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Process-dependent Nanostructure and Crystallinity Competition in All-Conjugated Poly(3-hexylthiophene) Block Copolymers YEN-HAO LIN, RAFAEL VERDUZCO, Rice University, VERDUZCO LAB TEAM — The nanostructure of active layer in organic photovoltaic (OPV) is critical to charge transfer and power conversion efficiency (PCE). This study elucidates a model example of crystallinity competition and process-dependent nanostructures in various composition of an all-conjugated block copolymer, poly(3-hexylthiophene)-*b*-poly(9′,9′-dioctylfluorene) (P3HT-*b*-PF) synthesized from a combination of Grignard metathesis and Suzuki-Miyaura polycondensation. In contrast to previous studies of P3HT-based all-conjugated block copolymer where P3HT typically dominates the final morphology through crystallization. Grazing-incidence X-ray scattering (GIXS) measurements verify that thermally annealed P3HT-b-PF spun-cast films show a morphology dominated by crystallization of P3HT or PF, depending on the size of block ratios. However, all solvent annealed films show primarily an out-of-plane stacking ($q \sim 0.15$n Å^{-1} where n =1,2,3,4,5,6,7) on the substrate and with strong (020) π-stacking parallel to substrate surface. This expanded small lamellar domain is about 4 nm which is designated to alkyl-chain stacking within block copolymer. Subsequent thermal annealing at high temperatures results in loss of the expanded spacing, indicating that the observed orientation and structure of P3HT-*b*-PF is in non-equilibrium status so that proper processing condition is important in determining final nanostructure and potentially enhanced PCE in all-polymer OPVs.

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