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Synthesis, Morphology, and Optoelectronic Properties of All-Conjugated Block Copolymers[1] KENDALL SMITH, RAFAEL VERDUZCO, YEN-HAO LIN, JORGE MOK, Rice University — Recent work has demonstrated the potential of all-conjugated block copolymers for solution-processed photovoltaic devices, with power conversion efficiencies near 3%. However, optoelectronic properties and structure-property-processing relationships are poorly understood for this class of materials. Here, we present systematic studies on the processing, morphology, and optoelectronic properties of model all-conjugated block copolymer systems. All-conjugated block copolymer poly(3-dodecylthiophene)-*block*-poly(9,9-dioctylfluorene) (P3DDT-*b*-PF) exhibit simultaneous crystallization of both blocks but no clear evidence of microphase segregation. By contrast, under solvent annealing, poly(3-hexylthiophene) –*b*–poly(9,9-dioctylfluorene) (P3HT-*b*-PF) exhibit lamellar ordering, evidenced by multiple reflections under GIWAXS and GISAXS analysis, including an in-plane reflection indicative of strong π-π stacking for both P3HT and PF blocks. The characteristic lamellar domain spacing (4.2 nm) is found to be independent of block ratio or total molecular weight. Optoelectronic measurements and photovoltaic device results are presented for all-conjugated block copolymers that incorporate ambipolar PFTBT polymer block and high-performance *p*-type PTB7 polymer. These results provide guidelines for optimizing the morphology of all-conjugated block copolymers through materials design and processing.

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Rafael Verduzco
Rice University

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