	Experiment title: **GID investigations at thin film for organic field effect transistors**	**Experiment number**: SC 2102
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Report:

Recent research on organic and polymeric semiconductors is directed towards highly ordered molecular structures for the thin film organic field-effect transistors (OFETs). Poly-3-hexylthiophene (P3HT) is one of the promising materials for new OFETs. In order to study structural properties of P3HT thin films we applied grazing incidence x-ray diffraction (GID) which is a powerful technique for the structural investigations of the surface and subsurface regions [1]. In particular, GID is sensitive to the in-plane structure and allows extract an information about in-plane molecular ordering as a function of depth. Thin films of highly conjugated P3HTs were studied for low (LMW) and high (HMW) molecular weight fractions [2]. Our measurements were focused on LMW fraction. We expect that both polymorphs disappear at different temperatures close to the glass transition temperature.

First of all, the thicknesses of thin LMW films were probed by reflectivity and observations of 10-50 nm thick P3HT films were observed (see figure 1). For the LMW fraction, x-ray diffraction data show difference depending on concentration. For the low concentration most dominates amorphous broad humps with very weak (100) signal from stacked sheets oriented parallel to the substrate (red and blue curves, figure 2). Despite of the low concentrations of these films we found quite intense intralayer stacking (010) peaks. For the higher concentration GID surface scans reveal small crystalline domains embedded in amorphous

matrix. Here, additionally to a broad amorphous hump many crystalline peaks are visible. In order to interpret measured reflections (hkl-indexes) we assumed that the small crystalline domains are orthorhombic having lattice parameters **a** = 16. 5 Å, **b,c** = 7. 7 Å. A similar unit cell was suggested in [3].

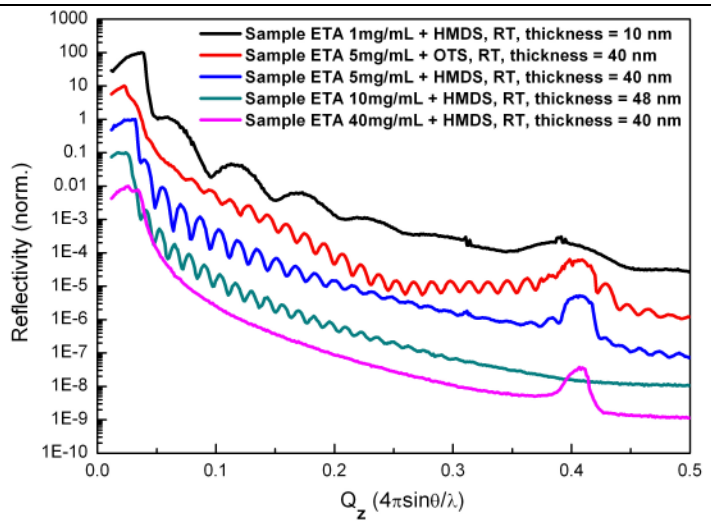

Figure 1: Reflectivity measurements of the 10-40 nm nm thick P3HT films with the different concentrations.

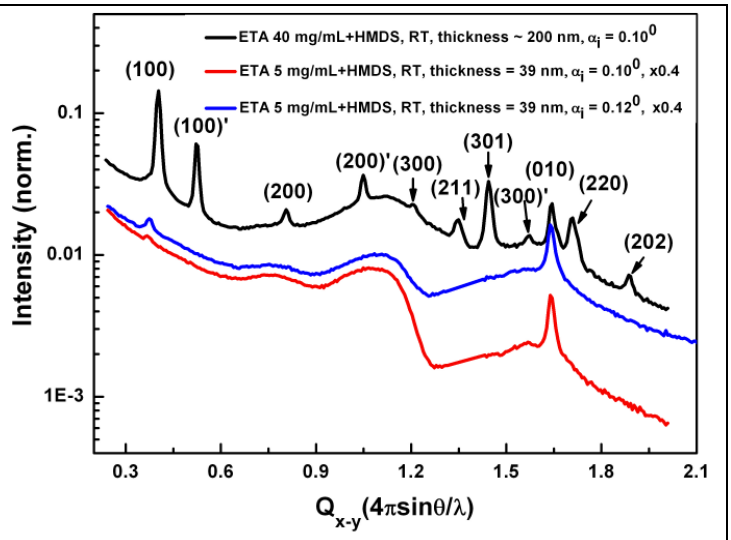

Figure 2: In-plane scan for different concentration of LMW samples with different angle of incidence (α_i).

Second part of the experiment was conducted with GID setup at in-situ annealed samples by Anton Paar DHS 900 domed hot stage. Performing out-of-plane scans in the large **Q** range later, simultaneously, the fine scans were probed in the vicinity of the (100) and (010) (see figure 3,4). We found a glass transition temperature of about 100° C and only slightly modified within concentration. These two peaks reveal an opposite nature of the thermal expansion. As one can see from the figure 4 that shift of (010) peak causes an decrease of intralayer distances with increase of temperature, while the (100) 'd' spacing is increasing which ultimately shrink the lamella laterally and expand it in normal direction.

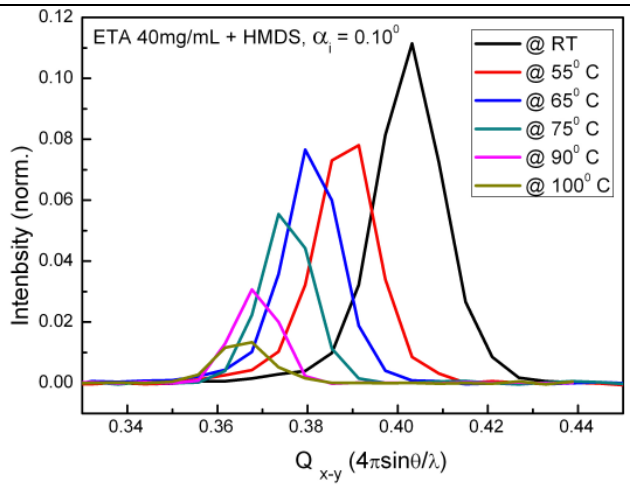

Figure 3: Influence of the temperature on the intensity of out-of-plane (100) peak at various temperatures for 40 mg/mL and films with the different concentrations.

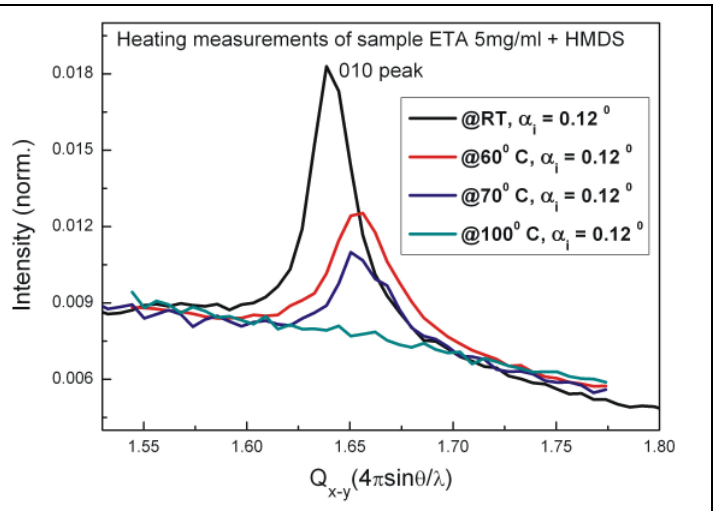

Figure 4: Out-of-plane 1st order (010) peak at various temperatures for 3 mg/mL LMW thin film.

Additional structural peaks shown in figure 5 confirm an existence of 2 crystalline forms for the LMW P3HT films. However, second (less intense) form is not stable with temperature and disappears after temperature treatment.

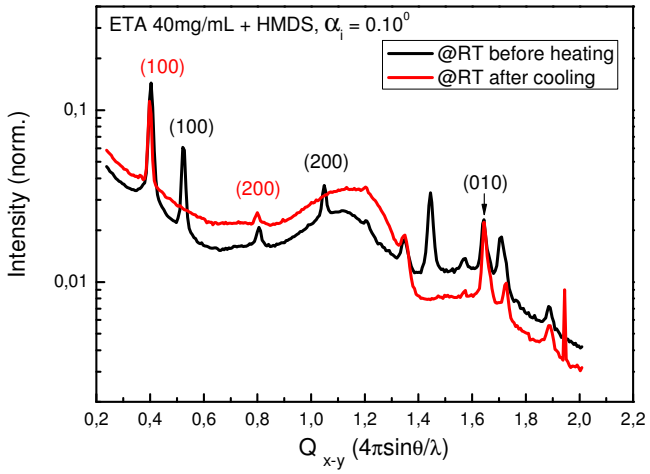

Figure 5: Out-of-plane GID profiles before and after (black and red curves, respectively) heating at 100°C for 40 mg/mL LMW thin film.

Therefore by temperature measurements for the LMW fraction for the first time two polymorphs have been clearly seen. Finally we have to mention that because of low scattering power such thin polymer films only can measured by use of synchrotron radiation in grazing-incidence geometry.

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References

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[2] A. Zen et al. Macromolecules 39, 2162 (2006)
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