AA}^{-1}$ ($d_{001'} = 7.06 \text{ \AA}$) respectively (see Supplemental Information). The experimentally determined (001) repeat distance is in good agreement with the 14.3 \AA chain backbone repeat distance determined from ChemDraw®. Such in-plane polymer ordering, including an unusual number of higher order reflections, is unprecedented in the realm of semiconducting polymer thin films, especially due to the inherent disorder and fluctuations often found in the crystalline phases of these materials.

X-ray diffraction features of different sets of reflections provide insight into the local spatial arrangement of the polymer chains. The lamellar stacking peaks tend to arc (Figure 2a,b) with an out of plane distribution approximately equal to that of the π -stacking peak, while the chain backbone repeat peaks (Figure 2a,c) are more rod-like. This suggests that the chain backbones lie flat on the substrate, while the in-plane lamellar stacking is less oriented, with significant deviations from strict in-plane texture. Coupled with the broad, weak, specular π -stacking peak, the complete X-ray data suggest that P(NDI2OD-T2) packs in a platelet-like geometry with only poor order out of

plane; nevertheless, one direction of the flat plane of the platelet (along the chain backbone) is very well aligned (parallel) with the substrate (Figure 3). Due to the broad π -stacking peak ($\Delta q = 0.14 \text{ \AA}^{-1}$), the crystallite thickness is estimated to be $\sim 3.7 \text{ nm}$ as determined from the Scherrer equation. It should be noted that this figure is a rough estimate due to the likely defective nature of the packing in the π -stacking direction. We also note that no mixed index peaks are readily observed in any of our diffraction data. This result, coupled with the broad π -stacking peak, indicates that there is poor registry between chains along the a - and b -directions of the lattice (suggesting poorly ordered alkyl side-chains). These findings are consistent with the microstructure sketched in Figure 3.

The data from both grazing incidence and specular diffraction clearly show a predominantly face-on molecular packing for P(NDI2OD-T2) films, which is surprising given its high mobility. Most high performance semicrystalline p-type polymers show a largely edge-on packing arrangement.^[15,16,23,24] Hence, until now, it has been assumed that edge-on packing for polymer FETs is advantageous and, indeed, necessary for high performance due to the fast 2D charge transport along the chain backbone and in the π -stacking direction. Face-on packing is sometimes found in films of low regio-regularity or low molecular weight polymers, and those processed from low boiling point solvents and on certain treated surfaces. This face-on packing is often cited as an inherently detrimental configuration causing poor device performance.^[8,10,11] Our X-ray characterization of P(NDI2OD-T2) films demonstrates that the relationship between edge-on packing and high mobility is far from general and that excellent in-plane transport properties can be obtained with a face-on packing texture. The question remains: how does P(NDI2OD-T2) attain such a high mobility if it has such a seemingly disadvantageous microstructure?^[25]

We note that in a transistor configuration, the largest contribution to charge transport is known to occur within the first few nanometers of the semiconductor near the dielectric interface.^[26,27] For well ordered liquid crystalline lamellar packed polymers that orient edge-on, such as poly(3-hexyl thiophene) (P3HT) or poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-b]thiophenes) (PBTTT), where the lamellar stacking distance is $\sim 1.5 \text{ nm}$, transport is largely dominated by the first interfacial monolayer and is essentially two-dimensional. Thus, any

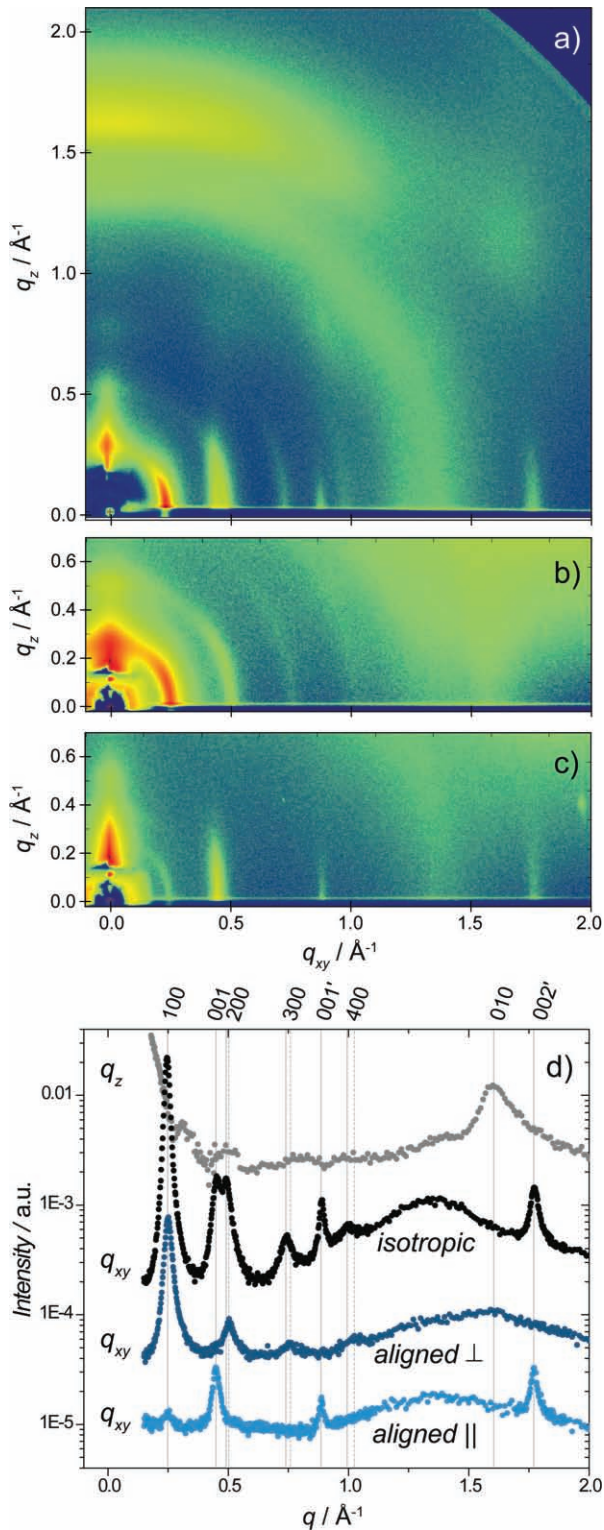


Figure 2. X-ray characterization of P(NDI2OD-T2) structure. a-c) 2D grazing incidence diffraction pattern from spun cast, isotropic film (a), dip coated, aligned film with scattering vector q nominally perpendicular to the fiber direction (b), and q nominally parallel to the fiber direction (c). d) high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

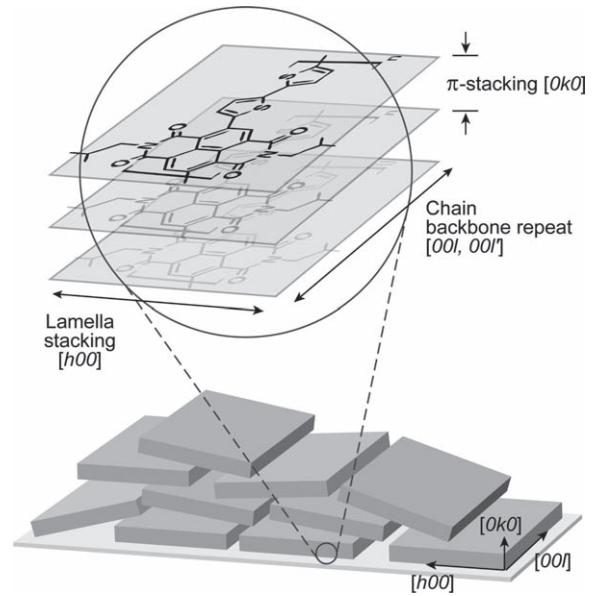


Figure 3. Schematic of face-on molecular packing of P(NDI2OD-T2) inferred from X-ray data (top) indicating the repeat directions referenced. Proposed microstructural arrangement of the crystallites (bottom) indicating slight disorder in the π -stacking and lamella stacking directions of the flat, platelet-like crystallites and alignment of the chain backbone direction with the substrate. The complete, branched octyl-decyl side chains are omitted from the schematic due to their unknown relative orientation and order.

barrier to charge transport, such as a chain end or kink must be avoided by hopping around the barrier within that interfacial monolayer. In a face-on packed system such as P(NDI2OD-T2), transport is more microscopically three-dimensional as charge carriers can escape a transport barrier near the dielectric interface by hopping to subsequent layers coupled by π -stacking out-of-plane. Indeed, with the observed π -stacking separation of 3.93 Å, the electrostatics of the transistor allows charge to populate at least 2–3 layers of semiconductor. At high molecular weights, (here, 300kD, determined by GPC), the chain length is approximately 15–20 times the grain size estimated from AFM and preliminary peak width analysis, suggesting extensive inter-grain connectivity, where one polymer likely belongs to a number of grains.^[28] Thus, if a charge hops to a neighboring layer along the π -stacking direction, it will likely find its way to an adjacent grain, thereby maintaining an efficient transport pathway.

Interestingly, the crystalline texture may affect band alignment in these materials. For instance, it has been shown by photoelectron spectroscopy and modeling that the magnitude of the ionization potential depends on the orientation of molecules relative to the surface of an ordered assembly.^[29] It is noted that the surface of a face-on assembly of oligothiophenes has an associated 0.6eV increase in the ionization potential, as compared to typical, upright packing of such oligomers.^[29] A 0.4eV increase in ionization potential has also been predicted in P3HT when a monolayer of the polymer is in the face-on rather than the typical edge-on arrangement.^[30] Thus, even if a slight increase in ionization potential exists for face-on vs.

edge-on packing in P(NDI2OD-T2); due to the collective surface dipole formed by the π -orbitals, a net benefit may arise with respect to charge injection in this electron transporting materials. Nevertheless, it would be interesting to investigate if the charge transport benefits of edge-on packing would persist in P(NDI2OD-T2) if such a texture could be obtained by controlling processing conditions.^[25]

The current understanding of this polymer's molecular packing does not provide specific information about the molecular packing at the top interface, the air/polymer interface, where the high performance top-gate device channel operates. Thus, atomic force microscopy was used to investigate the top surface, as well as the delaminated bottom interface, with the goal of comparing their morphologies (See Supplemental Information). In both the top and bottom surface, features on the order of 10–30 nm are evident and are likely due to the crystalline grains. This is supported by X-ray peak width analysis where the bulk crystalline grains in the chain backbone and lamellar stacking directions are estimated to be 25–30 nm (not shown). Thus, AFM characterization is consistent with the top and bottom interfaces being crystalline and displaying similar grain sizes as the bulk of the film.

In conclusion, we have investigated the molecular packing and microstructure of P(NDI2OD-T2) using a series of synchrotron X-ray diffraction geometries, and interface microstructure analyses. We suggest a basic packing motif for this polymer, showing predominant in-plane ordering and only weak out-of-plane π -stacking order. Although this packing motif is often considered counter productive for high performance thin film transistors, we propose a mechanism by which this packing may not be detrimental to in-plane electrical transport.

The implications of the high performance yet face-on packing of this polymer is important for further development of related n-type and ambipolar materials. The out of plane π -stacking also suggests an enhanced diode mobility, which was indeed recently observed.^[31] Nevertheless, the potential for high electron mobility out-of-plane, as well as the already observed high in-plane field-effect mobility, make the structural understanding of these materials important for both transistor and photovoltaic applications.

Experimental Section

Materials: poly{[N,N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bithiophene)}, (P(NDI2OD-T2)), Polyera ActivInk N2200), and the dielectric Polyera ActivInk D2200, was used as received (Polyera Corp, Skokie, IL). Synthesis and purification is described elsewhere.^[9]

Film Fabrication: Isotropic films were spun cast from solution (1–10 mg mL⁻¹) from 1,2-dichlorobenzene (DCB) at 1000 rpm, and annealed at 150 °C for 30 min. Aligned films were dip coated from 0.1 mg mL⁻¹ DCB solution, and withdrawn at a rate of 1.2 $\mu\text{m s}^{-1}$ in an enclosure with a nitrogen atmosphere. Films used for XRD were spun on silicon with native oxide; those for devices were prepared as described below. All substrates were treated with an octadecyltrichlorosilane (OTS) self assembled monolayer after a 20 min UV-ozone treatment. Spun film preparation was done in a N₂ glove box (<1 ppm O₂), and dip-coated films were prepared in a N₂ backfilled enclosure.

X-ray and AFM Characterization: X-ray scattering was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 7-2 (high resolution grazing incidence), 2-1 (high resolution specular scan

with a point detector), and 11-3 (2D scattering with an area detector, MAR345 image plate, at grazing incidence). The incident energy was 8 keV for beam lines 7-2 and 2-1, and 12.7 keV for beam line 11-3. The diffracted beam was collimated with 1 milliradian Soller slits for high resolution in-plane scattering and with two 1mm slits for specular diffraction. For both grazing incidence experiments, the incidence angle was slightly larger than the critical angle, ensuring that we sampled the full film depth. Scattering data are expressed as a function of the scattering vector $q = \frac{4\pi}{\lambda} \sin \theta$ where θ is half the scattering angle and λ is the wavelength of the incident radiation. Here, q_{xy} (q_z) is the component of the scattering vector parallel (perpendicular) to the substrate. AFM characterization was performed with a PARC Systems XE-70, in non-contact mode.

Transistor Fabrication and Testing: Films for device characterization were spun on Si/SiO₂ substrates with bottom Au contacts (channel dimensions of W = 100 μm and L = 3–10 μm). After spinning the active layer, the top gate dielectric, Polyera D2200 ($C_d = 5.59 \text{ nF cm}^{-2}$), was spin cast followed by the deposition of a top Au gate electrode. Samples were annealed at 100 °C for 10h before and 1–2h after spinning of the dielectric. Mobility was evaluated in the saturation regime, at a drain voltage $V_d = 60 \text{ V}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. A.S. and J.R. gratefully acknowledge financial support from the National Science Foundation in the form of, respectively, a Career Award and a Graduate Student Fellowship. This publication was partially based on work supported by the Center for Advanced Molecular Photovoltaics (Award No KUS-C1-015-21), made by King Abdullah University of Science and Technology (KAUST).

Received: April 3, 2010

Revised: May 10, 2010

Published online: July 9, 2010

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