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Supporting information

In-situ visualization of the enzymatic growth of surface immobilized DNA block copolymer micelles by scanning force microscopy

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SEM imaging of a cantilever tip after the *in-situ* measurement

Variations in the width of structure could arise from tip abrasion; however the height of structures is not depending significantly on the shape of the tip. To exclude tip artifacts we imaged every AFM tip by scanning electron microscope (SEM) after the measurements and the radii of curvature were measured. In all SEM data reported, we found tip radii between 8 – 20 nm (Figure S-1).

Figure S-1: Scanning electron microscope image of a tip after an *in-situ* measurement. The radius of curvature of this tip is 8 nm.

Comparison of the histograms for *in-situ* and *ex-situ* experiments

Figure S-2: Histograms of height of micelles after *ex-situ* enzymatic reaction of 60 min and *in-situ* enzymatic reaction of 52 min. The histograms were fitted by Gaussian equation.

AFM imaging of 42mer DNA-*b*-PPO

Figure S-3: Height topography of 42mer DNA-*b*-PPO micelles imaged by tapping mode in buffer.

The data scale is 10.0 nm.

Figure S-4: Scanning electron microscope image of the tip after a measurement with DNA(42mer)-*b*-PPO micelles. The radius of curvature of this tip is 17 nm.

Enzymatic reaction of 42mer DNA-*b*-PPO

Figure S-5: *In-situ* observation of the enzymatic reaction of 42mer DNA-*b*-PPO micelles and height distribution of surface structures. (A) Before injection of dTTP. (B) 10 min after injection of dTTP. (C) 28 min after injection of dTTP, and (D) 46 min after injection of dTTP. The lateral scale is 200 nm and the height scale is 10 nm for all images. (E) Histograms of height of globular structures obtained from SFM measurements. Each histogram was fitted by two Gaussian distributions.

Height distribution of surface structures in the experiment “continuous monitoring of selected micelles”

Figure S-6: Histograms of height of globular structures obtained from the images shown in Figure 3. Each histogram was fitted by two Gaussian distributions. Both the peak of TdT and the peak of DNA-*b*-PPO micelles could be distinguished clearly. The peak of TdT remained constant at approx. 3 nm for all images analyzed. The peak of DNA-*b*-PPO shifted from 4.7 nm at 23 °C to 7.6 nm 72 min after 37 °C was reached.

Gel electrophoresis pictures of DNA-*b*-PPO micelles after different reaction times in the presence and absence of Ni^{2+}

Figure S-7: Gel electrophoretic analysis of the DNA-*b*-PPO block copolymers after different reaction times with TdT a) in the presence b) in the absence of Ni^{2+} .