

Phase behaviour and Self-assembly beyond cellulose I

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Liquid crystalline (LC) ordering in colloidal suspensions provides a framework for linking particle anisotropy and interparticle interactions to emergent hierarchical structures. Cellulose nanocrystals (CNCs) represent a model lyotropic system, spontaneously forming chiral nematic (cholesteric) phases in aqueous media [1]. CNCs are rigid rod-like nanoparticles obtained via acid hydrolysis of cellulose, typically measuring 100–300 nm in length for cotton- and wood-derived sources, whereas sisal-derived CNCs exhibit lengths of ~400 nm and diameters of ~10 nm. Above a critical concentration, CNC suspensions undergo an entropy-driven isotropic–nematic transition, initially forming tactoids that subsequently coalesce into a fully developed chiral nematic phase [2]. This phase is characterised by a helicoidal rotation of the director, resulting in birefringence and a periodic modulation of the refractive index. The helical pitch decreases from micrometres in suspension to hundreds of nanometres upon drying, thereby enabling structural colour. Despite the intrinsic right-handed twist of individual CNCs, the mesophase is most commonly left-handed, and the origin of this chirality inversion remains unresolved [3]. Previous studies have predominantly focused on CNCs derived from native cellulose I, with comparatively limited attention given to alternative crystalline allomorphs and their influence on phase behaviour. Transformation to cellulose III via ethylenediamine (EDA) treatment alters hydrogen bonding, chain packing and surface chemistry, thereby affecting particle morphology, surface charge and interparticle interactions that are critical for mesophase formation. In this work, we investigate the self-assembly of CNCs derived from filter paper and sisal, extending beyond the native cellulose I allomorph. Particular emphasis is placed on cellulose III-derived CNCs obtained through allomorphic transformation followed by post-sulphation via sulphuric acid hydrolysis. The aim is to elucidate how variations in crystalline structure, particle morphology, and intrinsic twist influence the formation, handedness and pitch of LC phases, and how these features translate into solid-state photonic films. A comparative analysis between post-sulphated cellulose III nanocrystals and their parent cellulose I systems is conducted. Liquid crystalline phase diagrams for both systems are presented, enabling direct comparison of their phase behaviour. Corresponding films obtained via evaporation-induced self-assembly are also examined to correlate mesophase structure with optical response (Figure 1). Characterisation techniques include Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and zeta potential measurements. This work establishes a link between nanoscale structure, phase behaviour and optical properties, thereby advancing the understanding of chirality transfer in CNC-based lyotropic liquid crystals.

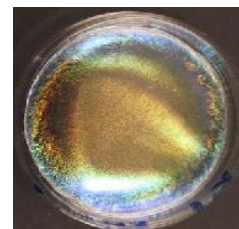


Figure 1: iridescent film of cellulose I of sisal derived CNCs

References

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