Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Control of Crystallization to Promote Microphase Separation in Fully Conjugated Block Copolymers YOUNGMIN LEE, THINH P. LE, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, ZACH SEIBERS, S. MICHAEL KILBEY, II[1], Department of Chemistry, University of Tennessee, Knoxville, TN 37996, QING WANG, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802,, ENRIQUE D. GOMEZ[2], Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802 — Donor−acceptor fully conjugated block copolymers, where donor and acceptor conjugated polymers are covalently bonded together, are interesting as single-component active-layer materials for photovoltaics because it can adopt mesoscale microphase separated structures with length scales comparable to the exciton diffusion length. Nevertheless, due to the strong crystallization of poly(3-hexylthiophene-2,5-diyl) (P3HT), morphologies of fully conjugated block copolymers containing P3HT are predominantly driven by crystallization as opposed to microphase separation. We control the crystallization in block copolymers to promote microphase separation in fully conjugated block copolymers through the addition of small amounts of 3-octylthiophene to the polymerization of P3HT. Poly(3-hexylthiophene-2,5-diyl-*r*-3-octylthiophene-2,5-diyl)-*block*-poly((9,9-dioctylfluorene-2,7-diyl)-*alt*-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5"-diyl) (P3HT-*b*-PFTBT) copolymers were prepared by Grignard metathesis for the alkylthiophene block followed by chain extension through a Suzuki-Miyaura polycondensation. We compare the crystallization, self-assembly and performance in devices of P3HT-b-PFTBT with a few mole percent of 3-octylthiophene in the P3HT block.

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Date submitted: 03 Nov 2015 Electronic form version 1.4