Core-crystalline wormlike micelles (CCWMs): A toolbox for complex surface-compartmentalized nanostructures

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The self-assembly of block copolymers into one-dimensional so-called "nanofiber micelles" has gained increased interest over the last few years [1]. Recently, we have produced CCWMs with a patch-like microphase-separated corona via solution self-assembly of a polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) triblock terpolymer (SEM) with a crystallizable PE middle block (Fig. 1A) [2]. Here, structure formation is accomplished by cooling down a toluene or THF solution from > 60 °C to room temperature, i. e. inducing PE crystallization.

As a general procedure this generation of CCWMs can be applied to other triblock copolymers with a polyethylene middle block, e.g. polystyrene-*block*-polyethylene-*block*-polystyrene (SES) (Fig. 1B) and polystyrene-*block*-polyethylene-*block*-poly(ethylene oxide) (SEEO). One-dimensional growth can be further observed for polyethylene contents of at least 20 wt-% to 40 wt-%.

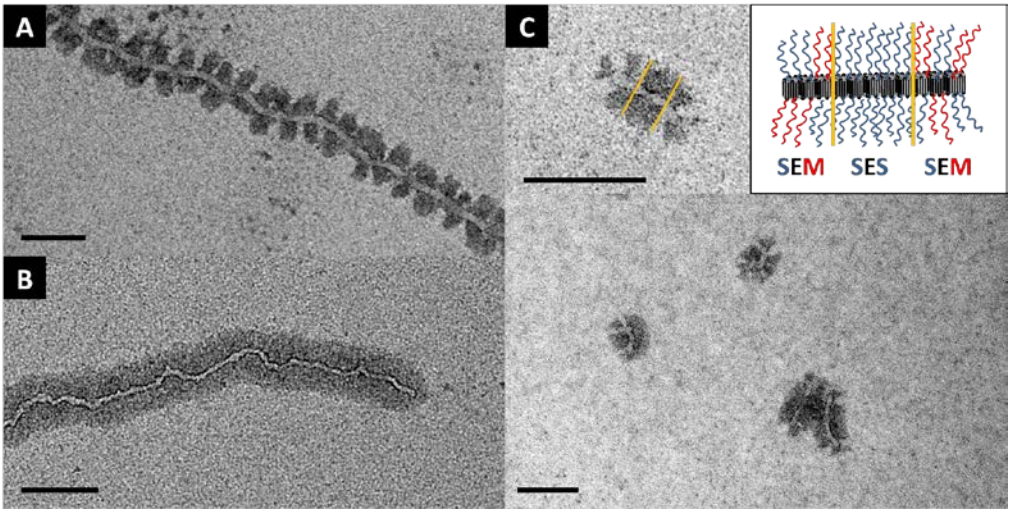

Fig. 1: A,B) Wormlike micelles formed by a $S_{381}E_{875}S_{389}$ (A) and a $S_{340}E_{704}M_{363}$ (B) triblock terpolymer, respectively; C) block-co-micelles of $S_{381}E_{875}S_{389}$ and $S_{340}E_{704}M_{363}$; in all TEM images scale bars correspond to 100 nm and PS is selectively stained with RuO_4.

Using mild sonication, the length of the CCWMs formed from SES can be tuned from over 1 µm to about 50 nm. By now adding a solution of unimolecularly dissolved SEM, block-co-micelles with a corona of pure PS in the middle part and a surface-compartmentalized corona of PS and PMMA on the outer parts are formed by epitaxial growth. To the best of our knowledge this is the first time that the recently discovered principle of block-co-micellization [3] is extended from metal-containing block copolymers to a purely organic system, proving its universal applicability.

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[2] Schmalz, H.; Schmelz, J.; Drechsler, M.; Yuan, J.; Walther, A.; Schweimer, K.; Mihut, A. M. *Macromolecules* **2008**, *41*, 3235.
[3] Wang, X.; Guerin, G.; Wang, H.; Wang, Y.; Manners, I.; Winnik, M. A. *Science* **2007**, *317*, 644.