Self-assembly of asymmetric and symmetric end-grafted cellulose nanocrystals

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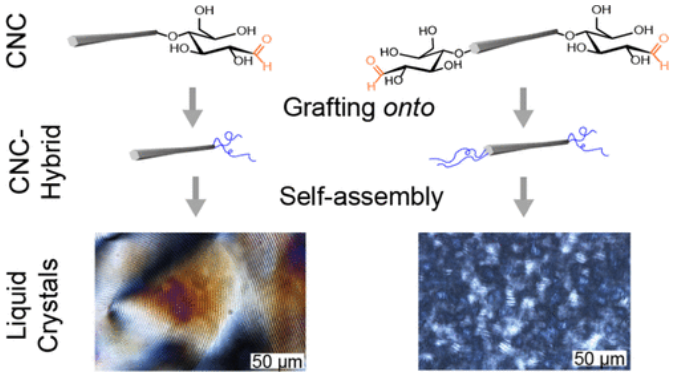
ABSTRACT

Cellulose nanocrystals (CNCs) are intriguing nanomaterials, not only due to their outstanding thermomechanical properties, but also by virtue of their self-assembly into chiral liquid crystal (LC) phases. Such chiral LC phases of CNCs have been observed primarily in aqueous suspensions above a critical concentration, at which mesophases with a "fingerprint" texture, associated with their chiral nematic pitch, begin to appear. Among the external factors that can be used to manipulate the chiral nematic pitch of CNCs, such as ionic strength, ultrasound, *etc.*, reducing end group (REG) modification of different CNC allomorphs remains less explored. The REGs on CNCs extracted from cellulose I (CNC-I) allomorphs are exclusively located at one end of the crystallite, whereas CNCs extracted from cellulose II (CNC-II) allomorphs feature REGs at both ends of the crystallite. In this work, a neutral hydrophilic polymer, poly[2-(2-(2-methoxy ethoxy)ethoxy)ethylacrylate] ($POEG_3A$), was grafted onto the REGs of two different CNC allomorphs via reductive amination [1]. The grafting of $POEG_3A$ onto the CNCs was evidenced by Fourier transform infrared (FTIR) spectroscopy, atomic force microscopy (AFM), and through the observation of the coil-globule conformational transition of the grafted $POEG_3A$ chains. Furthermore, we investigated the self-assembly of end-tethered CNC-hybrids to discover the formation of chiral nematic phases observable by polarized optical microscopy. We hypothesize that the introduction of $POEG_3A$ to the REGs of CNC allomorphs does not disturb the surface of the CNCs along the rods, allowing the modified CNCs to effectively pack and form helicoidal assemblies in spite of the presence of the end-grafted polymers.



[1] Delepierre, G., Traeger, H., Adamcik, J., Cranston, E.D., Weder, C., Zoppe, J.O., *Biomacromolecules*, 22 (8), 3552–3564, 2021