



Experiment title:

Analysis of nanocrystalline structure in thin Poly(3-hexylthiophene) films

Experiment

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Report:

Regioregular poly(3-hexylthiophene) (P3HT) is one of the most promising polymer material having high charge carrier mobility. In particular low (LMW) and high molecular weight (HMW) fractions of P3HT provide different structural and optoelectronic properties [1, 2]. The aim of the experiment was understanding and improvement of the structural properties of HMW fraction for a bulk as well as for thin films via surface engineering and recrystallization phenomena [3,4].

All the X-ray measurements were performed at ID10b of ESRF ($\lambda = 0.824 \text{ \AA}$) utilising an Image plate with 2048x2048 pixels of 65 μm size set at 30 cm apart from the sample. The beam size was 0.1x0.3 mm^2 . In all measurements, the incident angle and the angle of exit within the incident plane are α_i and α_f , resp., and the in-plane scattering angle is 2θ . For better comparison all angular coordinates are transformed into q-space [1]. All X-ray measurements were performed under vacuum conditions ($\sim 10^{-3}$ mbar) using the DHS 900 domed hot stage provided by Anton Paar GmbH, Graz, Austria. For temperature resolved measurements the temperature has increased in steps of 10 $^\circ\text{C}$ from room temperature to the melting point of the individual sample with an accuracy of $\pm 0.5^\circ$. Data were taken after stabilization of the respective temperature at sample surface. HMW P3HT ($M_n = 30,000$ g/mol) thin films of having different concentration exposed to X-ray on top of various substrates (Si/SiO₂, Si/SiO₂/HMDS, Si/SiO₂/OTS).

Typical temperature dependent structural variations of HMW P3HT on OTS modified substrate have shown in Fig.1 recorded by image plate exposure [3]. Unfortunately under shallow angle the furnace material was hit by the x-ray beam as well which explains the appearance of wide rings in the 9 nm^{-1} range, In addition, one can see the bulk sample has shown a typical wide angle reflections in 100 direction referring to alignment of micro-crystallites along the surface normal with certain angular width in the direction perpendicular to the surface normal.

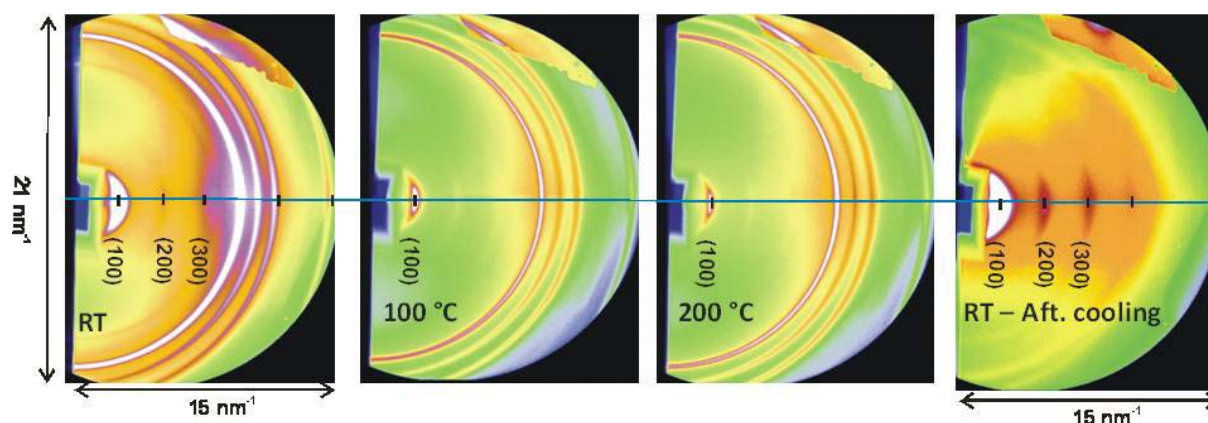


Figure 1 Temperature dependent structural improvement for OTS bulk sample for $\alpha_i = 0.05^\circ$

The width of this angular distribution decreases for increasing temperature. The ordering of the crystallites is improved after the 1st heating cycle which is visible by the increased intensity of 200 and 300 reflections comparing with the as-prepared state. Similar behaviour also was found for HMDS coated substrate for bulk samples having multiple heating cycles.

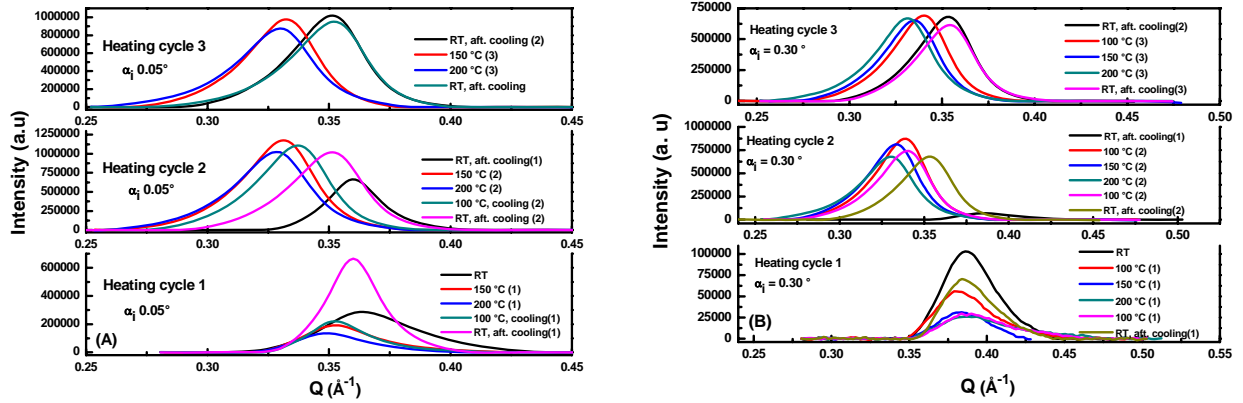


Figure 2 Temperature dependent cycles and (100) peak expansion along the normal direction for thick HMW P3HT on HMDS coated substrate for (A) $\alpha_i = 0.05^\circ$ and (B) $\alpha_i = 0.30^\circ$

These measurements allow to analyze the variation of (100) peak intensity as a function of temperature as shown in Fig.2. In general we observe a bi-modal behaviour. Whereas in 1st and 2nd cycle the peak positions changes rather continuous there are two distinct peak positions after the 3rd heating cycle, one refers to the room temperature and a second to the high-temperature. Inspecting the details in the 1st cycle the curve taken at an incidence angle below the critical one ($\alpha_i = 0.30^\circ$) shows an increase of intensity between RT and 100 °C followed by a decrease at higher temperatures. The other curves ($\alpha_i < 0.05^\circ$) provide continuous decrease in intensity with raising temperature as found for thin films. The continuous decrease of intensity with increasing temperature for smaller α_i ^s compared to the bulk film show that temperature induced morphological changes starts from the air-film interface and propagate towards the film-substrate interface. The process of thermally induced reorganization appeared less pronounced for OTS treated substrate, which ultimately gives hint that OTS could be good material for as spun samples. This point can also be confirmed from Fig. 3. Here the effect of annealing for samples with films thickness of about 200nm and different surface treatment is summarized. Without discussing further, one can see that HMDS or SiO₂ treated samples show best structure ordering after annealing whereas OTS treatment is good for as prepared samples only.

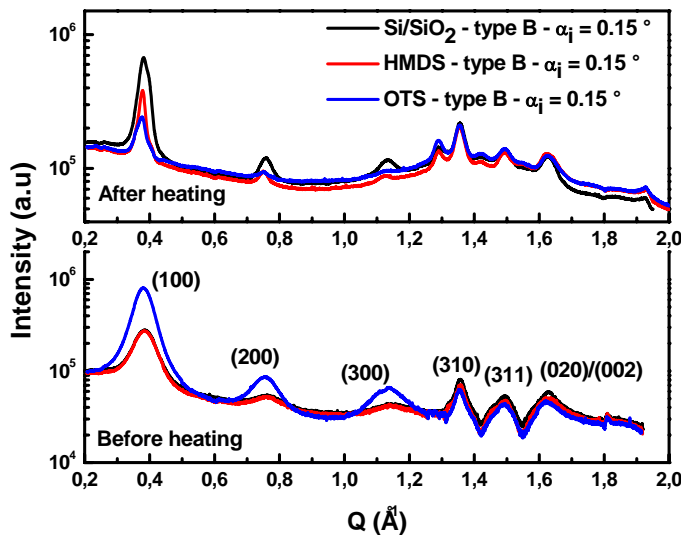


Figure 3 Out-of plane scans for three different substrates for before heating (bottom) and after heating (upper) for $\alpha_i = 0.15^\circ$

Fig. 4 shows the depth dependence of the angular distribution of out-of plane (100) peak orientation for thick and thin films along the in-plane direction. This information is taken from 2D diffraction maps as shown in Figure.1, measuring the widths of the (100) peak along Q_{\parallel} (vertical axis in Fig.1). In case of a complete random orientation of crystallites the 2D pattern will show closed Debye-Scherrer rings, but a uniform orientation would appear as single spot on Q_z axis (horizontal axis in Fig.1). Again, we exploited the depth resolution of x-ray beam tailored by choosing α_i larger or smaller α_{cf} . Here $\alpha_i = 0.05^\circ$ corresponds to measurement ~ 10 nm below the surface whereas the total film is measured for $\alpha_i = 0.30^\circ$. Comparing thick and thin films we see major differences. For thick films the orientation distribution of (100) peak is smaller at high temperature (HT) within the whole film. The room temperature (RT) values (before and after heating) are same at top surface and decrease towards the bulk. For large penetration depth the FWHM is decreased after annealing. This can be interpreted by temperature induced reorganization within the film. At HT the size of crystallites along (100) increases collecting polymer material from their vicinity. Reducing the temperature the crystallites becomes partially destroyed only with the effect that the orientation distribution is improved after annealing. The behaviour is opposite for thin films. Due to small film thickness we are no more depth dependence and the FWHM is by factor 4 larger at HT compared to RT values before and after annealing. Small variation of orientation distribution at HT is in accord with the larger number of small sized crystallites shown in Fig. 4A which is a strong hint for the influence of the film-substrate interface.

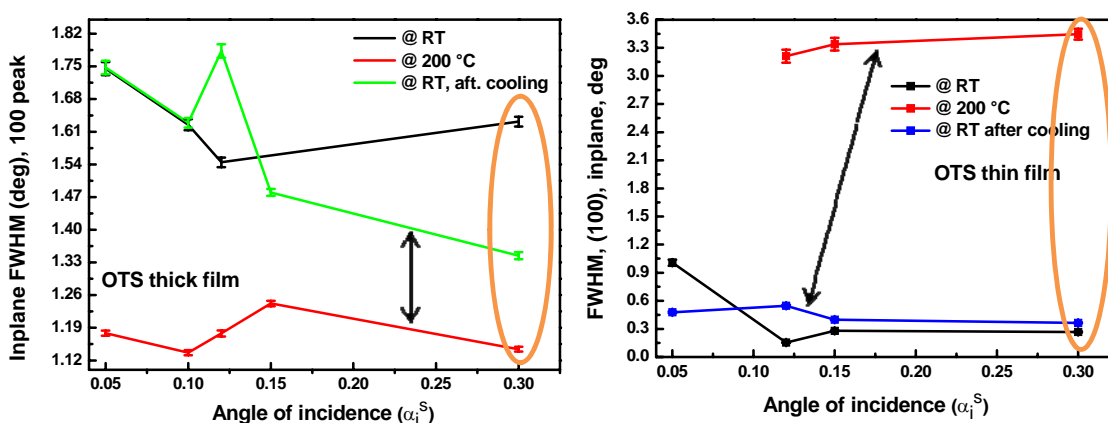


Figure 4 Depth dependence of FWHM for in-plane 100 peak for thick (left) and thin (right) films on OTS substrate.

Combining all these one can conclude, we have seen structural improvement with step up heating, where the number of heating cycle can play an important role for optimization of as-prepared films. It became obvious that the 1st heating cycle is not sufficient to transform the film morphology into the thermodynamically equilibrium. After 3 cycles we have noticed a dual-form behaviour of HMW P3HT fraction, where one face can be access at elevated temperature while other at RT. The HT structure can be characterized as a thermotropic phase appearing in addition to the phase found at RT [5]. Films made from HMW fraction have shown crystal growth only along surface normal direction. However, no specific interface layer has been found. Thin films of 10 nm thickness behave as a whole, while bulk films have shown that changes of morphology have started from the air-film interface. Our results are important for the improvement of electronic performance of respective OFET devices made from HMW P3HT.

References

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