

Supporting Information

Splitting of Surface-Immobilized Multicompartment Micelles into Clusters upon Charge Inversion

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Surface Immobilization – Adsorption Kinetics

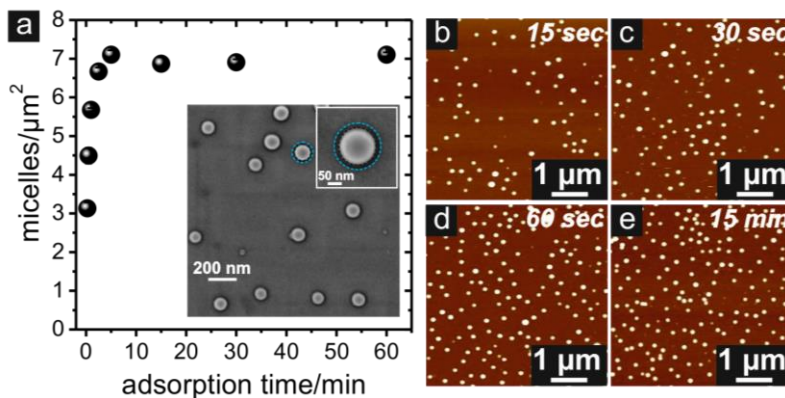


Figure S1. Micelle density on a silica surface as a function of adsorption time, inset: SEM image (PB core: black dashed line, PMAA shell: blue dashed line) (a) and exemplarily the corresponding AFM height images (z -scale: 0-100 nm) after 15, 30, 60 sec, and 15 min adsorption time (b-e).

pH-Response – Incubation at pH 10.5 and pH 12

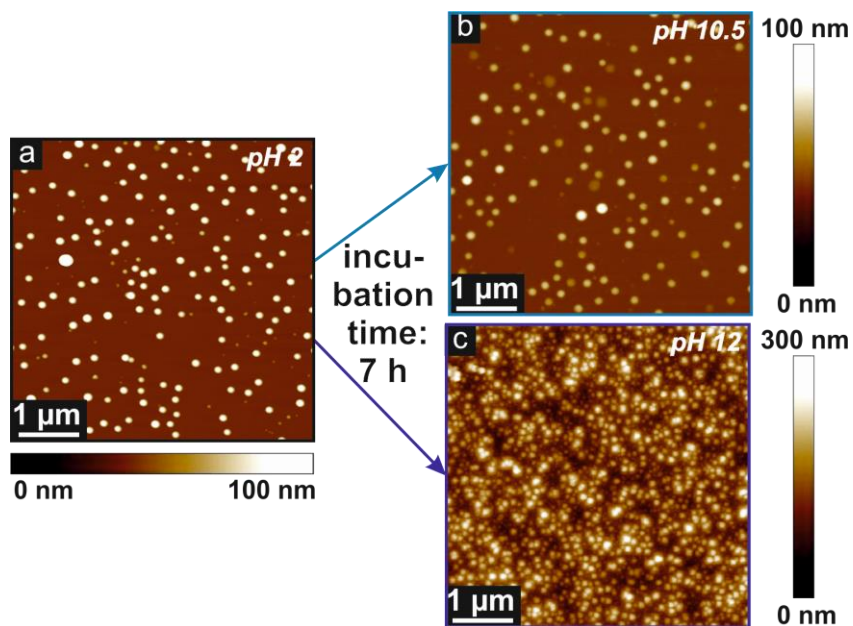


Figure S2. AFM height images of a reference sample (exemplarily) with surface-immobilized BMAAD micelles adsorbed from pH 2 solution (a) and samples after immersion/incubation at pH 10.5 (b) and pH 12 (c).

Splitting Kinetics

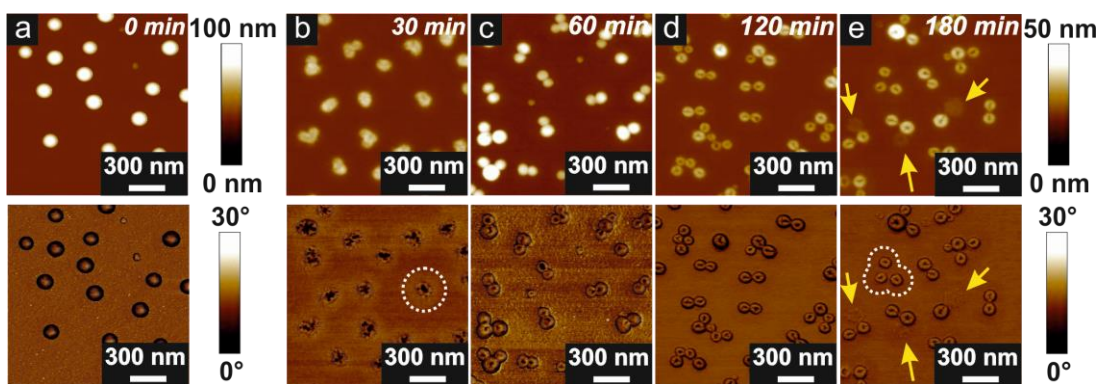


Figure S3. AFM height (top row) and phase (bottom row) images of BMAAD micelles adsorbed from pH 2 before (a) and after exposure to pH 11 for 30, 60, 120, and 180 min (b-e), respectively. The “finger prints” of the corona in the phase images are highlighted by dashed white lines (b,e) and the “finger prints” of desorbed subunits are pointed out by yellow arrows (e).

Successive Exposure to Basic and Acidic Solutions

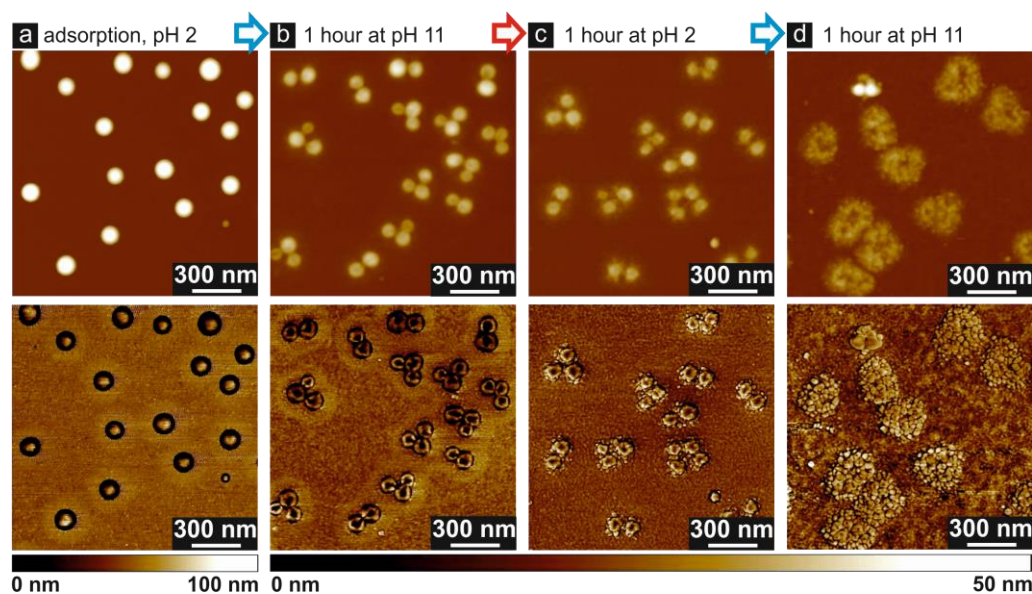


Figure S4. AFM height (top row) and phase (bottom row; z -ranges: (a) 0-30°, (b) 0-10°, (c) 0-10°, (d) 0-30°) images of surface-immobilized BMAAD micelles in dry state directly after adsorption from pH 2 solution (a), and after subsequent exposure to pH 11 (b), pH 2 (c) and again pH 11 (d), each for the duration of 1 hour.

Diameter, Height, Radius of Curvature and Surface Area

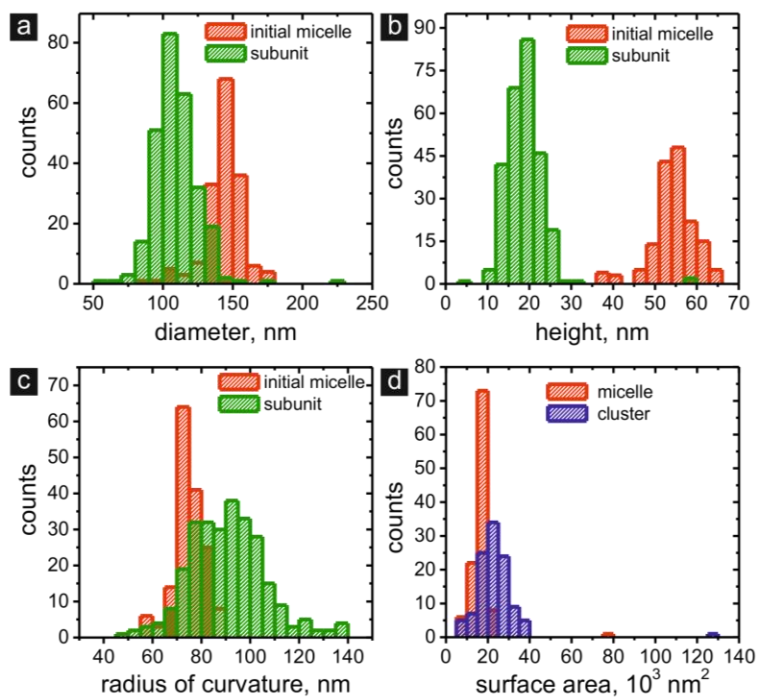


Figure S5. Distributions of AFM raw data such as diameter (a) and height (b) of the initial micelles before splitting (red) as well as of the resulting subunits (green) after splitting. Using the raw data the distributions of the radius of curvature (c) and contact area between the micelles or clusters (= sum of subunits, blue) and the silica substrate (d) can be calculated.

Distances Within the Clusters

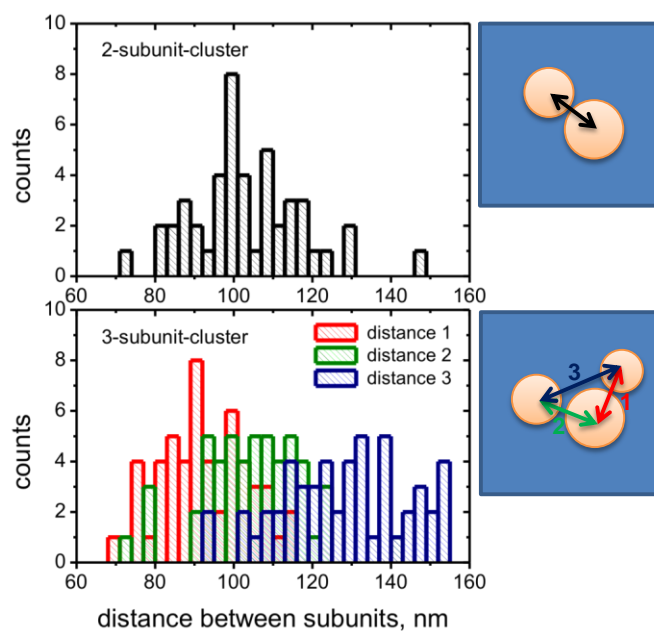


Figure S6. Distributions of center-to-center distances in 2-subunit and 3-subunit clusters with schemes illustrating the corresponding distances.

Polymer Desorption During Splitting

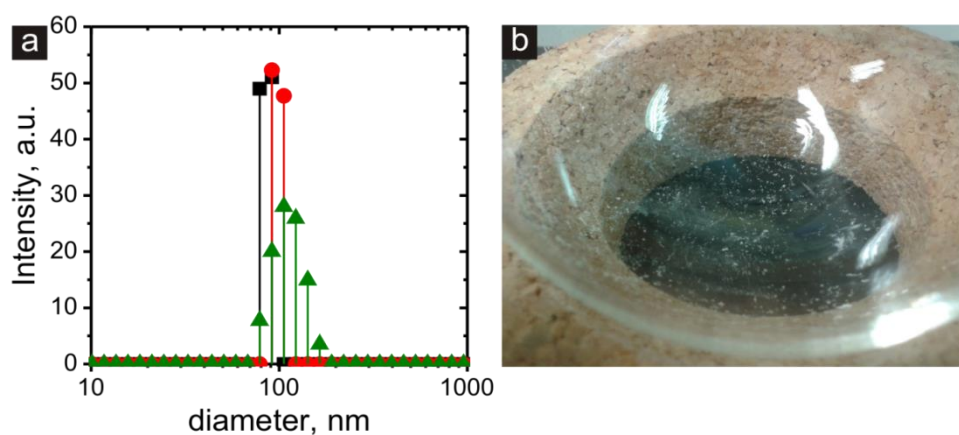


Figure S7: Hydrodynamic diameters (DLS) of micellar aggregates detected in the supernatant after incubation of surface-immobilized BMAAD micelles for one hour at pH 11 (a). Freeze-drying of the supernatant (collected from 3 samples) resulted in a white powder (b) which corresponds to the polymer desorbed from the surface.

Cluster Size and Aggregation Number

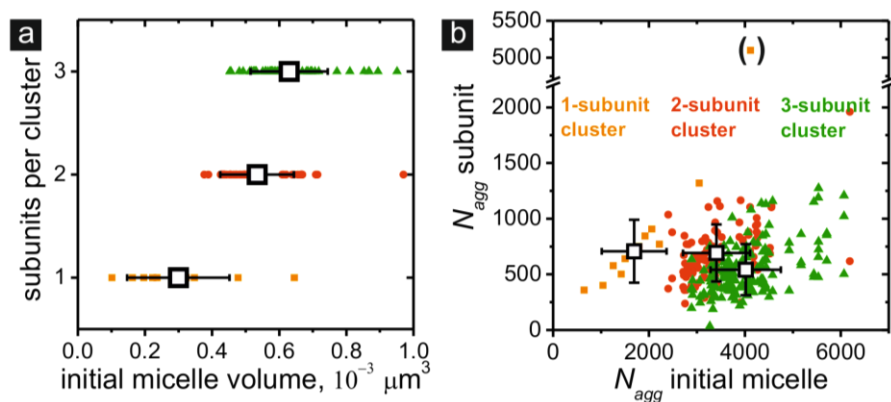


Figure S8. Cluster size (= number of subunits per cluster) as a function of the initial micelle volume (a) and aggregation number of subunits after splitting as a function of the initial micelle aggregation number (b). Different colors correspond to a different number of subunits per cluster (1: orange squares (■), 2: red circles (●), 3: green triangles (▲)). Black open squares (□) represent the mean values and the corresponding standard deviations.

Cryo-TEM in pH 2 and 11

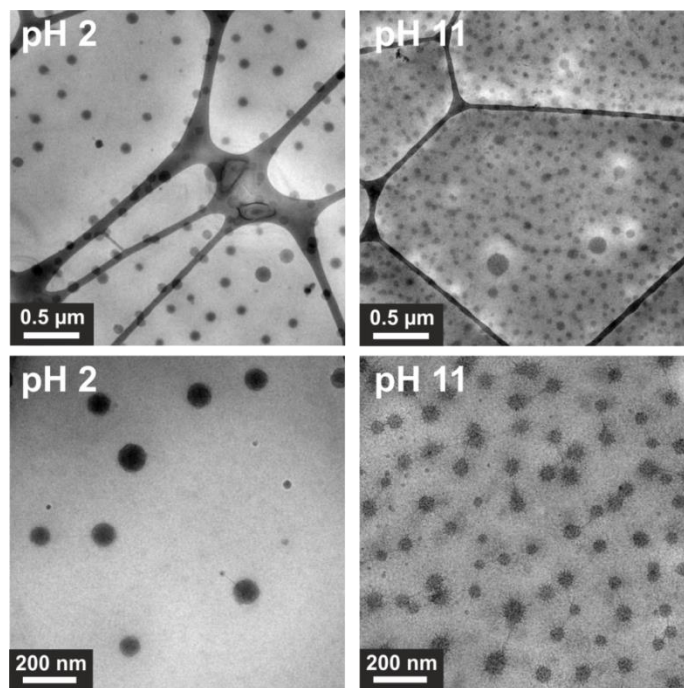


Figure S9. Cryo-TEM micrographs of BMAAD micelles in pH 2 solution and after dialysis against pH 11.

Theoretical Consideration of Micelles Splitting

Consider ABC triblock terpolymers with degrees of polymerization N_A, N_B, N_C of A, B and C blocks, respectively. Block C is hydrophobic and forms a dense core of the micelle. v_C and v_B are the volumes of C and B monomer units, respectively. Blocks B and A are weak polyacid and weak polybase, respectively. We analyze the aggregation number in micelles assuming that in both limiting cases (acidic and alkaline conditions) the micelles retain spherical star-like shape, that is, the radius of the dense core is smaller than that of the hydrated corona.

Acidic conditions:

At strongly acidic conditions (pH=2) block B (that is, PMAA) is uncharged and collapsed due to the intrinsic hydrophobicity, whereas block A (PDMAEMA) is fully ionized (positively charged), the fraction of charged monomer units $\alpha \cong 1$.

The micelles have a core-shell-corona shape with the central core formed by hydrophobic block C surrounded by a spherical shell formed by collapsed and uncharged block B and decorated by (positively) charged corona formed by extended blocks A.

Let φ_C and φ_B be the volume fractions of C and B monomers in the core and in the shell, respectively. Then $R_C = \left(\frac{3}{4\pi} \frac{pN_C v_C}{\varphi_C} \right)^{1/3}$ and $R_B = \left(\frac{3p}{4\pi} \left[\frac{N_C v_C}{\varphi_C} + \frac{N_B v_B}{\varphi_B} \right] \right)^{1/3}$ are the outer radii of the C-core and of the B-shell in a micelle with aggregation number p , respectively.

The free energy (in $k_B T$ units) of the core-shell-corona micelle can be presented as

$$F = F_{\text{corona}} + F_{\text{interface}} \quad (1)$$

The term

$$F_{\text{interface}} = 4\pi R_C^2 \gamma_{BC} + 4\pi R_B^2 \gamma_B \quad (2)$$

accounts for the excess free energy of the core-shell (C/B) and shell-corona interfaces, γ_{BC} and γ_B are the corresponding surface tensions (in $k_B T$ units).

Then eq. 2 can be presented in the form

$$F_{\text{interface}} = (36\pi)^{1/3} p^{2/3} \left(\frac{N_C v_C}{\varphi_C} + \frac{N_B v_B}{\varphi_B} \right)^{2/3} \left[\gamma_B + \gamma_{BC} \left(\frac{N_C v_C / \varphi_C}{N_C v_C / \varphi_C + N_B v_B / \varphi_B} \right)^{2/3} \right] \quad (3)$$

The free energy of the corona comprises as the main contribution translational entropy of ideal gas of counterions confined in the corona,

$$F_{corona} = pN_A \ln \left(\frac{pN_A}{R_{corona}^3 - R_B^3} \right) \quad (4)$$

(where we have omitted p -independent terms). Minimization of the free energy per chain,

$$\frac{\partial}{\partial p} \frac{F_{corona} + F_{interface}}{p} = 0 \quad (5)$$

leads to the following expression for the aggregation number in the equilibrium micelle

$$p_{core-shell} = \left(\frac{N_C v_C}{\phi_C} + \frac{N_B v_B}{\phi_B} \right)^2 N_A^{-3} \left[\gamma_B + \gamma_{BC} \left(\frac{N_C v_C / \phi_C}{N_C v_C / \phi_C + N_B v_B / \phi_B} \right)^{2/3} \right]^3 \quad (6)$$

(a numerical coefficient is omitted).

Alkaline conditions

At strongly alkaline conditions (pH=11) the block B is fully ionized and negatively charged whereas block A is uncharged, but remains soluble in water.

The excess free energy of the C-core/corona interface assumes the simple form:

$$F_{interface} = 4\pi R_C^2 \gamma_C \quad (7)$$

The corona consists of inner hydrated “shell” formed by fully ionized and strongly extended B-blocks, and outer region formed by non-ionized and weakly extended A-blocks. The ionized inner part of the corona provides the main contribution to the coronal free energy,

$$F_{corona} = pN_B \ln \left(\frac{pN_B}{R_B^3 - R_C^3} \right) \quad (8)$$

By applying eq. 5 we obtain an expression for the aggregation number in a star-like micelle with ionic coronal chains

$$p_{star} = \left(\frac{N_C v_C}{\phi_C} \right)^2 \gamma_C^3 N_B^{-3} \quad (9)$$

We remark that this is an upper estimate for the aggregation number, an account of repulsive interactions under good solvent conditions between A-blocks would lead to a smaller value.

Hence,

$$\frac{p_{core-shell}}{p_{star}} = \left(1 + \frac{N_B v_B \phi_C}{N_C v_C \phi_B}\right)^2 \left(\frac{N_B}{N_A}\right)^3 \left(\frac{\gamma_B + \gamma_{BC} \left(1 + \frac{N_B v_B \phi_C}{N_C v_C \phi_B}\right)^{-2/3}}{\gamma_C} \right)^3 \quad (10)$$

If this ratio is larger than unity, one can expect splitting of micelles upon switching from acidic to alkaline conditions in solution.