# Interface Structure of Semiconducting Polymer Films

Abstract

Near-edge X-ray absorption fine structure (*NEXAFS*) spectroscopy reveals surprisingly little surface dichroism in high-molecular-weight regioregular poly(3-hexylthiophene) (*rreg-P3HT*) thin films spin-cast from a range of good to bad solvents. The thiophene ring orientation at both the air- and substrate-interfaces shows only a weak preference for the edge-on orientation, that depends little also on solvent conditions. The average orientation angle <α> is *57–62º* from normal for the ring $C_{1s} \rightarrow \pi^*$ transition. The alkyl side chains are disordered with <α> of *49–52º* for the alkyl $C_{1s} \rightarrow \sigma^*$ transition. This contrasts with published results from grazing-incidence x-ray diffraction studies which suggest a predominant edge-on orientation in the sub-surface or bulk. Friction-mode atomic force microscopy reveals a surface heterogeneity uncorrelated with topography that indicates the co-existence of various surface packing and orientation forms. The dominant spatial wavelength of this texture varies strongly with casting solvent from *10 nm* to few hundred nm, and tracks the solvent dependence of the hole-carrier field-effect mobility (μ_{FET}). π-stacking in all spin-cast films is significantly better at the substrate than the air interface, as evidenced by enhancement of the Rydberg intensities, and this broadly correlates with μ_{FET}. Therefore μ_{FET} in this material is still dominated by heterogeneity, particularly by a distribution of surface orientation and packing states. A further marked increase in mobility beyond *0.1 $cm^2V^{-1}s^{-1}$* should be possible.

Background

Semicrystalline semiconducting polymers typically adopt a local crystalline order in which the polymer backbones are aligned parallel to each other in the *c*-direction, the aromatic units are stacked in the *b*-direction, and the side chains occupy the *a*-direction. This is the case for *rreg-P3HT*. See cartoon below.
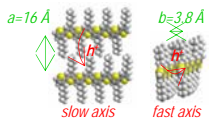
Due to their *1D* and disordered nature, charge transport must involve frequent hopping across chains. The hopping rate is dependent on the wavefunction overlap integral and is expected to be considerably slower in the *a*-direction (*ie., slow axis*) than in the *b*-direction (*ie., fast axis*).

Two possible local orientations of this fast *b*-axis relative to the sample plane have been identified in the last several years from grazing-incidence x-ray diffraction (*GIXRD*): edge-on and face-on (see left cartoon). *GIXRD* concluded that the predominant orientation of *rreg-P3HT* is edge-on in the sub-surface and bulk. Furthermore, it was assumed that this orientation persists to the interfaces where the interesting field-effect charge transport properties of these films are localised. This provides a nice explanation of the known high μ_{FET} (0.1–0.01 cm^2/Vs) in these films.

We show here using *NEXAFS* that this picture is incorrect: The orientation of polymer chains at the interfaces is considerably more random and thus far less optimal than previously held. Also the side chains are disordered. Hence it should be possible to obtain even higher mobilities from these polymers. Attempts to do so are underway.

## Near-edge x-ray absorption fine structure

In *NEXAFS* spectroscopy, soft x-ray photons are used to probe the transition energy, intensity and polarisation direction of core level electrons to empty states. In molecular and polymer systems, these empty states correspond to unoccupied molecular orbitals. The core hole thus produced is highly localised. This leads to strong excitonic effects, but otherwise makes simple interpretation of the spectra energies, intensities and polarisation possible.
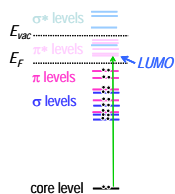
We conducted our measurements on *100-nm-thick* spin-cast *rreg-P3HT* films ($M_n \approx 20k$) at the *SINS* beamline of the Singapore Synchrotron Light Source (*SSLS*) with energy resolution ≈ *0.6 eV*. See left panel. Linearly-polarised and monochromatised x-ray photons were incident on the sample at preselected angles and the total electron yield *TEY* (photoemission + Auger + loss electrons) was collected as a function of the incident photon energy.
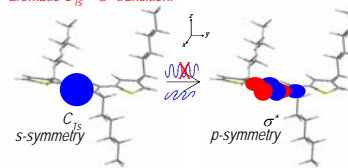
Surface x-ray dichroic ratios: dipole selection rules

aromatic $C_{1s} \rightarrow \pi^*$ transition:

aromatic $C_{1s} \rightarrow \sigma^*$ transition:
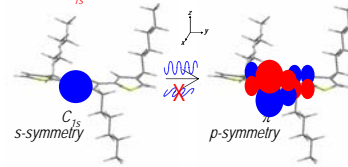
· The initial state C_{1s} is spherically symmetric. Thus the transition dipole moment µ for the *aromatic* $C_{1s} \rightarrow \pi^*$ transition is in the same direction as the final-state p_z orbital, which is normal to the plane of the thiophene ring.

· µ for the *aromatic* $C_{1s} \rightarrow \sigma^*$ transition, on the other hand, is in the same direction as the final-state p_y orbital, which is parallel to the plane of the thiophene ring.

· By measuring the surface dichroic ratios (*ie.,* polarisation dependence) for these transitions, the local bond orientation of the atoms involved is thus revealed.

· This information is averaged over the electron emission depth, which is extremely surface-sensitive, (frontier *2 nm*), for the *TEY* measured here.

· The challenge is to extract this information from the vast number of overlapping transitions that are observed. Here we found a way of extracting the σ* transition for the alkyl chains from the aromatic rings. Together with the well-resolved π* transition, this gives unambiguous information on the surface orientation of both the backbone thiophene rings as well as the alkyl side chains.

Dichroic ratios near unity: weak orientation preference

An unexpectedly weak polarisation dependence of the *NEXAFS* spectra was found, giving x-ray surface dichroic ratios near unity. Therefore only a weak orientation preference of the thiophene rings and the alkyl *CC* bonds occurs at the interfaces. A typical set of spectra collected for the chloroform spin-cast film is shown below. The resonances are assigned to *CC* π* (285.2 eV), *CS** (fitted, 287.0 eV), CH* (fitted, 287.4 eV), CH σ* and Rydberg resonances (fitted, 288–291 eV). Reliable angular dependence can be extracted for the *CC* π* and *CC* σ* transitions. The *CC* π* resonance is free from overlapping transitions while the *CC* σ* resonance (290–315 eV) requires curve fitting using empirical data to isolate the transitions from the alkyl side-chains and the aromatic rings that are also superimposed on the C_{1s} ionisation continuum background.
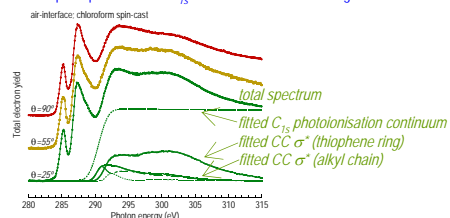
Air and substrate interfaces: order vs orientation
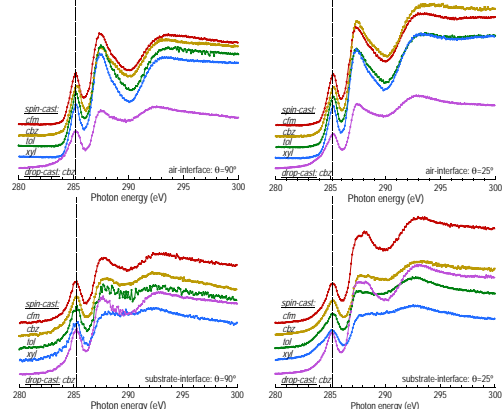
From the dichroic ratios, we deduced ring <α> values which give the average ring tilt angle with respect to the surface normal of the film. The values fall within a narrow range of 57–60º (±2º). The expected <α> values for isotropic orientation of the rings subjected to in-plane chain alignment is 45º; for pure edge-on orientation, <α> is 90º; and for pure face-on orientation, 0º. These polymer chains have a small preference for the rings to stack edge-on, but this preference is not overwhelming (65% edge-on *vs* 35% face-on), in contrast to published *GIXRD* studies. All the solvents investigated and both interfaces, even of the drop-cast chlorobenzene film. Therefore chains are the interfaces are oriented differently than the bulk. The p* band shows a red tail and the Rydberg intensity is markedly enhanced at the bottom interface (and at both interfaces for the drop-cast film). This indicates generally better π–π stacking at this interface. Therefore slow equilibration of the drying solvent produces better order but not better orientation.

brought to you by a partnership of the ONDL team and the SSL team:

ONDL: Lay-Lay CHUA, Peter HO (phyhop@nus.edu.sg)
SSL: Mandal DIPANKAR#, Xingyu GAO, Dongchen QI, Andrew WEE (phyweets@nus.edu.sg)
joint student of SSL and ONDL