Structural Interplay in Block Copolymer-Bile Salt Complexes: From Globules to Ribbons

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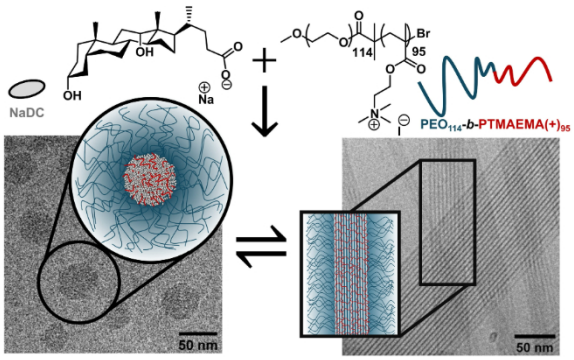
The supramolecular structures resulting from the complexation between the neutral–cationic block copolymer poly(ethylene oxide) –*block*– poly(2-(trimethylammonium)ethyl methacrylate iodide) (PEO114 –*b*– PTMAEMAI95) and the bile salt sodium deoxycholate (NaDC) were investigated by dynamic light scattering, small-angle X-ray scattering, cryogenic transmission electron microscopy and proton NMR techniques.[1] Complexes were produced using different preparation protocols: the direct mixing of the pure solutions of block copolymer and bile salt, containing their respective simple counterions, and the dispersion in water of a freeze-dried complex salt, free of simple counterions. While the direct mixing protocol produced a mixture of ordered ribbon-like aggregates and globular particles with disordered cores, the complex salt protocol yielded exclusively ordered "ribbons". The globular particles resembled classical spherical "complex coacervate core micelles" with a core of anionic deoxycholate micelles complexed with cationic PTMAEMA(+) blocks, the core radius being limited by the PTMAEMA contour length, and a shell composed of neutral PEO blocks. The drastically different ribbon morphology was found to result from (1) the organization of DC anions into hexagonally packed helices in the core and (2) the limitations on the ribbon thickness imposed by the lengths of the copolymer blocks. By varying temperature and sample treatments, it was found that the ordered ribbon morphology represents the equilibrium structure at 25 °C, while the globular morphology is favored at 50 °C. The results suggest strategies to design the morphology and tune the dimensions of aqueous block copolymer–bile salt aggregates.



Supramolecular structures controlled by the delicate balance between the bile salt self-assembly and the geometric characteristics of the block copolymer.

References:

[1] Suelen Gauna Trindade, Guanqun Du, Luciano Galantini, Lennart Piculell, Watson Loh, Karin Schillén. Structural interplay in block copolymer-bile salt complexes: from globules to ribbons. *Soft Matter* **2025** , *21* , 3814-3828.

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