Role of confinement and corona crystallinity on the bending modulus of copolymer micelles measured directly by AFM flexural tests

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Supporting Information:

Force Curve Acquisition and Conversion

The non-destructivity of the measurements was ensured by repeating the force curves several times on the same suspended micelles and verifying that the same results would be obtained through consecutive measurements. This can be seen from the overlay of eight consecutive force curves overlaid in Figure 2. Moreover, the micelles could still be imaged in topography scans after the force curve acquisition.

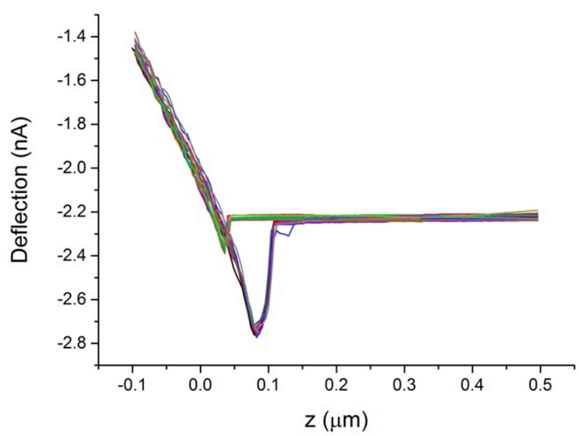

Figure S1 Overlay of eight force curves consecutively performed on a single suspended micelle. The same slope was obtained from all the measurements.

The force curves were converted into Force vs bending depth by knowing the spring constant of the cantilever used and the deflection sensitivity of the cantilever. The latter was evaluated by performing a force curve on a bare silicon substrate and obtaining the slope of the curve. For reference, an overlay of a force curve on bare silicon, and one on a suspended micelle are shown in Figure S2.

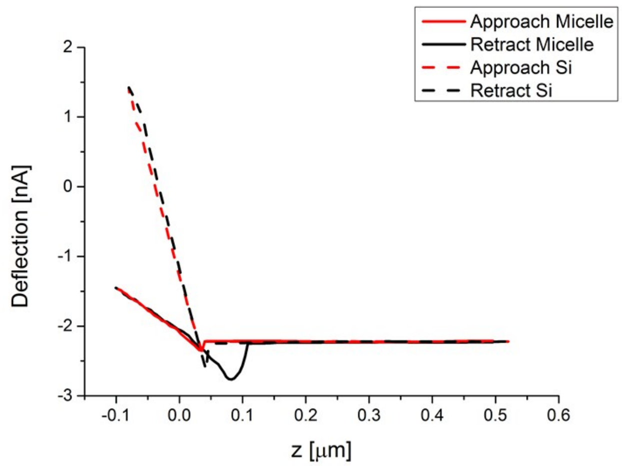

Figure S2 Overlay of the same force curve shown in figure 1 together with a force curve performed on a bare silicon substrate. The contact point of both approach curves was matched.

From these it was possible to obtain the force curves expressed as Force per indentation depth. This was done only for the approach curves which were the ones necessary to estimate the spring constant of the suspended micelles. Moreover, only the portion following the contact between the tip and the micelle was shown. An overlay of the converted curves is shown in Figure 4.

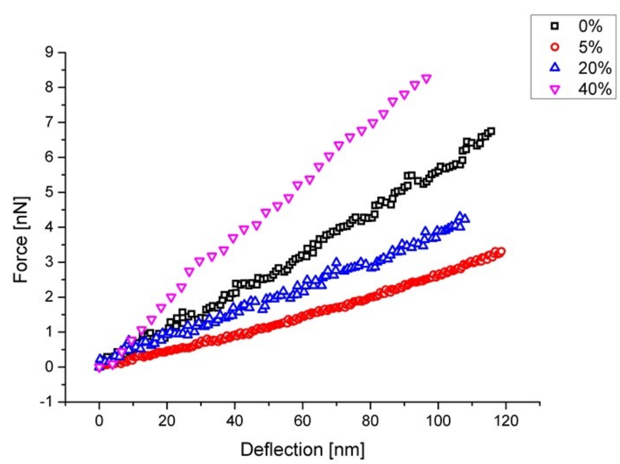

Figure S3 Force vs deflection for each different suspended elongated micelle. Each curve shows an elongated micelle with a different homopolymer concentration.

The slope of these curves corresponds to the spring constant *(k_m)* of the micelles which can be used to evaluate their elastic modulus using the following equation:

$$E_{app} = \frac{192\,IF}{L^3\;\;d} = \frac{192\,I}{L^3} k_m$$ *Equation 1*

The major contribution to the error on the moduli is given by the uncertainty on the diameter measurement which appears in the area modulus of inertia.

Diameter characterization TEM and AFM images

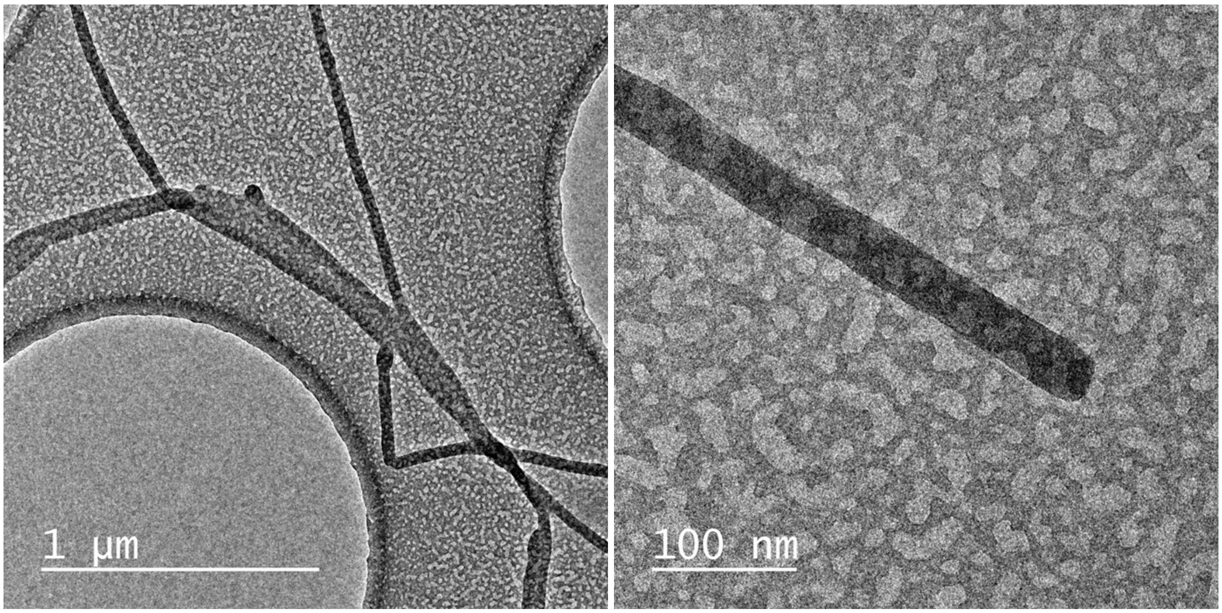

Figure S4 Representative TEM images used to measure the diameter of the raw copolymer micelles. On the is a lower magnification image showing how the micelle diameter is approximately constant along their length, while on the right is one of the high magnification images used to determine the diameter.

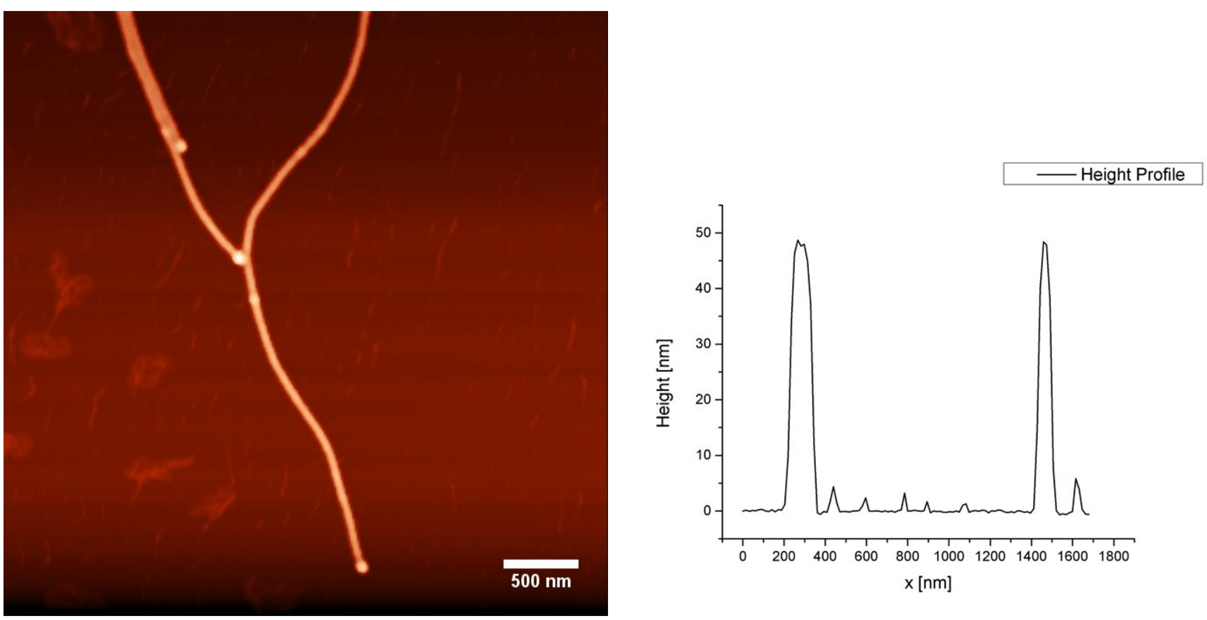

Figure S5 AFM topography scan of a raw PS-PEO micelle on a flat silicon substrate (left). On the right is a height profile drawn on the top part of the image crossing all three of the micelles. From the height of the peaks we can obtain an estimate of the micelle diameter in their dry state which is of 48 nm.

AFM topography scans of suspended micelles

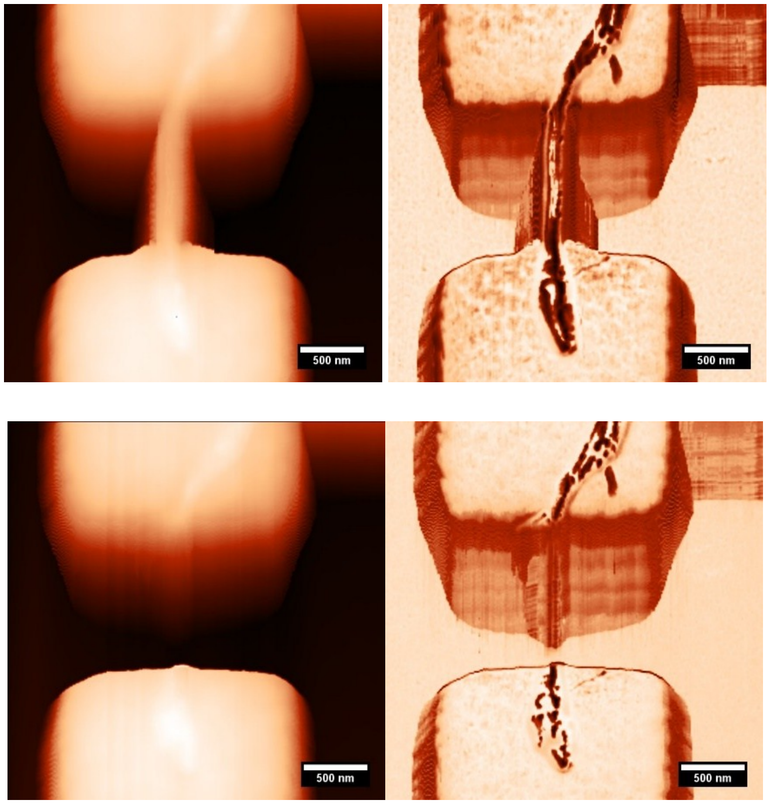

Figure S6 Top row: AFM topography (left) and phase (right) scans of a suspended micelle. This is an example of the topography scans used to find the central portion of the micelle to perform the force curves. Bottom Row: Topography (left) and phase (right) scans performed after a series of, destructive, force curves were performed on both the micelle's suspended part and on the one supported by the pillars. It can be seen that force curves performed on the micelle on top of the pillars can fracture the micelle without it moving from its original position. Moreover, imparting a high deflection to the suspended part of the micelle will cause it to fracture at the pillar edges. Even under such destructive conditions, the position of the micelle at the edges of the pillars is not changed.