

Supplementary Information

Alkyl Side Chain Length Modulates the Electronic Structure and Electrical Characteristics of Poly(3-alkylthiophene) Thin Films

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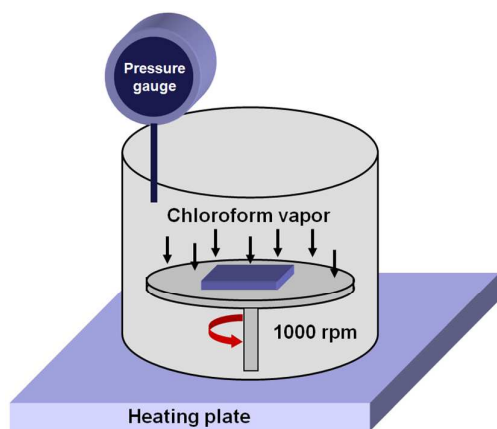
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Insights into the inner structures of the P3AT nanowire thin films were sought by collecting synchrotron grazing-incidence wide angle X-ray scattering (GIWAXS) profiles in the out-of-plane mode. The GIWAXS profiles revealed that as the solvent vapor pressure increased, the first Bragg peak (100) grew stronger (Figure S2). The morphology of the P3AT films produced by spin-coating under ambient conditions, in which the degree of molecular order is low, was quite different from the morphology obtained under a high vapor pressure. Film fabrication under a high chloroform vapor pressure allowed the solvent to evaporate slowly, which dramatically improved the degree of ordering within the crystalline domains.

The preferred orientations of the ordered domains in P3BT nanowires deposited on an insulator substrate were found to be along the (100)-axis normal to substrate and along the (010)-axis in the plane of the film. The schematic diagram shown in the inset presents the crystallographic structure of a P3AT nanocrystallite with respect to the insulator substrate, where the (100), (010), and (001) axes correspond to the directions of the side chains, π - π stacking, and main chains in P3BT. We propose that high vapor pressures induce these domains to orient themselves nominally edge-on, with the π -stacking interactions oriented in the plane of the substrate. This structure gives rise to two-dimensional charge transport properties in the film.^{23,24} Based on the morphological studies and X-ray studies, we proposed that the P3AT chains in the nanowires were packed such that their π -systems were parallel to one another and the alkyl lateral chains were perpendicular to the plane of the substrate. This π - π stacking orientation would be consistent with the high mobilities observed in the FET measurements, although the exact structural details at the dielectric/organic interface are not available at this point. The fabrication of P3HT and P3OT films under high vapor pressures also improved the degree of ordering (data not shown); however, we could not obtain good GIWAXS profiles in the in-plane mode. It was very difficult to compare the peak intensities quantitatively in the in-plane mode due to the large baseline noise in the very thin P3AT film (6–7 nm).



Scheme S1. Schematic representation of the modified spin-coater in a closed chamber fitted with a pressure gauge.

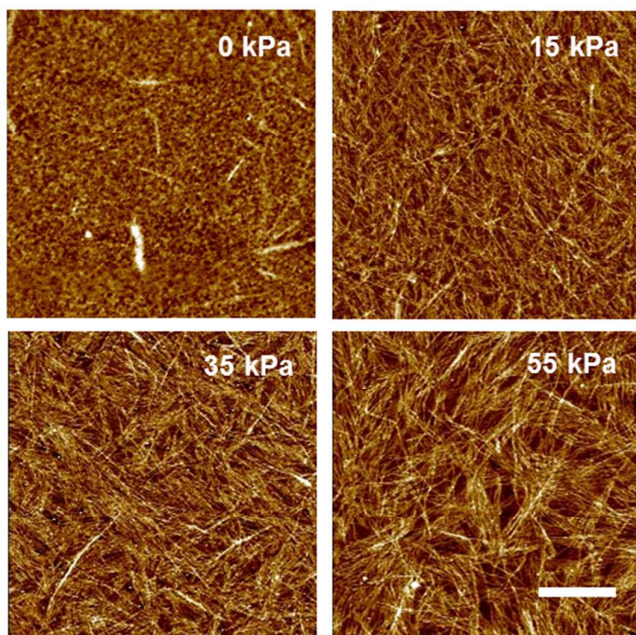


Figure S1. AFM topographical images ($5 \times 5 \mu\text{m}^2$) of spin-coated P3BT films prepared under various solvent vapor pressures: ambient conditions, 15 kPa, 35 kPa, and 55 kPa. (the scale bar is $1 \mu\text{m}$.)

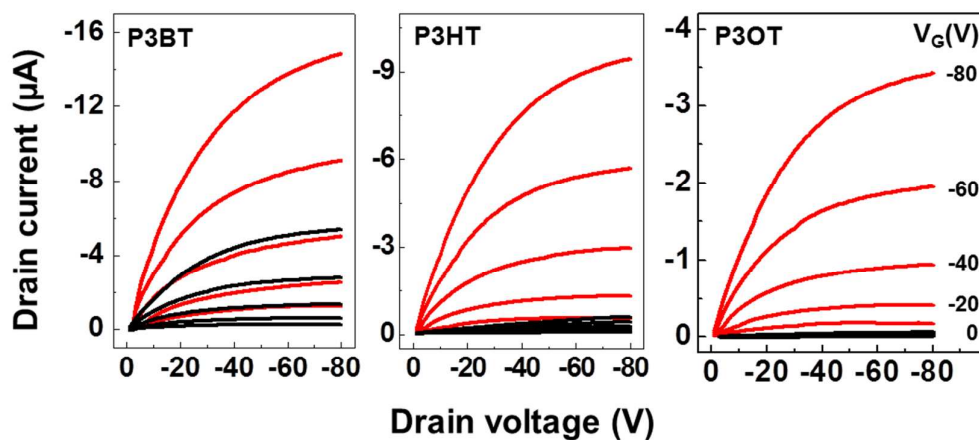


Figure S2. Current-voltage output characteristics of the FETs based on P3AT films spin-coated under an ambient atmosphere (black line) or under a high solvent vapor pressure, 55 kPa (red line).

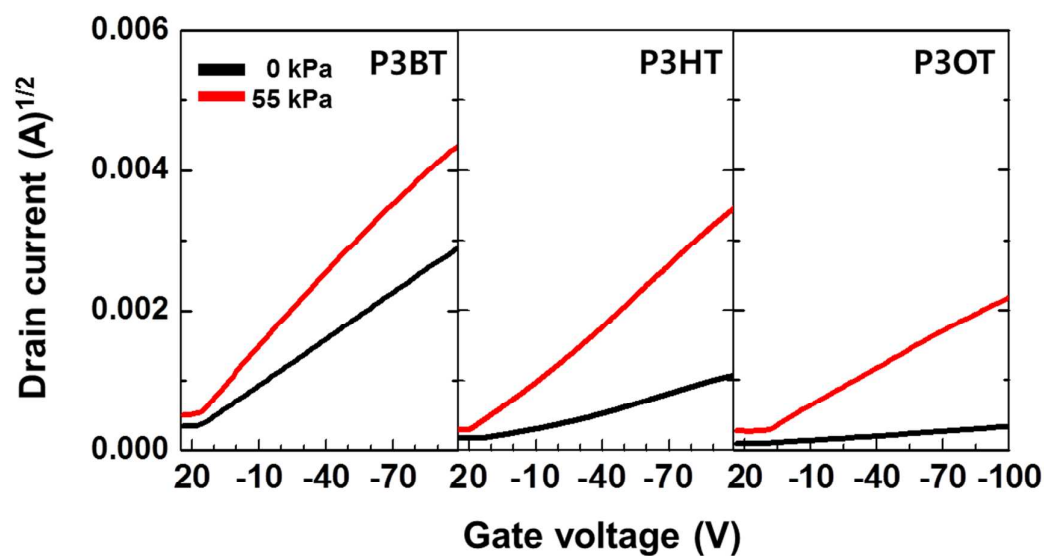


Figure S3. The transfer characteristics of an FET based on P3AT films spin-coated under an ambient atmosphere (black line) or under a high solvent vapor pressure, 55 kPa (red line).

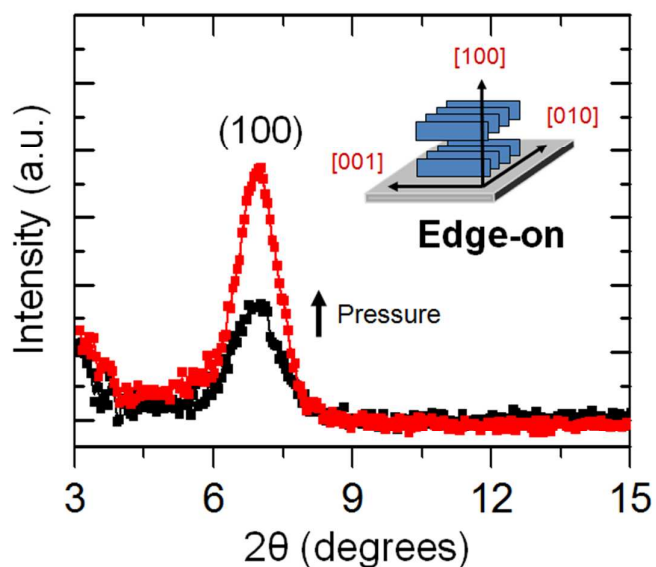


Figure S4. GIXD patterns obtained as a function of the scattering angle 2θ for P3BT thin films self-assembled on insulator substrates under the following solvent vapor pressures (black line, 0 kPa; red line, 55 kPa).

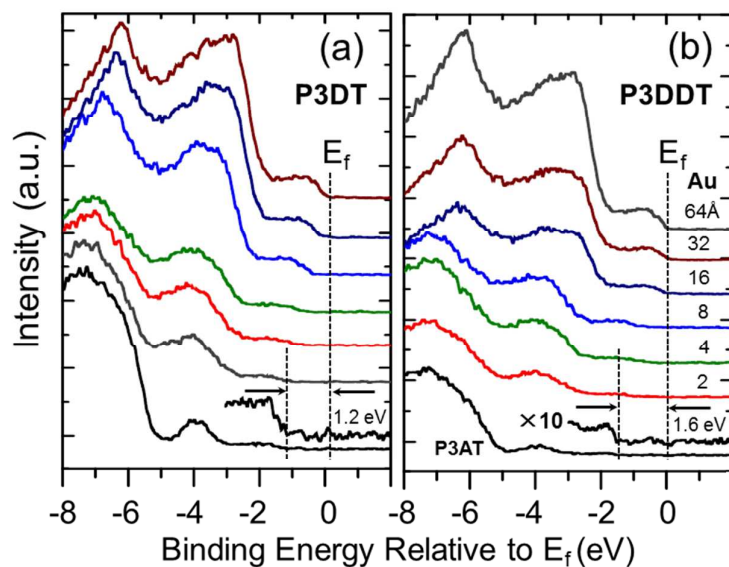


Figure S5. X-ray photoelectron spectra of Au deposited on a P3AT film. Changes in the valence band spectra of the (a) P3DT, and (b) P3DDT films as a result of Au deposition.