

## CRYSTAL STRUCTURES AND BONDING IN CELLULOSE POLYMORPHS

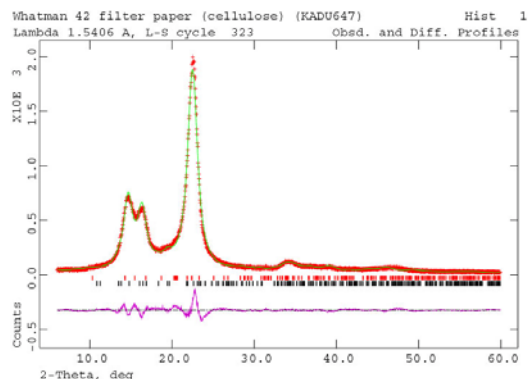
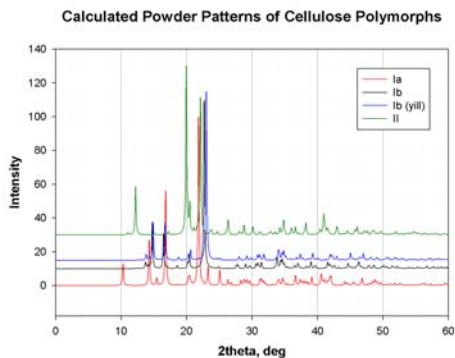
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Quantum chemical geometry optimizations have been carried out for celluloses I $\alpha$ , I $\beta$ , and II using density functional plane wave pseudopotential techniques. The resulting improved structural models provide insight into the intra-chain and inter-chain hydrogen bonding (which includes both O-H $\cdots$ O and C-H $\cdots$ O hydrogen bonds) in these three polymorphs.

Cellulose is a linear poly(1-4)- $\beta$ -D-glucan, and is probably the most abundant biomacromolecule. Cellulose is encountered in the powder diffraction laboratory as the filter paper which has trapped deposits, and also (as microcrystalline cellulose) as the binder in many pharmaceuticals. The increasing use of the Rietveld method for quantitative phase analysis provides the impetus for developing improved structural models for the various forms of cellulose.

Despite its abundance, the crystal structure of cellulose is not yet completely known. The normally-encountered form, native cellulose (cellulose I), occurs as metastable partially-crystalline microfibrils. These microfibrils are composed of mixtures of two different crystalline polymorphs, designated cellulose I $\alpha$  and I $\beta$ . Cellulose I can be converted into a stable crystalline form, cellulose II, by two different processes: regeneration and mercerization.

The geometry optimizations (using CASTEP) were based on initial models from the literature and new structural determinations of celluloses I $\beta$  and II [1,2].



- [1]. Y. Nishiyama, P. Langan, and H. Chanzy, *J. Amer. Chem. Soc.*, **124**, 9074-9082 (2002).
- [2]. P. Langan, Y. Nishiyama, and H. Chanzy, *Biomacromolecules*, **2**, 410-416 (2001).