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In-situ characterization of the mesophase of a high performance semiconducting polymer L.J. RICHTER, A.J. MOAD, D.M. DELONGCHAMP, R.J. KLINE, D.J. GUNDLACH, D.A. FISCHER, NIST, Gaithersburg, MD — Poly(2,5-bis(3-alkylthiophen-2yl)thieno[3,2-b]thiophene) is a semiconducting polymer with exceptional hole mobility in thin film transistors upon annealing into a mesophase. We have identified the structural motifs of both the mesophase and the high performance, thermally processed film with a variety of in-situ techniques: NEXAFS, spectroscopic ellipsometry (SE), and IR absorption. Upon cooling from the mesophase, the films exhibit pi-stacked lamella with molecular terraces (AFM) with a high degree of order of the conjugated backbone (NEXAFS). The side chains are well ordered (IR) and interdigitated, which may be a driving factor in the growth of large crystals. Upon re-heating, the side chains (IR) and conjugation length (SE) monotonically disorder until entry into the mesophase which is characterized by highly disordered side chains and moderate torsional disorder of the backbone but near ideal in-plane order of the polymer long axis. Side-chain order is reestablished upon re-cooling into the ordered phase. The hysteresis of the side chain order mimics the DSC of powders. As-cast films exhibit greater disorder in all degrees of freedom; entry into the mesophase is necessary to achieve high order. The spectroscopic data can be correlated with in-situ mobility measurements.

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