587g Nanocomposites under Shear: Alignment of Inorganic Nanoparticle and Protein Arrays Templated in Block-Copolymer Mesophases

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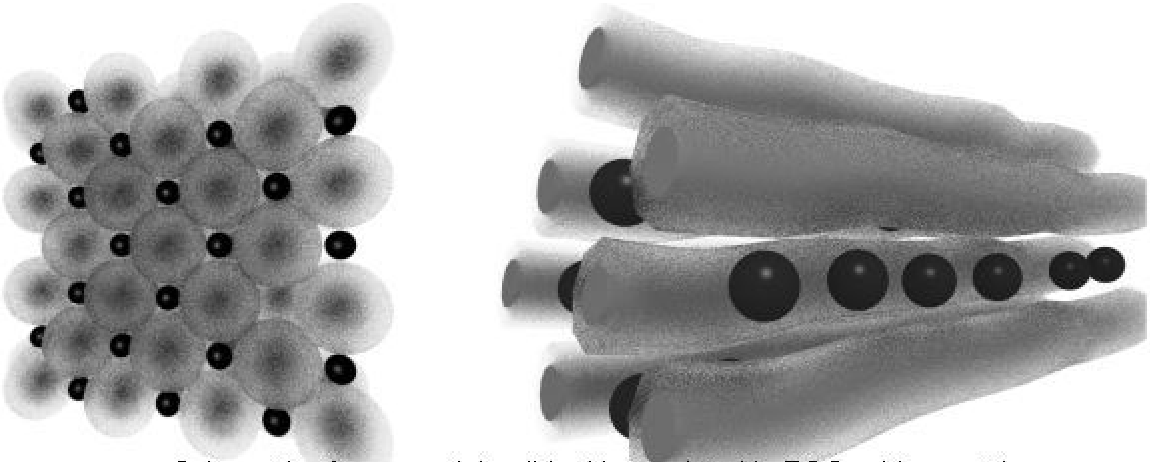
Block copolymers form highly organized structures when they are dissolved in solvents that are selective (having different solubility) to the different polymer blocks. A simple and general method to template nanoparticle and globular protein arrays using thermoreversible PEO_n-PPO_m-PEO_n copolymer cubic crystals (Pluronic) has been recently presented.[1,2] Although the crystalline domains of unaligned block copolymer templates exist over micron lengthscales, the orientation of their lattices is usually different. Shear orientation of block copolymer cubic crystals into macroscopic single crystals has been previously demonstrated.[3] In this work, we show that this shear orientation is also possible for block copolymer nanocomposites containing nanosized additives (silica nanoparticles or serum albumin) intercalated in the interstitial cavities of the micelle crystal. The shear-aligned nanocomposite is a single crystal macro-domain where the templated particles have the same lattice orientation. Using small angle neutron scattering (SANS) under shear, we show that alignment is possible in mesophases of face-centered-cubic (FCC) micelle crystals and in close-packed arrays of cylindrical micelles. Contrast variation allows us to probe the alignment of the nanoparticle array and the polymer template independently. We characterize the effect of shear rate, relative size of nanoparticle and polymer template, relative concentrations and temperature on the final state of alignment of the nanocomposite. The formation of aligned single-crystal arrays of nanoparticles and proteins using shear represents a simple but significant improvement in our ability to manipulate materials at the nanometer scale. The results of this work are also important to emerging applications because orientation and persistence of order are crucial in the control of the properties of nanocomposites.

[1] Pozzo, D. C.; Hollabaugh, K. R.; Walker, L. M. Journal of Rheology 2005, 49, 759.

[2] Pozzo, D. C.; Walker, L. M. Macromolecular Symposia 2005 (in press).

[3] Eiser, E.; Molino, F.; Forte, G.; Pithon, X. Rheologica Acta 2000, 39, 201-208.



Schematic of nanoparticles (black) templated in FCC cubic crystal
and cylindrical block copolymer phases