Supporting Information

Thermally sensitive block copolymer particles prepared via aerosol flow reactor method: Morphological characterization and behavior in water

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This supporting material consists of fourteen figures and one video, which can be separately downloaded and viewed.

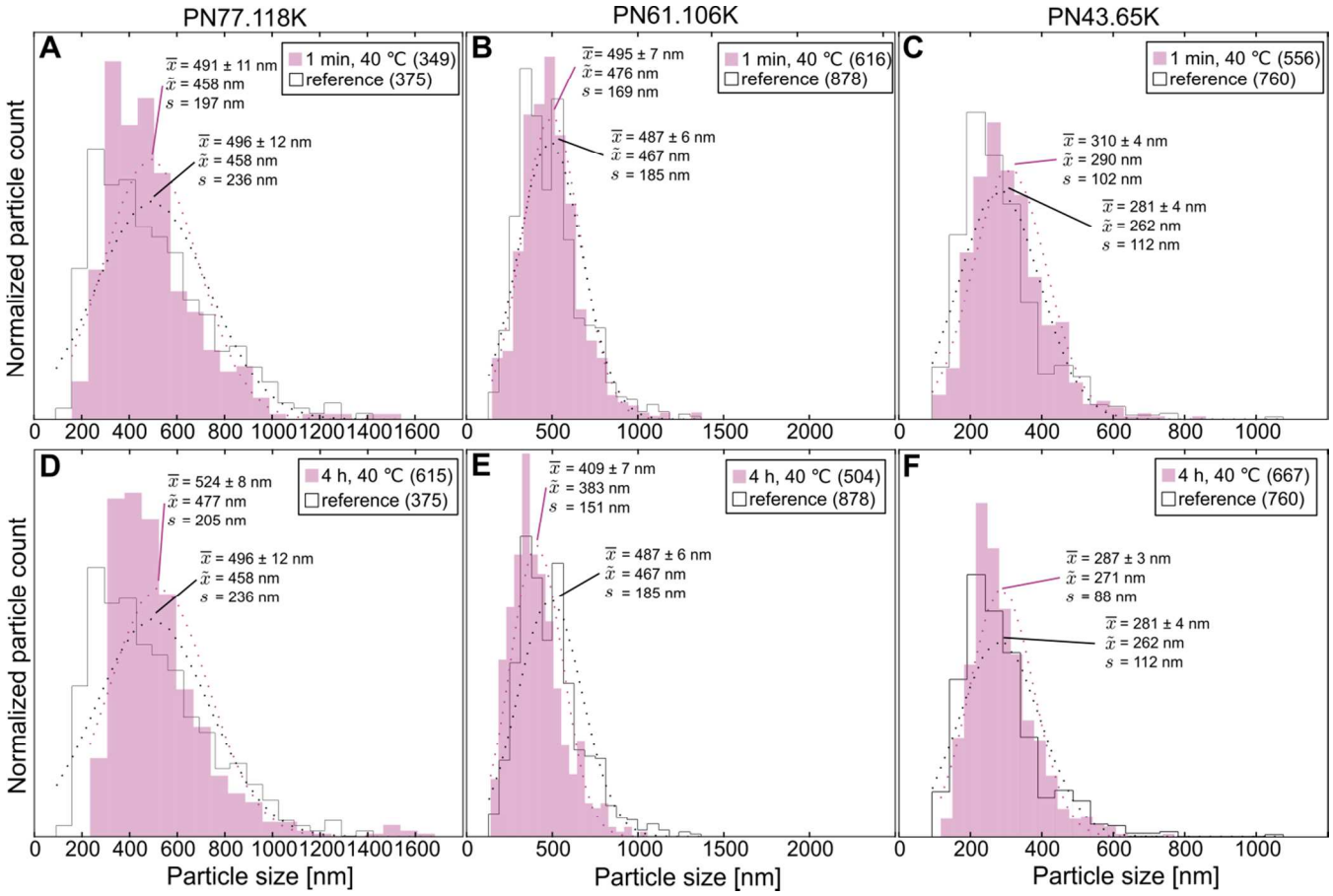


Figure S1. Particle diameter size distributions acquired from SEM micrographs for as-prepared particles (black line) and for freeze-dried particles after being one minute or four hours in water at 40 °C (violet area). Sample mean (x-bar), median (x-tilde) and standard deviation *s*, were calculated from the statistics. The amount of particles used for the statistics is written inside the parentheses in the label box. Normal distributions fitted to the data have been plotted with dashed lines.

In bulk the PN43.65K self-assembles into a lamellar morphology with periodicity of 395 Å as measured by SAXS as can be seen in Figure S2. It is possible to study the thickness of the PS lamella in the aqueous environment by using microtomed thin sections (ca. 100 nm of thickness). We found out that at

20 °C the width of the PS lamella is approximately 17 nm. This means that the PNIPAM lamella width in bulk would be approximately 22-23 nm. The PNIPAM domain width increases due to the swelling but the exact amount of swelling is difficult to resolve reliably because of the constraining effect of PS (see Figure S3).

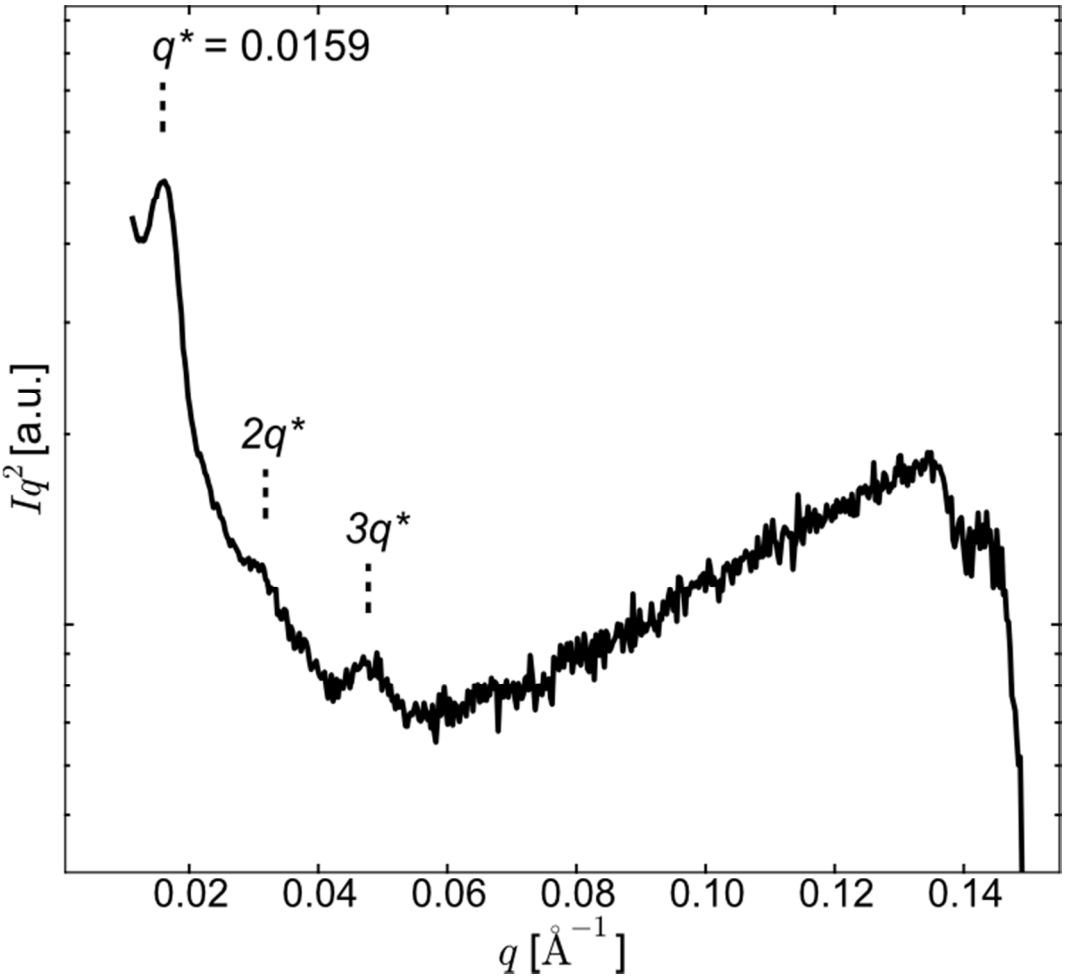


Figure S2. SAXS of annealed bulk PN43.65K. Lorenz-corrected intensity as a function of scattering vector. Three peaks support the lamellar morphology observed in TEM. Periodicity $d = 2\pi/q^* = 395$ Å.

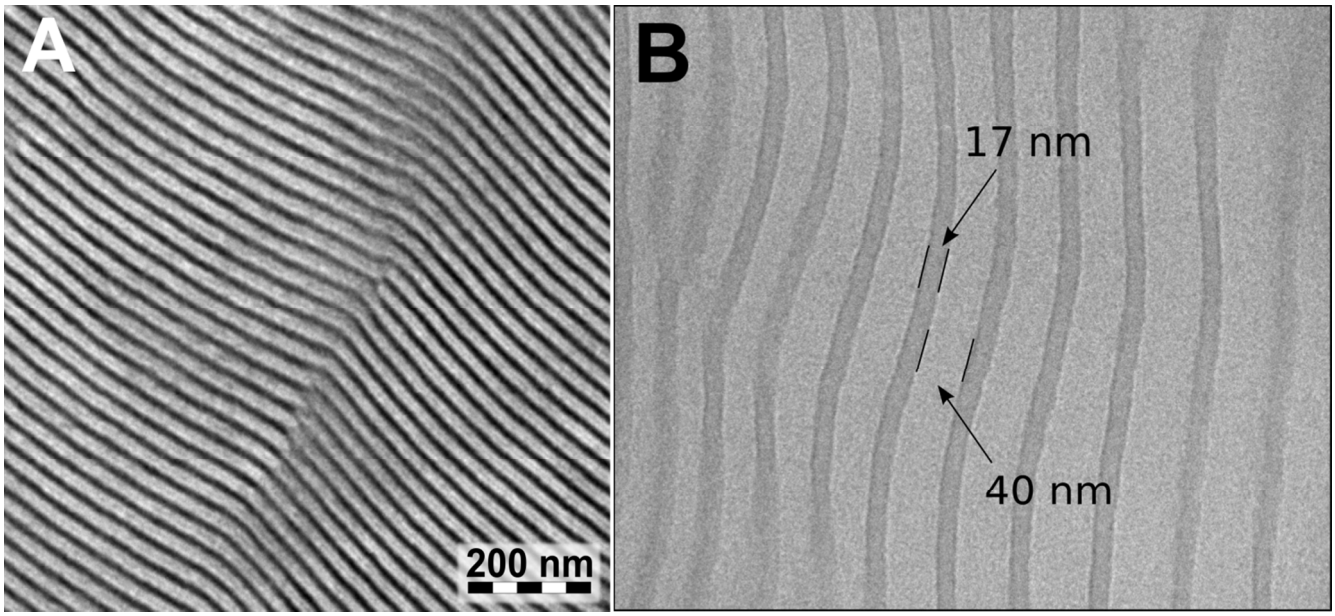


Figure S3. **(A)** TEM micrograph of iodine stained bulk section of annealed PN43.65K. Iodine stains PNIPAM domains, which appear dark in the micrograph. Periodicity was measured 30 nm, which is 23% less than measured by SAXS. One reason for this is the shrinking caused by the iodine staining. The other reasons can be the compression caused by microtoming. PS layer thickness was measured to be 20 nm. For comparison, the layer thickness in the cryo-TEM micrograph was measured to be 17 nm. One has to keep in mind that the layer thickness measurements made for onion-like particles are much more accurate, since no microtoming compression effect and possible section tilting effect are present. **(B)** Cryo-TEM of microtomed section of bulk PN43.65K prepared after equilibrating in water at 20 °C for 5-10 minutes. Sample is unstained. The lamellae widths of the PS and PNIPAM domains can be measured from cryo-TEM micrographs, resulting in 17 nm and 40 nm, respectively.

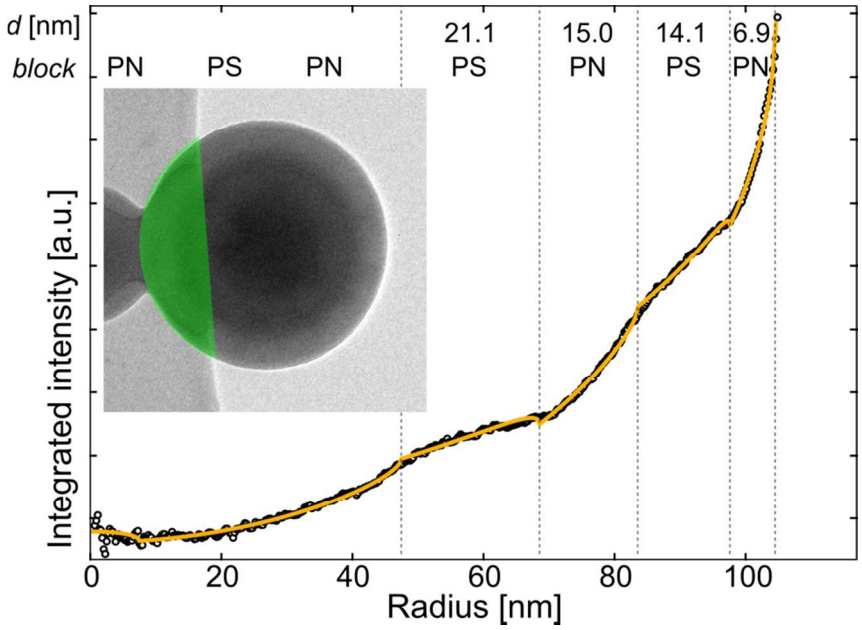


Figure S4. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been stained at iodine vapor for four hours. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

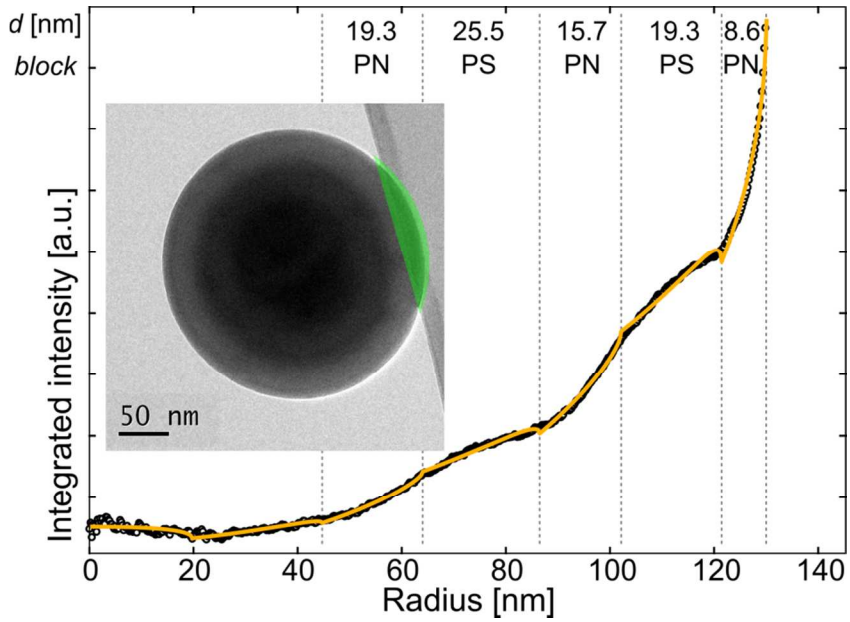


Figure S5. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been stained at iodine vapor for four hours. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

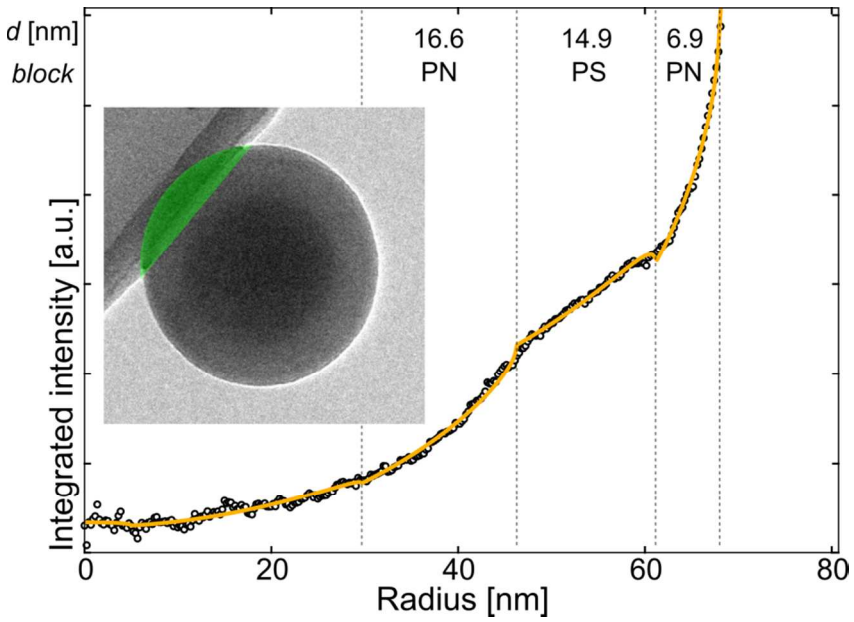


Figure S6. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been stained at iodine vapor for four hours. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

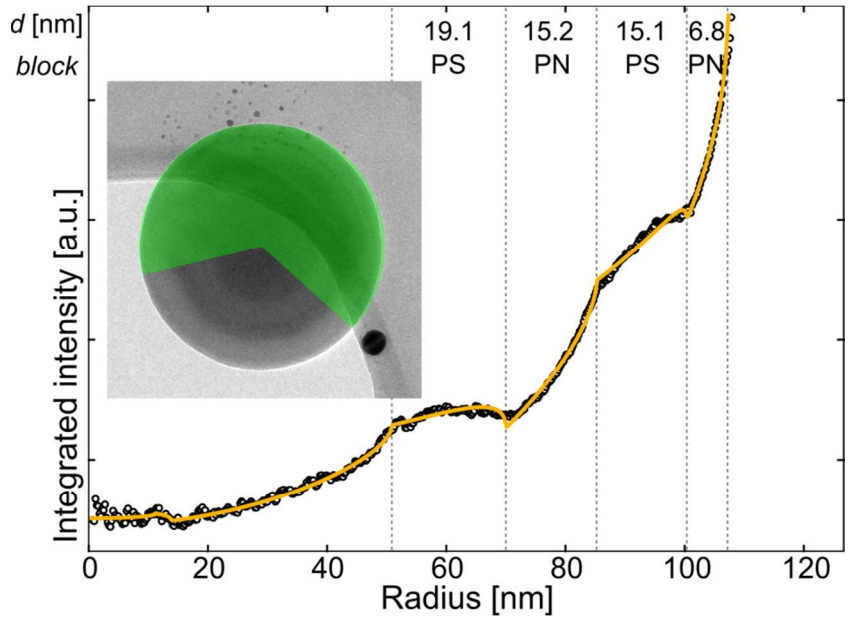


Figure S7. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been stained at iodine vapor for four hours. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

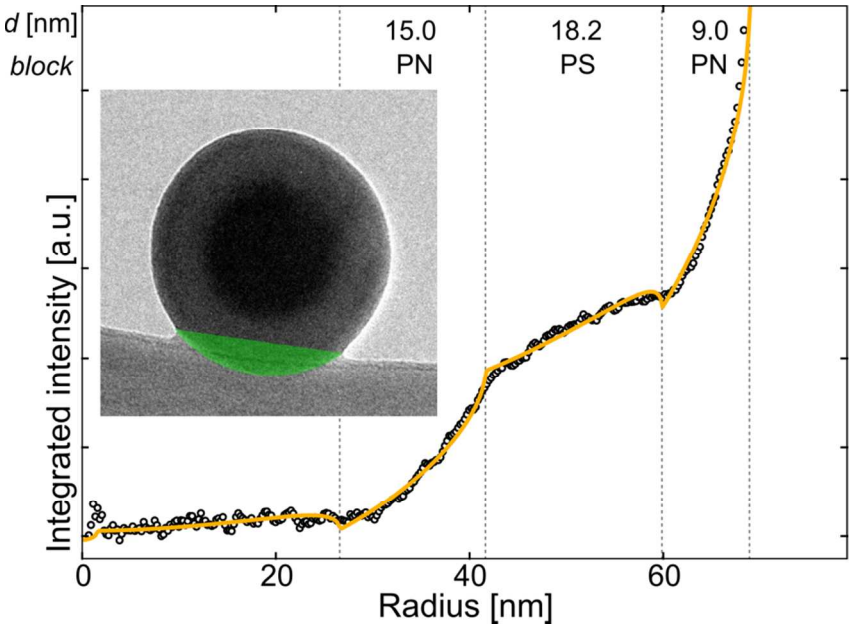


Figure S8. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been stained at iodine vapor for four hours. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

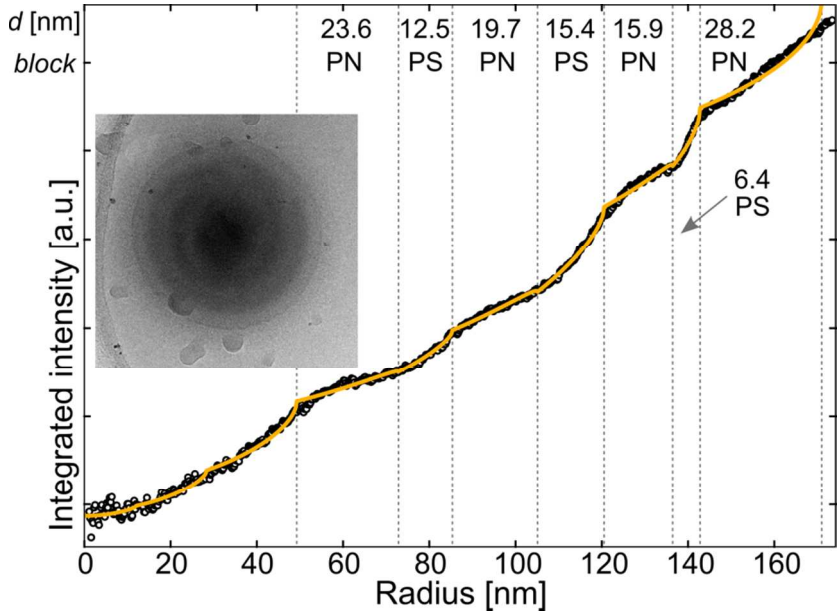


Figure S9. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been equilibrated in water at 20 °C for 5-10 minutes. No staining was used. Integration was performed around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

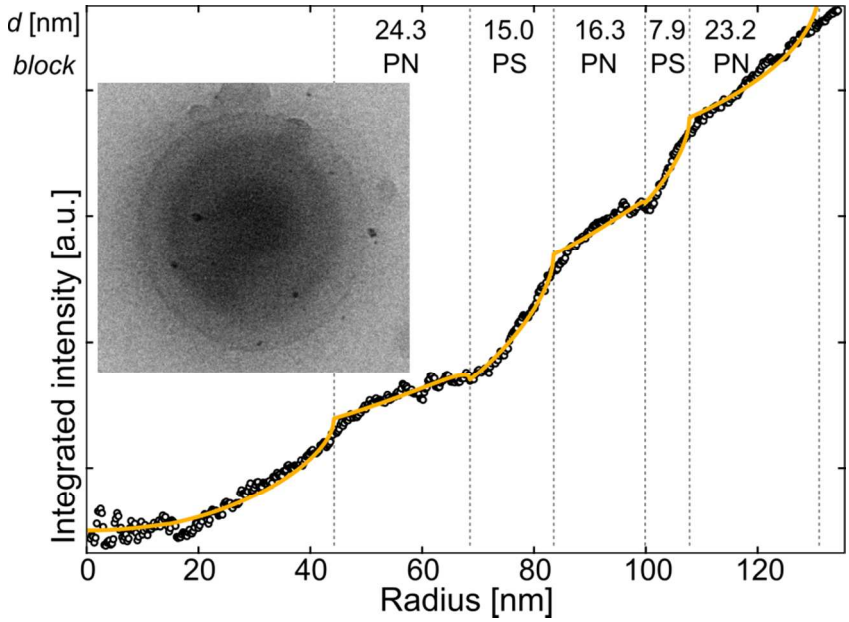


Figure S10. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been equilibrated in water at 20 °C for 5-10 minutes. No staining was used. Integration was performed around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

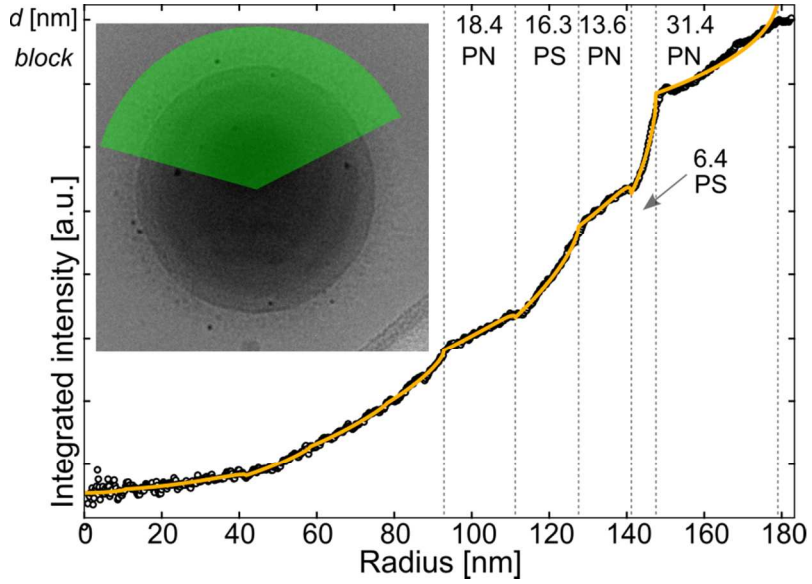


Figure S11. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been equilibrated in water at 20 °C for 5-10 minutes. No staining was used. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.

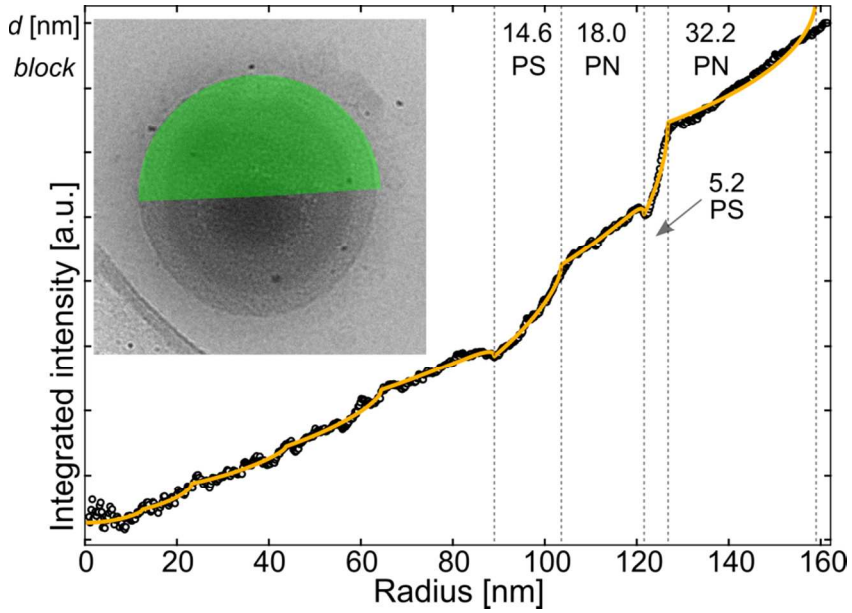
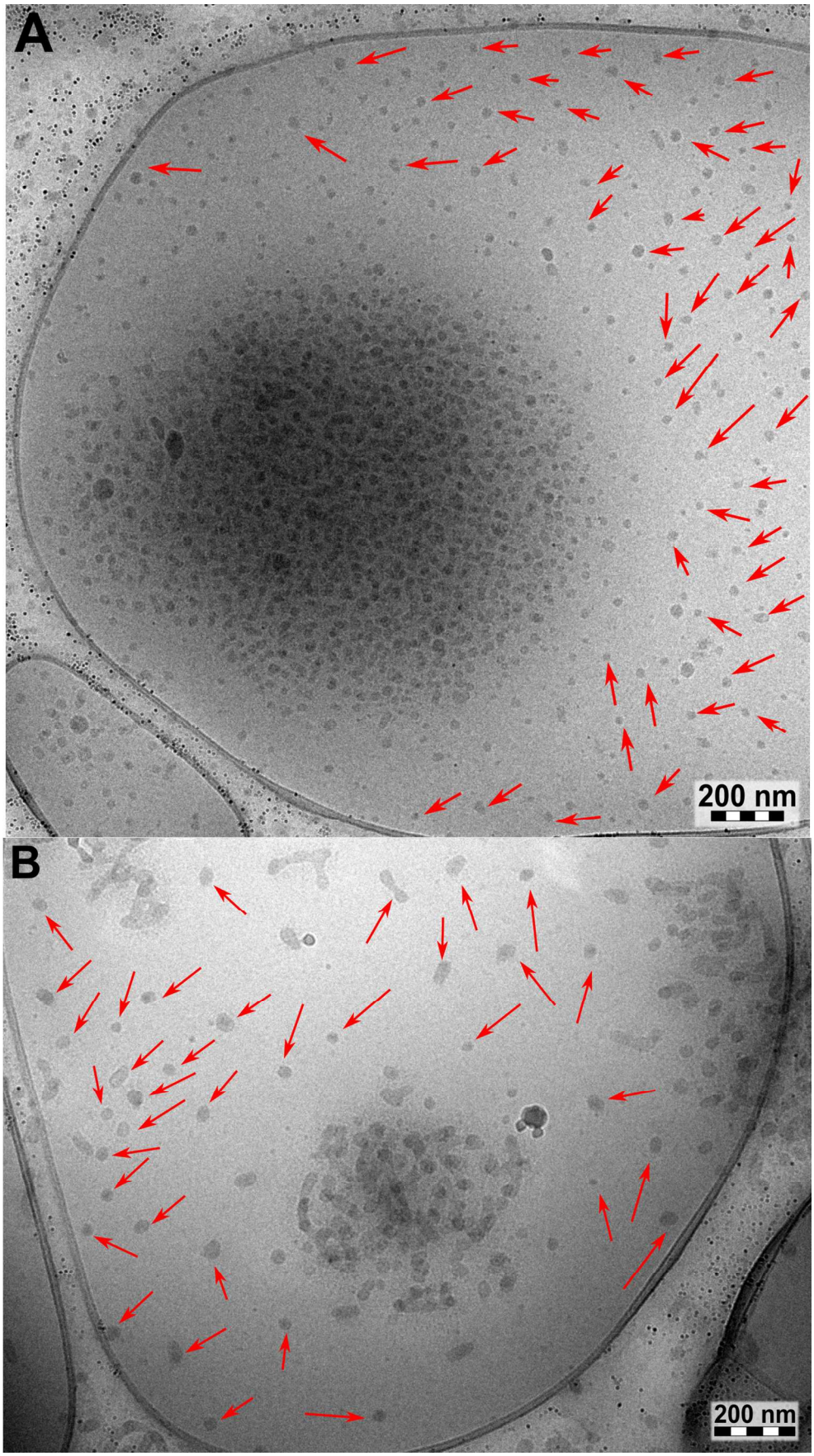
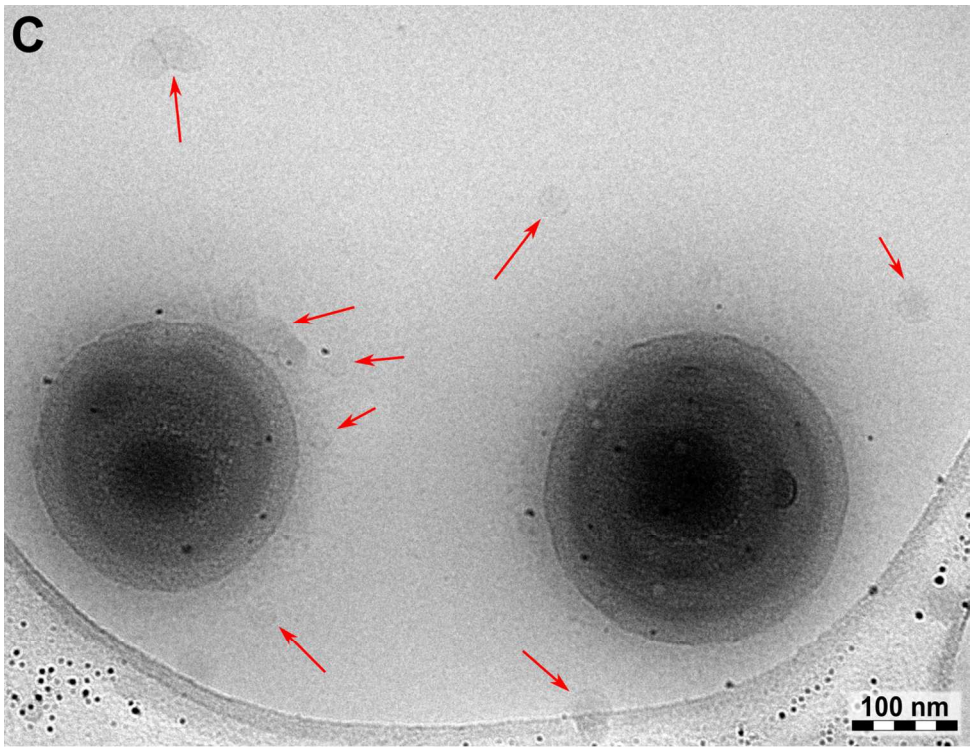


Figure S12. Integrated intensity of a projection of a spherical particle with onion-like morphology (open circles) and fitted model (yellow line). The sample has been equilibrated in water at 20 °C for 5-10 minutes. No staining was used. Integration was performed on the unmasked area and around the center point of the particle in the inset TEM-micrograph. The layer widths given by the model are listed on top of the graph.


A
200 nm
B
200 nm


C
100 nm

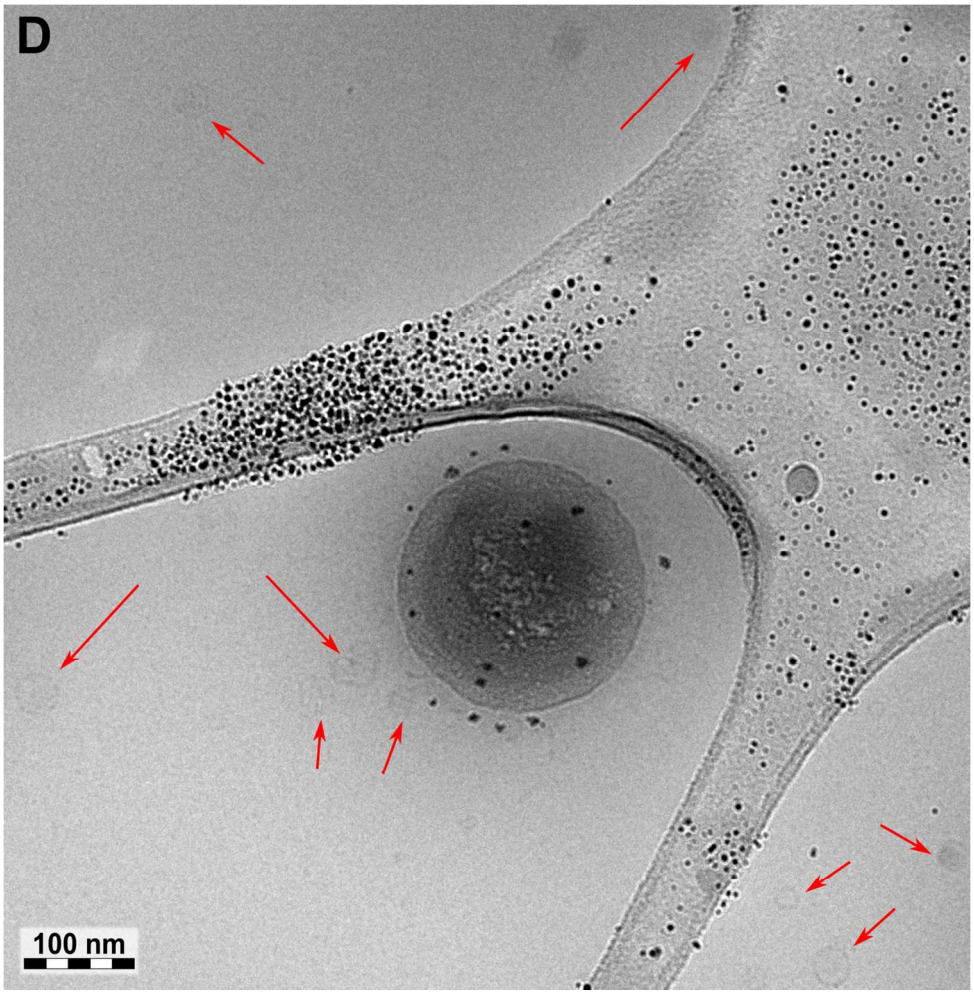

D
100 nm

Figure S13. Cryo-TEM micrographs taken from samples **(A)** PN77.118K, **(B)** PN61.106K, **(C)** and **(D)** PN43.65K. Samples were equilibrated in water at 20 °C for 5-10 minutes before vitrification. Separate micelles and vesicles have been marked by red arrows.

The aggregate sedimentation was verified for PN61.106K with UV-Vis and is plotted in Figure S14, where the temperature of the solution has been plotted with orange line and the measured light absorption has been plotted with green dots as a function of time. A particle dispersion, which has been prepared at room temperature, is first heated up to 40 °C with heating rate of 9.6 °C·h^{-1}. One can observe that this leads to the increase of light absorption due to the particle aggregation. The light absorption decreases during the next 22 hours, when the temperature stays constant at 40 °C. This is suggested to be due to the sedimentation of the particle aggregates. Next the temperature is dropped to the room temperature. At 32 °C a sudden drop of light absorption can be observed, which is due to the melting of the aggregates. After ten hours at 23 °C the temperature is again risen up to 40 °C. One can observe that the light absorption does not rise to the same level as during the first heating. This proves that the aggregation process is not totally reversible. In other words ten hours at 23 °C is not enough to melt all the aggregates that were formed during 20 hours at 40 °C.

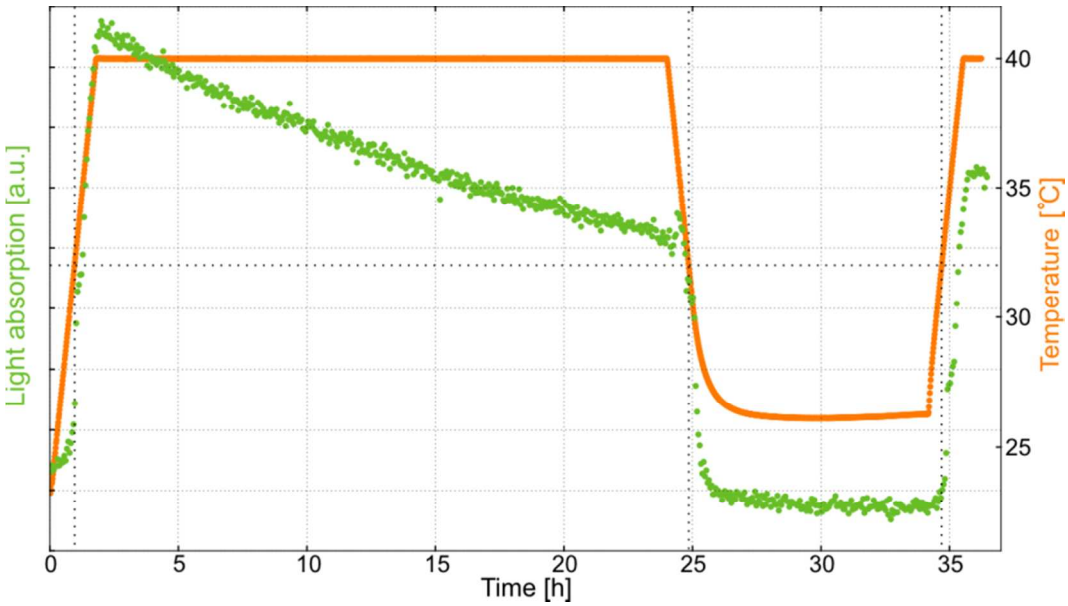


Figure S14. Light absorption of aqueous dispersion of PN61.106K as a function of temperature and time. Light absorption increases as a result of particle aggregation as the temperature is increased

beyond 32 °C. The solution has been kept static during the measurement without any mechanical stirring. At 40 °C light absorption decreases, which is due to the aggregate growth and subsequent sedimentation.