

## Solid State Structure of Poly(9,9-dinonylfluorene) - DTU Orbit (08/11/2017)

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We report on X-ray diffraction and grazing-incidence X-ray diffraction data of poly(9,9-dinonylfluorene) (PF9) in bulk, thin films and in the 1% methylcyclohexane gel. We denote the main crystalline phase as alpha phase and propose that the unit cell is monoclinic ( $a = 29.31$  angstrom,  $b = 23.65$  angstrom,  $c = 33.33$  angstrom, and  $\gamma = 84.70$  degrees) in bulk and orthorhombic ( $a = 28.70$  angstrom,  $b = 23.48$  angstrom, and  $c = 33.23$  angstrom) in thin films. This structure corresponds to the layered structure along the a-axis (along the elongated side chains and perpendicular to the seemingly stiff polymer chains) and to the stacking of aromatic main chain units along the b-axis. The polymer chains are aligned along the c-axis. Monoclinic structure agrees with the layer spacing of 14.6 angstrom, the stacking period  $d(040) = 5.89$  angstrom and the monomer repeat distance of 8.33 angstrom. The alpha phase experiences an order-disorder transition at 170 degrees C upon heating. In the 1% methylcyclohexane gel, this structural motif is maintained but with the loss of long-range order. This is interpreted as a formation of mesomorphic beta phase with an orthorhombic unit cell ( $a = 29.1$  angstrom,  $b = 28.1$  angstrom, and  $c = 16.7$  angstrom). Structural analogues to other 9,9-di-n-alkyl-substituted polyfluorenes are discussed in terms of unit cell parameters and backbone geometry.

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