LOW DOSE HIGH RESOLUTION ELECTRON MICROSCOPY (HREM) OF POLY(METAPHENYLENE ISOPHTHALAMIDE) (MPDI) TWISTED CRYSTALS

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Poly(m-phenylene diisophthalamide) (MPDI) is a polyaramide used to manufacture thermally stable high strength fibers (known commercially as Nomex® by DuPont). When MPDI dissolved in N,N-dimethylacetamide (DMAc) is slowly crystallized over several weeks by exposure to a non-solvent (H_2O), the polymer precipitates into uniform, regularly twisted crystalline bundles. Low dose HREM of the 0.38 nm lattice fringes perpendicular to the fiber axis are visible everywhere in the fiber whereas the lattice planes parallel to the fiber axis are only visible over a distance of 10-20 nm. The different sets of fringes appear periodically in agreement with regularly twisted fibers. The lattice spacings can be explained well by a hexagonal unit cell with a = b = 1.65 nm, and c = 0.38 nm. Molecular modeling shows that a flattened helical molecular structure explains the intensity distribution of the electron diffraction pattern as well as the high-resolution image data. This helical molecular conformation is similar to that seen in meta-phenylene ethynylenes and 2'-pyridyl-2-pyridinecarboxamide oligomers. The three-dimensional translational symmetry of a perfect crystal is geometrically incompatible with uniform twisting. The high-resolution images reveal that the twisted crystals accommodate this distortion by lateral shift-disorder of the helices parallel to the twist axis. This results in an overall symmetry similar to an ordered hexagonal columnar liquid crystal, resolving the geometrical incompatibility.