Supporting Information

Towards a Rational Morphology Control of Frozen Copolymer Aggregates

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Videos can be downloaded form the publisher's website.

1. Microscopy images of the spontaneous emulsification process

A video of the spontaneous emulsification in presence of PS_{16k} -PEO_{7.5k} can be downloaded from the publisher's website. Here is shown a montage containing four frames of the video taken 5 seconds apart from each other.



Figure S1. Montage from the video of spontaneous emulsification. From top left to bottom right each frame is taken 5 seconds after the previous one. In the initial frame we can see the chloroform phase containing PS_{16k}-PEO_{7.5k} and the water phase being deposited from the top. In the second frame, 5 seconds after the formation of the chloroform-water interface the spontaneous formation of droplets of water in chloroform is clearly visible.

2. Scanning Electron Microscopy Images of the Aggregates



Figure S2. Spherical micelles formed without evaporation from a planar interface between chloroform containing $PS_{9.5k}$ -PEO_{18k} and water: 5 µL of the upper clear water phase were dried on a silicon wafer and imaged by SEM. Upon drying the chloroform in water droplets transform into spherical micelles with diameters about 55 nm. Scale bar 100 nm.



Figure S3. Budding vesicle formed from an adsorbed droplet of chloroform containing PS_{16k}-PEO_{7.5k}. The adsorbed droplets form a budding vesicle and a series of smaller spherical vesicles and elongated

strings of vesicles. The former can be seen surrounding the larger aggregate while the latter are shown in more detail in Figure S4.



Figure S4. Detail of the strings of vesicles surrounding the budding vesicle formed from adsorbed droplets containing PS_{16k}-PEO_{7.5k}.

3. Laser Scanning Confocal Microscopy



Figure S5. (left) LSCM of chloroform/PS_{16k}-PEO_{7.5k}- droplets at the bottom of the imaging chamber (right) View of the same sample after the formation of micelles. Some droplets produced clearly visible

elongated micelles while most gave spherical micelles too small for optical microscopy. The chlorofom contains a small amount of Dil dye. See also the .avi files showing the data from different viewpoints.

4. List of videos

Seven videos are available on the publisher's website illustrating various aspects of our experiences:

Movie 1) Spontaneous_emulsification_planar_interface;

Violent penetration of upper water phase into the bottom chloroform phase containing 100 mg/mL PS_{16k} -PEO_{7.5k}.

Movie 2) Floating-droplets_ps16k-peo7_5k_elongated_formation:

Elongated micelles are formed from floating emulsion droplets containing $10 \text{ mg/mL PS}_{16k}$ -PEO_{7.5k}. The elongated micelles are clearly visible thanks to the fluorescent dye Dil.

Movie 3) Floating-droplets_ps9_5k-peo18k_spherical_formation:

Spherical micelles are formed from floating emulsion droplets containing 10 mg/mL PS_{9.5k}-PEO_{18k}. The droplets shrink in size until they disappear.

Movie 4) Adsorbed_droplets_ps16k-peo7_5k_budding-vesicles_formation: Vesicles and budding vesicles are formed from adsorbed emulsion droplets containing 10 mg/mL PS_{16k}-PEO_{7.5k}.

Movie 5) Adsorbed-droplets_ps9_5k-peo18k_elongated_formation:

Elongated micelles are formed from adsorbed emulsion droplets containing 10 mg/mL $PS_{9.5k}$ -PEO_{18k}.

Movie 6) LSCM_before

Figure S5 left, from different viewpoints

Movie 7) LSCM_after

Figure S5 right, from different viewpoints