Electronic Supplementary Information to the Manuscript

Interfacial activity of patchy worm-like micelles

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Synthesis of triblock copolymers. The used PE containing triblock co- and terpolymers were synthesized by catalytic hydrogenation of the corresponding PB containing block copolymers produced *via* sequential anionic polymerization in non-polar solvents, as can be found elsewhere.[1, 2] The preparation of the Janus cylinders used for comparison can be found in an earlier study.[3]

Preparation of worm-like crystalline-core micelles (wCCMs). Solutions of wCCMs in toluene or THF were prepared using the following procedure. The triblock copolymers were dissolved at a concentration of 1 g L^{-1} and then heated in a water bath to at least 65 °C, *i.e.* above the melting temperature of PE, resulting in unimeric solutions. Subsequently, these solutions were quenched to the desired crystallization temperature (T_c, Table 1, main manuscript) to form the wCCMs and kept at this temperature for 24 h followed by an additional annealing step at the temperature T_a (Table 1, main manuscript) for 3 h to obtain a more regular patchy structure of the corona, as published earlier.[1, 4] In 1,4-dioxane, wCCM solutions were obtained by dialysis, as direct self-assembly in 1,4-dioxane results in the formation of spherical CCMs. Therefore, the samples were first prepared in THF as described above and then dialyzed against 1,4-dioxane for several days by replacing the solvent twice. Subsequently, the wCCM solutions in 1,4-dioxane were diluted to 1 g L^{-1}. For all preparation steps gentle stirring or shaking was applied.

Pendant-drop tensiometry. Samples in toluene or 1,4-dioxane in a concentration range of 0.25 to 2 g L^{-1} were measured using a Dataphysics OCA 20 tensiometer at room temperature. The drop profile was recorded using a CCD camera and the fitting was performed with the Dataphysics software package. The low-concentrated solutions were prepared from 1 g L^{-1} solutions by dilution. The 2 g L^{-1} solution was prepared directly as described above. For all measurements clean and dust-free glass cuvettes were used. The droplet phase (water in case of toluene, or perfluorooctane (PFO) in case of 1,4-dioxane) was generated with a manual dosage system using 1 mL syringes with straight blunt tip (diameter 0.8 mm). All measurements were performed at least twice to check the reproducibility. The quasi-equilibrium interfacial tension was determined by averaging the values of the interfacial tension measured during the last 30 min of the experiment.

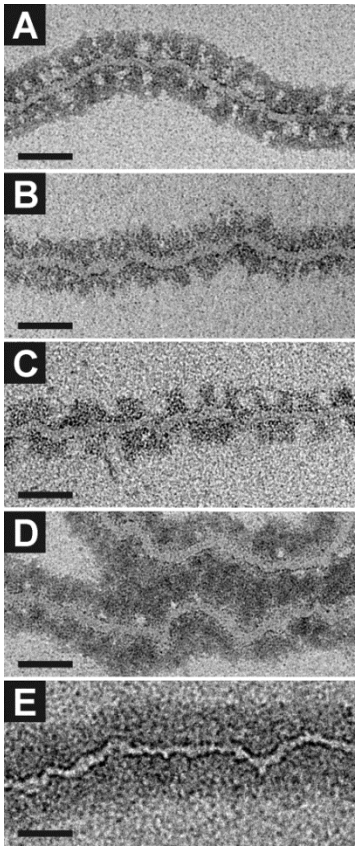

Fig. S1 Selected TEM micrographs (scale bars = 50 nm) showing the corona structure of A) SEM1, B) SEM4, C) SEM5, D) SEM6 and E) SES wCCMs formed in toluene (1 g L^{-1}). For all samples PS was selectively stained by RuO_4 vapour, resulting in dark PS domains. PMMA domains and the PE core appear bright. A more detailed characterization of the morphology can be found in our previous work.[1, 4]

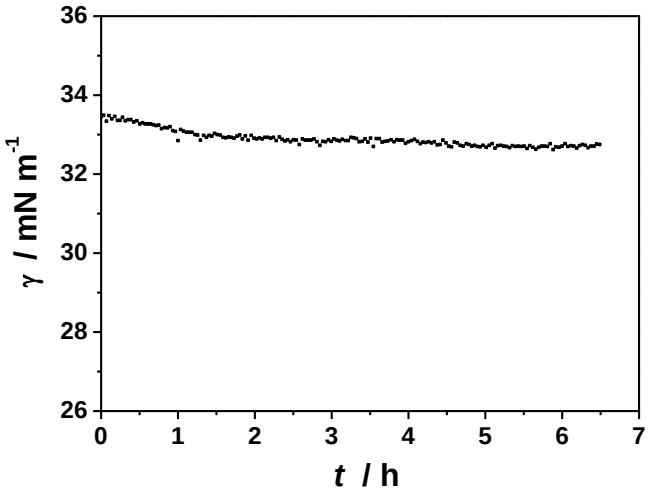

Fig. S2 Interfacial tension isotherm of the pristine toluene/water interface.

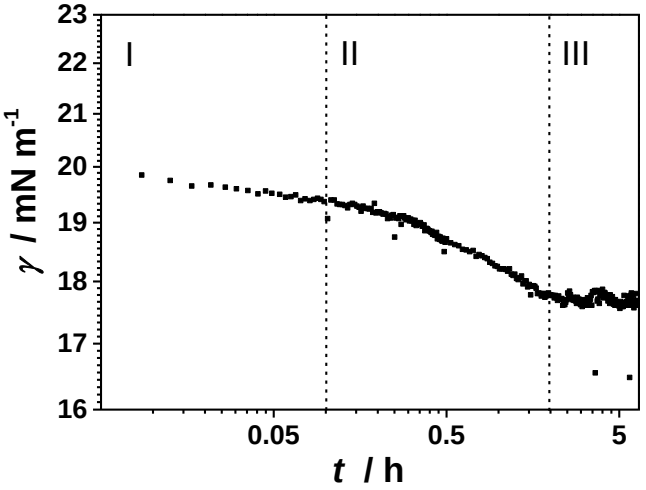

Fig. S3 Logarithmic presentation of the adsorption isotherm of a 1 g L^{-1} solution of wCCMs formed by SEM1 at the toluene/water interface, revealing three stages of adsorption (cf. Fig. 1 main manuscript).

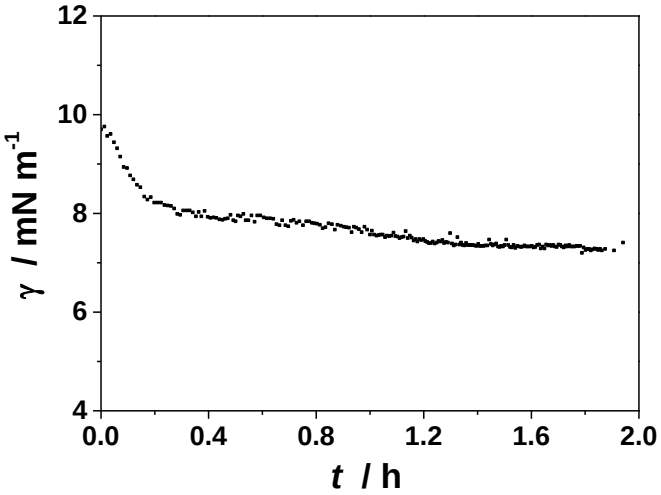

Fig. S4 Interfacial tension isotherm of a 1 g L^{-1} solution of wCCMs formed by SEM1 at the dioxane/PFO interface (γ_0(dioxane/PFO) = 10.75 mN m^{-1}).

References:

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