OP 9 - Chitin Colloidal Liquid-Crystals, Biomimetic Self-Assembly and Materials.

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Chitin nano- (or micro-) crystals are rigid rod-like particles known to form chiral nematic (N*) liquid crystalline phases when suspended in aqueous solutions. These mesophases remarkably mimic the long-range helical geometry observed in biological tissues, in which chitin, the fibrous component is associated to a mineral phase. The aim of the present work was to decipher the interplay between competing forces that prevail to the emergence of order in chitin suspensions. We report a set of experimental data that compare well with predictions made by statistical physics theories for suspensions of rigid rods with an effective diameter arising from electrostatic interactions.
Coexistence of the two phases is a clear indication that the transition is of the first-order type. Temperature has no effect on the phase separation up to 100°C, and the system is therefore athermal. In contrast, pH and ionic strength strongly influence the critical concentrations in the isotropic (PhiI) and nematic (PhiN) phases at coexistence. The critical concentrations go through a minimum at [HCl] ~ 5 $x10^{-4}$ M with PhiI = 1.96+/-0.25% and PhiN = 3.51+/-0.35%. In the nematic phase, the chitin particles interact strongly enough, over distances up to 120 nm, to produce an interference peak identified by small angle x-ray scattering. The position of the intensity maximum varies linearly with Phi exp(-1/2), indicating that the rods centers-of-mass are set on a hexagonal lattice despite short-range liquidlike local order. The azimuthal spread of the interference peak is directly related to the particles orientational distribution function. Fitting the intensity profiles gives an order parameter S~0.8, as predicted by theory. The cholesteric pitch P0 ranges from 27.5 +/- 3.5 µm to 140 +/- 17 µm in the biphasic domain, depending on the composition of the suspension medium. Materials can be prepared from these complex fluids with long-range chirality, for instance by in-situ polymerization of acrylamide, and/or formation of a silica matrix through sol/gel condensation. Transient liquid-crystal ordering was selected by evolution for the assembly of extracellular matrices like arthropods cuticles, plant cell wall and compact bone. The major biological macromolecules of these tissues (chitin, cellulose and collagen) all form chiral liquid-crystal phases in vitro. Structural modulations can be achieved by fine-tuning the particles interactions or applying an external field, making self-assembly a highly versatile way of preparing ordered materials.