

気液界面上に作製したポリチオフェン薄膜における分子配向の研究 Investigation of molecular orientation in thin films of polythiophenes fabricated on air-liquid interface

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Introduction: Performance and operational lifetime of organic material based electronic and optoelectronic devices depend on the degree of electron delocalization and its stability. Apart from material properties, another challenge in exploiting the potential of organic electronics is its cost, user-friendly, and ordered/crystalline thin film fabrication techniques. Therefore, a facile deposition technique is highly desired to have precise control over polymer chain ordering along with large area homogeneous thin film fabrication. In this work, the floating-film transfer method (FTM) has been utilized, which provides a large area, highly oriented, crystalline, and smooth polymer thin films. In the case of self-assembled conjugated polymer thin films, the edge of the crystalline domains corresponds to the folded polymeric chains. These folding introduces constraints in the growth of crystalline domains by limiting the successive molecular chain packing as well as causes lattice parameter fluctuation. Therefore, local alignment of polymeric chains in close proximity via π - π stacking can counterbalance disorders like backbone twisting, chain ends, stacking faults, etc. This work provides a novel technique to fabricate highly edge-on oriented thin solid films of polythiophene and its derivatives.

Experimental: Chloroform solution of polythiophene and its derivatives like PBTTT, PQT and P3HT were allowed to spread spontaneously over the liquid mixture of Ethylene glycol and Glycerol (1:1 V/V). The thin film was then transferred to a desired substrate and dried at 70°C for 2 hours in vacuum. For OFET fabrication, in a bottom-gate top-contact structure, source drain electrodes were thermally deposited on the FTM films coated on Si/SiO₂ substrates. The thin films were characterized by UV-Visible spectroscopy, Transmission electron microscope (TEM), and X-ray diffraction (XRD) measurements.

Results and Discussion: The meridional XRD scan of the thin films show progressive diffraction (h00) peaks corresponding to side-chain interdigitation. The inter-planar spacing $d_{(100)}$ were found to be 21.05Å, 16.45Å and 16.27Å for PBTTT, PQT and P3HT respectively. The difference in d -spacing along a -axis for these three polymers can be attributed to the dissimilarity in sidechain length, degree of interdigitation and the tilting of polymer backbones across the c -axis. Probing surface tension gradient driven flow, we extend the average coherence length (i.e., average crystal size) along (h00) direction up to nearly 14.56 nm, 15.80 nm and 25.26 nm for P3HT, PQT-12 and PBTTT respectively. From the HR-TEM images, it is found that, chain folding is more likely in case of P3HT as compared to PBTTT. This is because of side chain density in P3HT is nearly twice than in PQT-12 and PBTTT which makes its backbone more flexible as compared to others. Formation of low-energy planar backbone conformation in PBTTT, due to reduced steric hindrance among adjoined alkyl side-chain also facilitates domain size enhancement. A thorough analysis of the individual crystalline domain for all three polymer films reveal the existence of a periodic contrast modulation with a period of 3.50 ± 0.10 Å, 3.64 ± 0.04 Å and 3.56 ± 0.12 Å for PBTTT, PQT and P3HT, respectively. These contrast modulation in the HR-TEM bright field image corresponds to the succession of electron-rich conjugated polythiophene backbones and the intervals are congruous with the inter-planar spacing $d_{(010)}$. Intense (020) equatorial reflection, as found in SAED pattern, in all of three polymers films evidenced the population of “edge-on” lamellae subjugated the local crystal orientation in the film plane. As grain boundary resists charge mobility, large coherence length justifies higher charge career mobility for PBTTT in comparison to other two polymers. Thus, FTM manipulates the relative orientation and spacing between molecules and enhances the electronic and optoelectronic functionality by assembling polymers at the air-liquid interface.

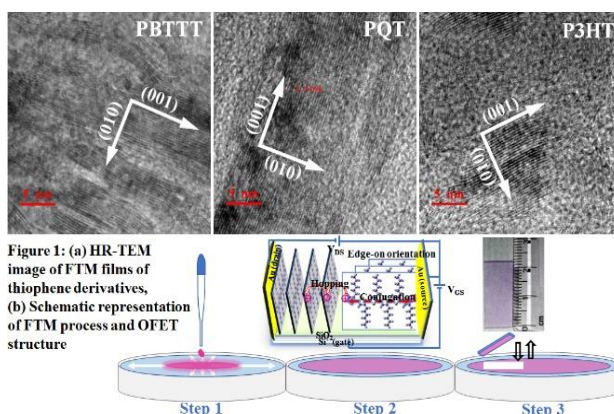


Figure 1: (a) HR-TEM image of FTM films of thiophene derivatives, (b) Schematic representation of FTM process and OFET structure