Patchy core-crystalline micelles: Self-assembly concepts, properties and applications

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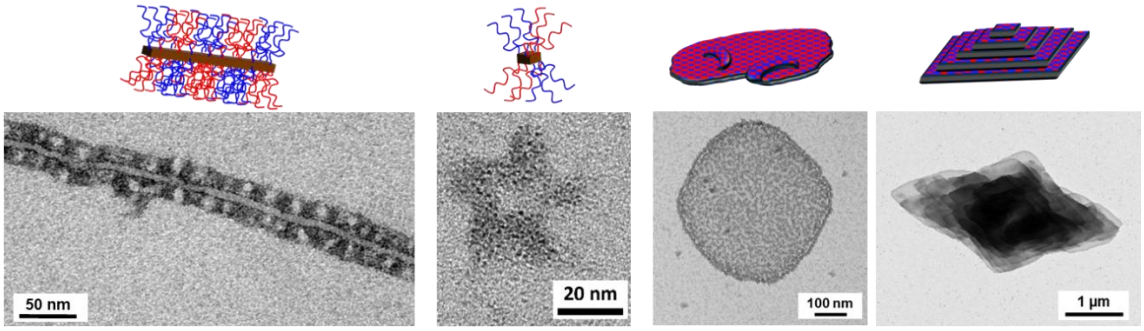

The unique corona structure of patchy micelles, featuring alternating, chemically distinct patches, opens various applications owing to their outstanding interfacial activity and potential for regio-selective functionalization. Crystallization-driven self-assembly (CDSA) of triblock terpolymers with a crystallizable polyethylene middle block and two incompatible end blocks (polystyrene (PS) and poly(methyl methacrylate) (PMMA)) is an efficient method for the production of patchy core-crystalline micelles (CCMs).[1] Depending on the solvent quality, either worm-like (wCCMs) or spherical (sCCMs) core-crystalline micelles with a patchy PS/PMMA corona are formed. Introducing tertiary amino-groups in one of the patches facilitates regio-selective loading with different metal and metal oxide nanoparticles. Immobilizing functional wCCMs on electrospun nonwovens employing coaxial electrospinning and subsequent loading with gold nanoparticles gives access to patchy hybrid nonwovens with excellent catalytic activity and reusability.[2] Moreover, wCCMs with functional patches can induce the molecular self-assembly of 1,3,5-benzenetricarboxamides (BTAs) to form well-defined, fir-tree-like superstructures if the tertiary amino-groups in the patches match with the peripheral substituents of the BTA.[3]

An alternative route to patchy sCCMs is stereocomplex-driven self-assembly (SCDSA) of diblock copolymers with enantiomeric poly(*L*-lactide) (P*L*LA) and poly(*D*-lactide) (P*D*LA) blocks, yielding sCCMs with a P*L*LA/P*D*LA stereocomplex core and a patchy PS/P*t*BMA corona (P*t*BMA = poly(*tert*-butyl methacrylate)).[4] These micelles are highly efficient compatibilizers for polymer blends.[5] This is attributed to their adaptive corona structure, resulting in a selective swelling/collapse of the respective miscible/immiscible corona patches at the blend interface.

Utilizing co-crystallization-driven self-assembly (CCDSA) of PS-*b*-P*L*LA-*b*-P*t*BMA triblock terpolymers with a P*L*LA homopolymer gives access to patchy platelet micelles with a non-concentric arrangement of the PS/P*t*BMA surface patches.[6] The platelets can be fluorescently labelled and used as stabilizers for emulsions owing to their excellent interfacial activity.

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[4] Schaller, R.; Hils, C.; Karg, M.; Schmalz, H. *Macromol. Rapid Commun.* **2023**, *44*, 2200682.

[5] Schaller, R.; Schmidt, M.; Schweimer, K.; Schmalz, H. *Polym. Chem.* **2024**, *15*, 3100.

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