ESRF	**Experiment title:** **Spatially dependent properties of π-π conjugated network in semicrystalline polymer thin films**	**Experiment number**: SC-3187
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Report:

Thiophene based polymers are promising candidates for OFET devices due to their easy processing conditions. They typically feature embedded in an amorphous matrix crystalline parts, which are assumed to be responsible for good device performance. Typically, experiments for structural investigation of thin films are carried out in grazing incidence diffraction (GID) under for x-ray total external reflection from the film surface. It provides depth resolved information on the structure but due to the large footprint obtained information is averaged accounting more than 10^4-10^5 crystalline nanodomains along whole film.

In the current experiment we have studied thin films nanoscale structural properties with special attention on the structural properties of the π-conjugated network. Quasi free standing thin thiophene based films (on thin SiN membrane) were investigated in transmission geometry which provides high nanosized spatial resolution. The films were spin coated or drop cast on silicon substrates of 100 nm thickness with rectangular windows of 2 mm x 50 µm size. The substrates including the windows were covered with a 15 nm SiN membrane to support the polymer film. Polymers under investigation during this experiment were poly(3-hexylthiophene) (P3HT) and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thio-phene) (pBTTT). The experiments were performed under ambient conditions at beamline ID13 at ESRF. The energy of the synchrotron beam was 15.25 keV and the beam size of 150 nm.

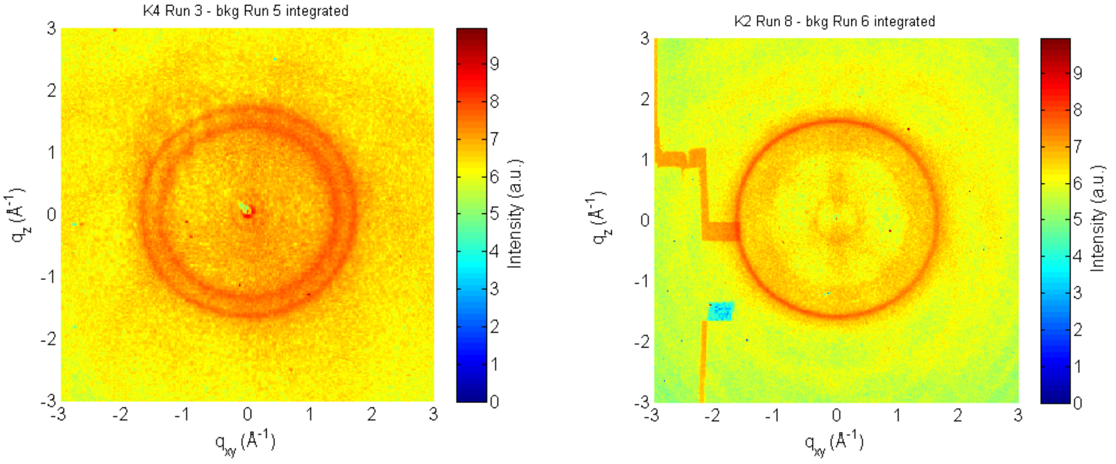

Figure 1: Transmission diffraction pattern for pBTTT (left) and P3HT (right)

The diffraction pattern observed in transmission mode at normal incidence for P3HT and pBTTT is shown in Figure 1. In the case of pBTTT (left) the inner (003) and the outer (020) rings can be seen indicating rather well 3D ordering [1], in contrast to the P3HT film (right) it shows only the (020) ring which is related to the π-stacking conjugated network.

As it is known from previously conducted experiments P3HT film is vulnerable to radiation damage [2]. However, the experimental setup did not allow keeping the sample under protective inert atmosphere in order to reduce radiation damage. Therefore, the stability of the polymers was checked in a separate measurement. Figure 2 shows the integrated Bragg peak intensities of P3HT and pBTTT. Both P3HT and pBTTT suffer significantly from radiation damage at long exposure times. The diffraction peaks of pBTTT decrease faster than P3HT. The exposure time for the following measurements was kept as short as possible (typically not longer than 5 seconds) to minimize radiation damage effects within single shot.

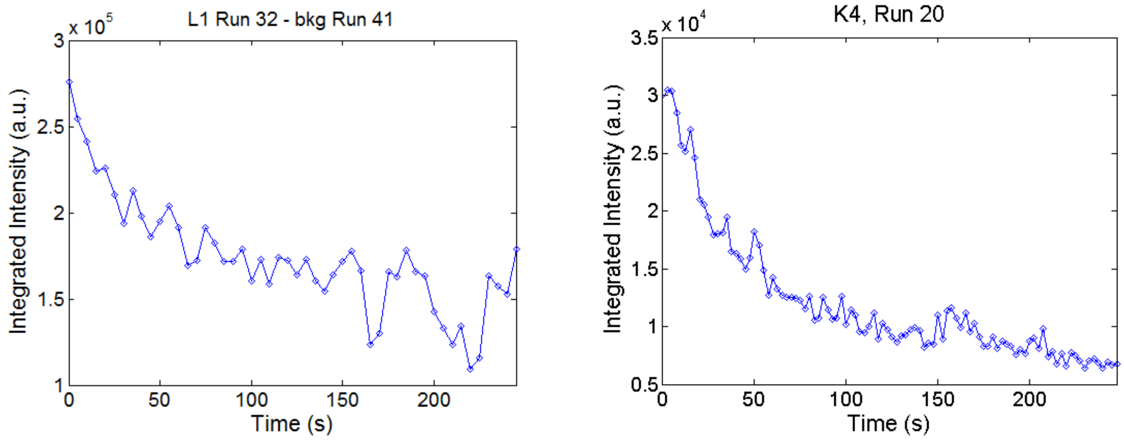

Figure 2: Radiation damage of P3HT in GID at $\alpha_i \approx 1°$ (left) and pBTTT at $\alpha_i = 20°$ (right)

In a second part of the experiment the samples were mapped spatially resolved in transmission geometry in order to resolve inhomogeneities within the film. The diffraction patterns of P3HT films showed slight variations in intensity along the diffraction ring as the beam was spatially scanned across the sample (thorough evaluation is under progress). In addition to the transmission experiments the diffraction patterns were also recorded at smaller incident angles (α_i up to 20°). Combination of the transmission and reflections under different inclination angles provide an unique possibility of the complete reconstruction of the 3D nanodomains embedded in amorphous matrix.

To summarize, we have demonstrated that transmission experiments at quasi free-standing polymer films are feasible with 150 nm sized beam nanobeam at beamline ID13. Moreover, a few tens of nm thick spin coated films have provided a clearly visible diffraction rings. Another positive issue is that diffracted pattern from polymer films proved to be stable with respect to radiation damage within fist few shots.

References

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