

Influence of Alkyl Side-chain Length on the Orientation and Crystallinity of Poly(3-alkylthiophene) Thin Films Prepared by Spin Coating as well as Low Temperature Drop Casting Technique

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In the day-by-day growing organic electronics field solution processable conjugated conducting polymers are becoming a building block for the fabrication cheap and ductile electronic equipments.[1, 2] Among the various conjugated polymers, solution processable poly(3-alkylthiophene)s (P3ATs) are widely in use for the fabrication of organic field effect transistor (OFETs) and solar cells etc. Current research is devoted to the influence of alkyl side-chain length on the structural and morphology of P3AT polymers which are grafted on the third position of the thiophene ring in order to make them soluble in common organic solvents like CHCl_3 , toluene, and xylene. The insulating alkyl side-chain grafted on the thiophene backbone hampers the charge transport along the alkyl side-chain stacking direction. Casting of P3AT films mainly results in two orientations while self-organizing called as edge- and face-on. The edge- and face-on oriented crystallites can be distinguished from the direction of π - π stacking i.e lying parallel and perpendicular to the substrate plane, respectively.[1, 2]

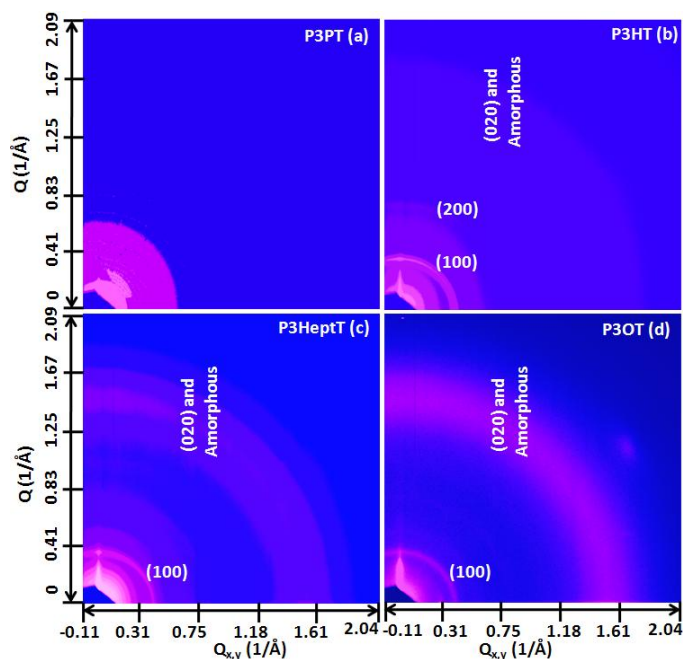


Figure 1: 2D diffraction pattern of spin coated P3AT thin films

During our last beam time at P08 (PETRA III), we have thoroughly analysed the influence of alkyl side-chain length on the crystallization and orientation of room temperature (RT) spin coated and RT and -30°C drop cast P3AT thin films. The analysis was carried out by choosing the following polymers; poly(3-pentylthiophene) (P3PT), poly(3-hexylthiophene) (P3HT), poly(3-heptylthiophene) (P3HeptT), and poly(3-octylthiophene) (P3OT). The 2D grazing incidence X-ray diffraction patterns

(GIXD) of as-spin coated P3AT thin films are shown in Figure 1. We could not observe any Bragg reflection for the as-grown P3PT thin film which confirms the absence any crystalline phases. On the other hand, P3OT results in two Debye-Scherrer rings indexed as (100) and (020) which confirm the presence of randomly distributed crystallites without any preferential orientations. The crystallites are becoming textured after the post growth annealing (undercooling of $\Delta T = 45^\circ\text{C}$ from the melting point), but they are having both the face- and edge-on oriented crystallites. A line profile along out-of- (GOD) and in-plane (GID) directions was extracted and they are presented in Figure 2a and 2b, respectively. The diffracted intensity of (100) reflection is getting weaker as decreasing the side-chain length along in-plane direction (Figure 2b). The same behaviour can be observed the RT cast P3AT thin films as well but the face-on oriented crystallites are completely absent while casting at -30°C and the percentage of face-on oriented crystallites are reducing with decrease of the cast temperature from RT. The increase of face-on oriented crystallites as increasing of the alkyl side-chain length might be attributed to the delay in initiation of the nucleation because of the increased solubility of P3ATs. The X-ray findings are in agreement with the high-resolution transmission electron microscopic images (HR-TEM) i.e increase of face-on oriented crystallites as increasing the side-chain length which is not favour for the fabrication of OFETs.[1, 2] The statistical nanodomain sizes extracted from the HR-TEM images of RT spin coated film confirm that P3OT (21nm) has the longest nanofibrils as compared to P3PT (11nm) ones after the post growth annealing and it reduces gradually as the side-chain length decreases. The post growth annealing mainly helps for the ripening of P3AT crystalline domains along alkyl side-chain stacking and π - π stacking direction but marginal effect was observed along stem direction i.e. along polymer backbone because of the folding and increased π - π interaction between the polymer backbones which can hinder the sliding diffusion of thiophene backbones.[3]

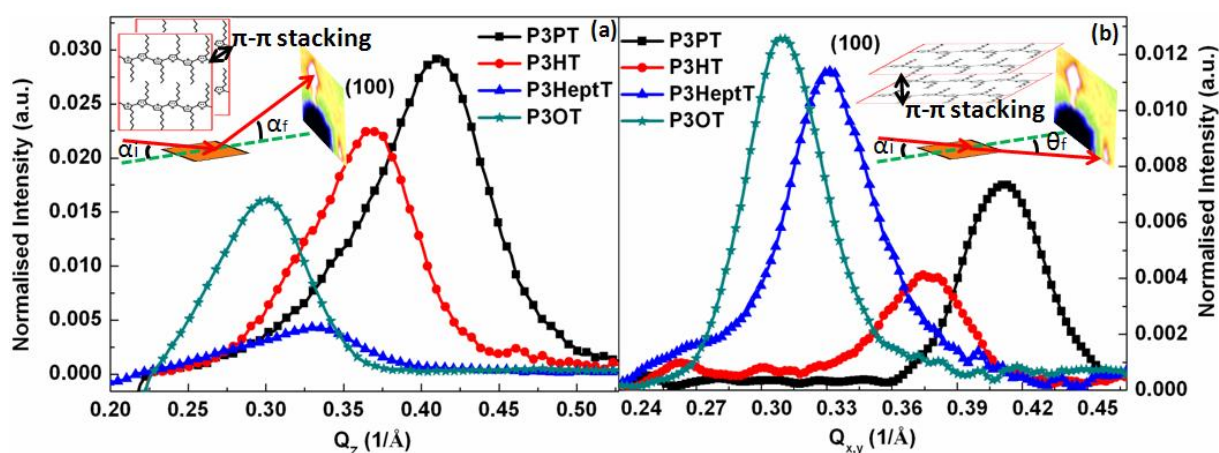


Figure 2. Shows the GOD and GID profile of annealed P3AT spin coated films which corresponds to the edge-on and face-on oriented crystallites, respectively

References

1. So, F., *Organic electronics: materials, processing, devices and applications*. 2009: CRC.
2. Wong, W.S. and A. Salleo, *Flexible electronics: materials and applications*. 2009: Springer Verlag.
3. Shabi, T.S., et al., *Impact of thermal annealing on the semi-crystalline nanomorphology of spin-coated thin films of regioregular poly(3-alkylthiophene)s as observed by low dose High resolution Transmission Electron Microscopy and Grazing Incidence X-ray diffraction*. *Macromolecules*, 2012 (submitted)