

THE STRUCTURE AND HYDROGEN BONDING OF A HIGHLY DISORDERED FIBER

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Poly(pyridobisimidazole) (PIPD), is a recent member of the polyareneazoles family of fibers developed for lightweight, high performance structural applications. It is a polymer with unusually high tensile and compressive strength. The essential difference between PIPD and other rigid rod polymers (PBO, PBZT) is that the structure of PIPD allows for extensive hydrogen (H) bonding. The presence of H-bonding is believed to be responsible for some of the unique properties of PIPD. Intramolecular H bonds impact the modulus and intermolecular H bonds impact the compressive strength. X-ray diffraction studies have shown that the as-spun PIPD fibers form a two dimensionally ordered crystal hydrate that is transformed into a high strength, H-bonded crystal form on heat treatment. Klopp and Lammers [1] (K&L) had difficulty in differentiating between a monoclinic structure, which results in a bidirectional H-bonded network, and a triclinic structure, which results in a sheet-like H-bonded network. Calculations of relative stability and comparisons of calculated mechanical properties with experiment indicate that the triclinic is more likely than the monoclinic structure.[2] On the basis of x-ray and limited neutron data on the native fiber (no isotopic labeling), Takahashi [3] concluded that the hydroxyl proton is rotated 180°, relative to K&L structure, forming an intermolecular O-H...N H-bond while the hydroxyl oxygen participates in an intramolecular H-bond, N-H...O. Recent work, [4] indicates that the details of the H-bonded structure in these fibers can have a profound impact on the axial compressive strength.

We are attempting to define the state of H-bonding in both AS (as-spun) and HT (heat treated) fibers to provide some insight into what changes are taking place to the H-bonded structure, both intra- and intermolecular, upon heat treatment. PIPD is also known to incorporate water, but the quantity, location and orientation of water molecules in the crystal structure have not been precisely identified. Finally, PIPD is a highly disordered fiber, but the various types of disorder have not been fully characterized. Structural description is presented in terms of two dimensional pair distribution functions, from synchrotron and neutron diffraction data.

[1] Klop E. A.; Lammers M. *Polymer* 1998, 39(24), 5987.

[2] J.C.L. Hageman, et al. *Polymer* 46 (2005) 9144–9154.

[3] Takahashi, Yasuhiro *Macromolecules* 2002, 35, 3942; *Macromolecules* 2003, 36, 8652.

[4] Leal, A. Andres, et al. *Polymer* 2009, 50, 2900.