

X-ray diffraction studies from surfaces and interfaces of high-molecular weight poly(3-hexylthiophene) P3HT fraction

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Regioregular poly(3-hexylthiophene) (P3HT) is one of the most promising polymer material having high charge carrier mobility. Up-to now high molecular weight (HMW) P3HT has shown the lower crystalline order compare to low-molecular weight (LMW) material^{1,2} but exhibit higher mobility $\sim (10^{-3} - 10^0) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, due to the presence of inter-chain and intra-chain networking system between the next neighbour molecules. One of the fundamental problems which still exist is to maximize the charge-carrier mobility of HMW P3HTs for polymeric electronic devices. Our current studies based on to correlate the enhancement of structure ordering from such HMW P3HT thin films to the improvement of charge carrier mobility.

All X-ray measurements were performed at Beamline BW2 as well as Beamline W1, Hasylab, Hamburg. 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 °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). All the results are summarized below –

From figure 1(A) one can see the general behaviour of out-of-plane diffraction scan (OOP) for 40 mg/mL. The presence of multiple peaks indicates the random orientation of the crystals inside in as prepared film. In addition one can observe the decrease of (100) peak FWHM after heat treatment indicating the increase of crystallite size along the normal direction. It ultimately indicates the increasing ordering of alkyl chains with the main thiophene chains for increasing temperature. Appearance of big amorphous halo centred on 1.4 \AA^{-1} indicates that such nano-crystallites are randomly distributed along the whole amorphous region. At the same time from figure 1(B) one can see the temperature dependence of (100) peak intensity, the (100) peak intensity increases up to some elevated temperature indicating the increase of alkyl chains ordering as well as the expansion of 100 d-spacing indicated by shift of Bragg peak position to smaller q-values. The opposite trend has been observed for in-plane (020) peak measuring the π - π stacking planes. Figure 1C shows development of integrated intensity of (100) peaks as function of temperature. It shows that number of such crystallites increases up to about 200°C. Also figure 1C shows the different recrystallization for samples with different interfaces. The development of FWHM vs temperature is shown in Fig.1D which is a measure for the size of crystallites. All these investigations have been performed also for samples, where the substrate surface was modified by OTS (Octadecyltrichlorosilane) and HMDS (Hexamethyldisilazane) and compared with films of pure SiO₂ interfaces (figure 1C & 1D). In summary of our investigation one can conclude that in HMW P3HT films the morphology consists of nano-crystallites of certain sizes (10-25 nm) embedded in an amorphous matrix.

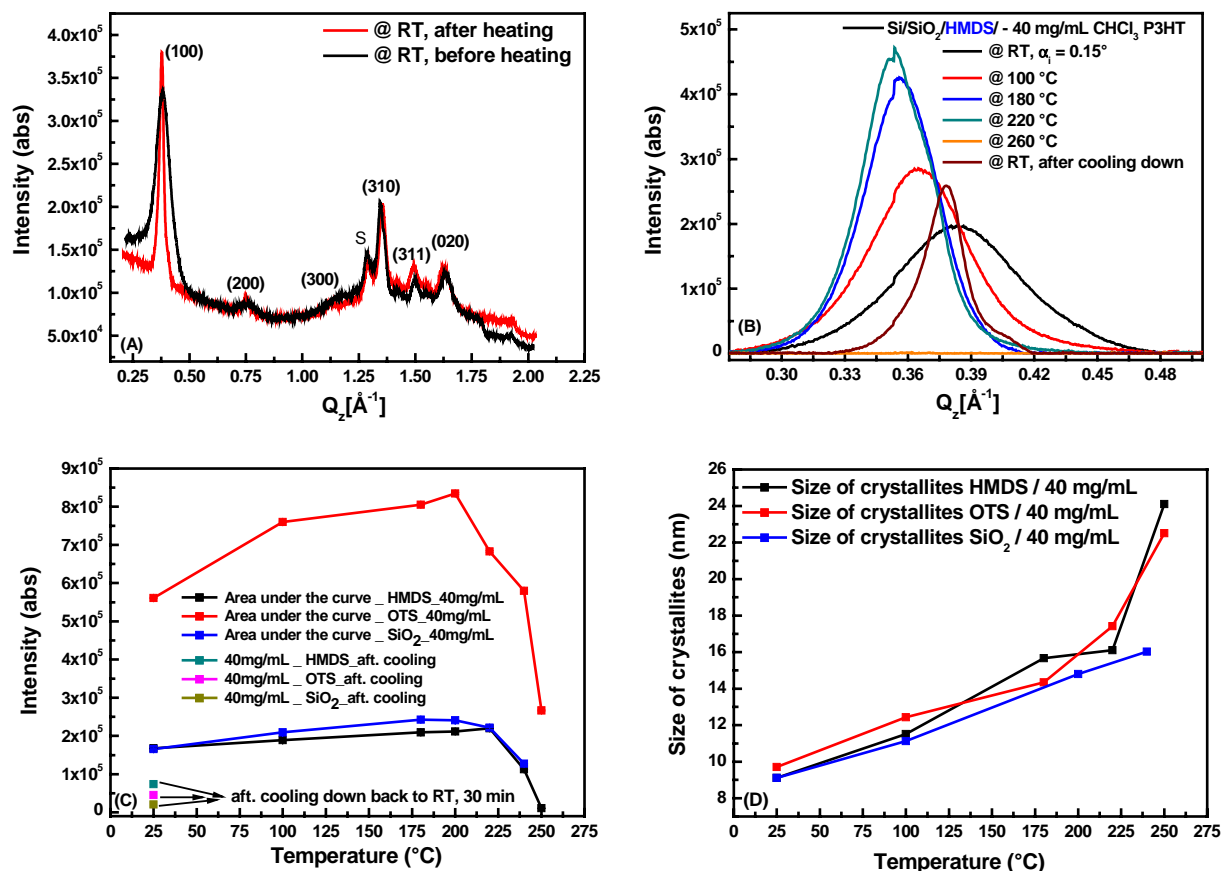


Figure 1. 1(A) Out-of-plane scan for 40mg/mL HMW P3HT on top of HMDS substrates, (B) temperature dependent variation of (100) peak, (C) Variation of area under the curve (volume of 100 peak) at elevated temperature for 40mg/mL P3HT concentration for different interface layers, (D) Variation of size of crystallites Vs elevated temperature for different interfaces.

The HMW fraction has shown an improvement of crystalline ordering and increase of size of crystallites at elevated temperature. Different crystal growth behaviour of thin and thick films prepared on same interface (HMDS) has been observed. The time of cooling or time of re-crystallization might also influence the re-crystallization behaviour. The 'd' spacing associated with the stacking of alkyl-chains increases, while the 'd' spacing corresponding to the π - π in-plane stacking decreases with increasing temperature. However the improvement of crystalline order has been found to certain temperature followed by a decrease of ordering at much higher temperature caused by melting of polymer material. This thermal behaviour of HMW material is in contrast to the properties found for films made from low molecular weight material where a continuous decrease of (100) intensity has been found for increasing temperature [1,2].

References:

- [1] Zen, A., et al., *Macromolecules*, 39, 2162, 2006
- [2] Joshi, et al., *PSS (a)*, submitted.

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