

Clustering of asymmetric dumbbell-shaped silica/polystyrene nanoparticles by solvent-induced self-assembly

By Weiya Li, Serge Ravaine and Etienne Duguet

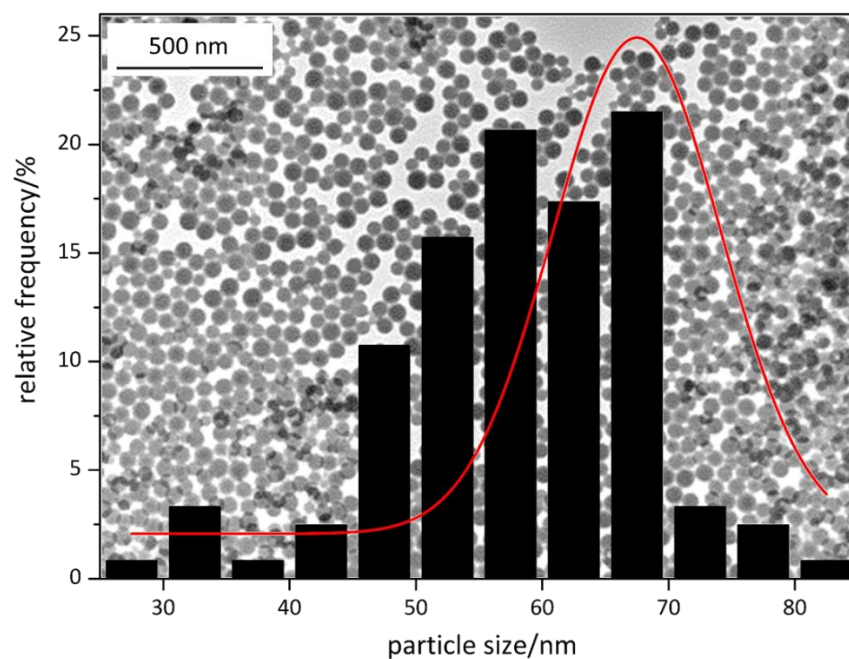


Fig. S1 Typical TEM image and size distribution of the precursor PS seeds.

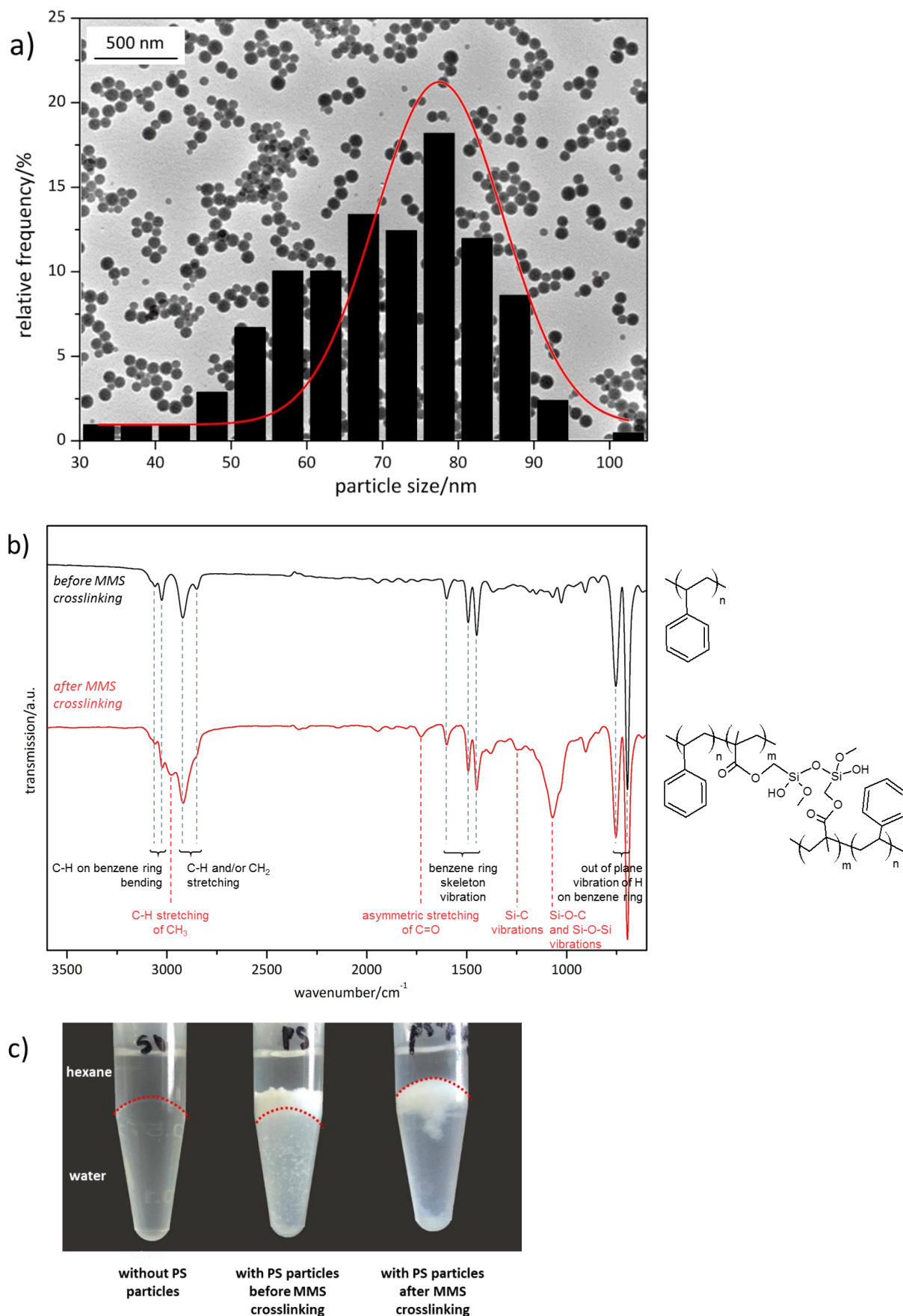


Fig. S2 a) Typical TEM image and size distribution of the MMS-crosslinked PS seeds; b) Fourier transform infra-red spectra of PS particles before and after MMS-crosslinking (performed on Shimadzu FTIR spectrophotometer IRAffinity-1S with MIRacle 10 single reflection ATR accessory; every sample was previously dried overnight under air at 70°C); c) dispersibility test of PS nanoparticles showing they are more readily dispersed in an aqueous phase after MMS-crosslinking.

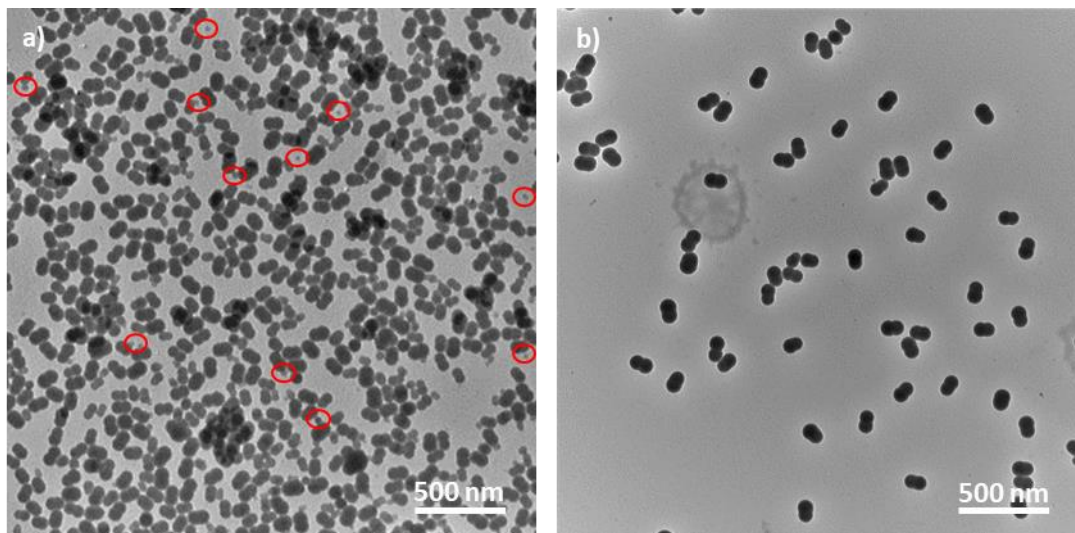


Fig. S3 Representative TEM images of PS dumbbell-shaped nanoparticles obtained for a swelling ratio $S = 2$ and swelling time of a) 2 h and b) 3 h. The red circles show extra PS spherical latex nanoparticles resulting from the incomplete styrene-swelling opening the possibility for non-seeded growth polymerisation of styrene.

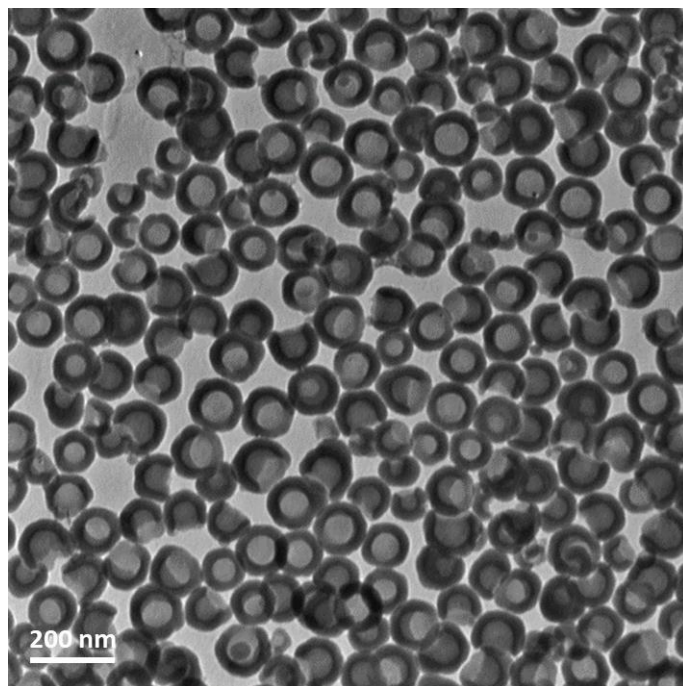


Fig. S4 Typical TEM image of the silica nanobowls obtained by calcination of the Silica/PS dumbbell-shaped nanoparticles (Batch #3) in a nacelle introduced in a furnace under air at 600°C for 6 h. The evidence of the nanobowl-like shape depends on the arrangement of the nanoparticles on the TEM grid.

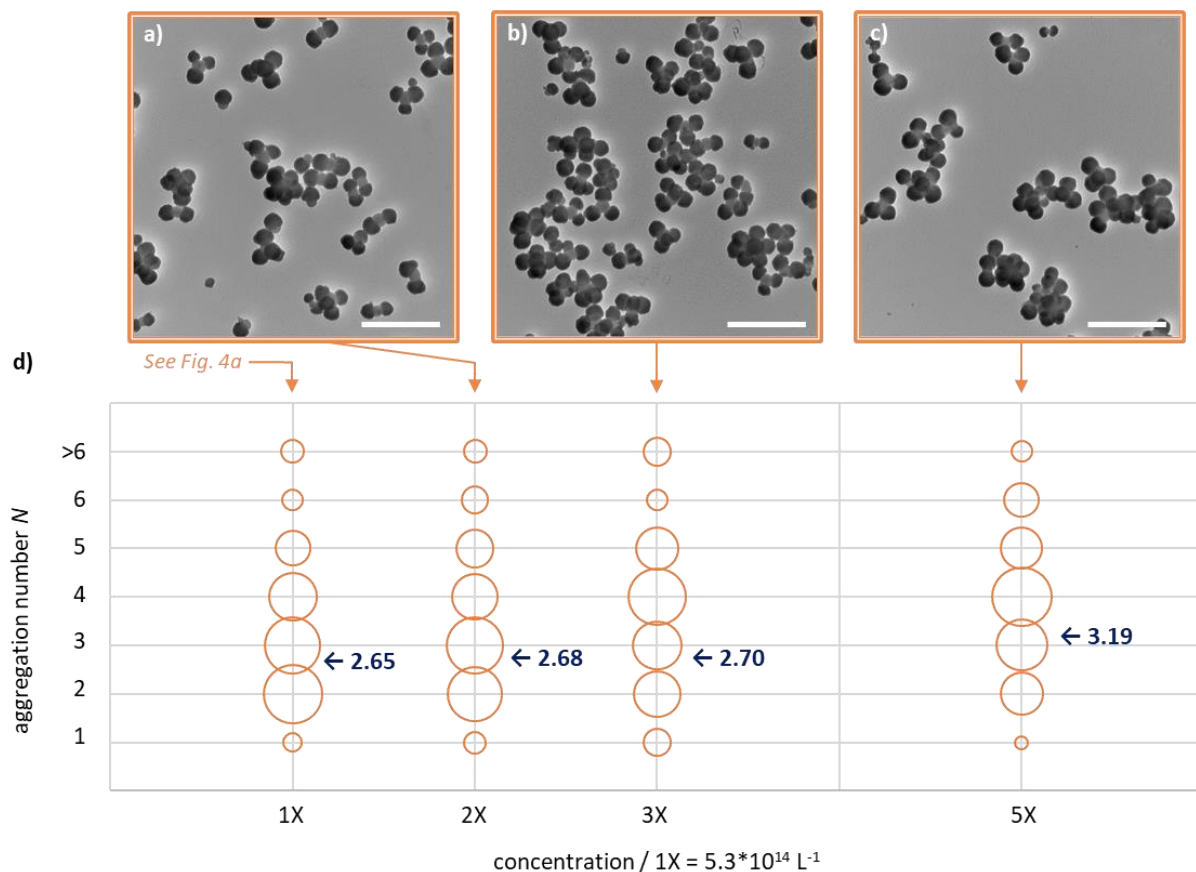


Fig. S5 a) to c) representative TEM images of the cluster mixtures obtained from Silica/PS dumbbell-shaped nanoparticles as a function of the nanoparticles concentration (scale bars: 500 nm); d) distribution of the nanoparticles within the clusters of aggregation number N as determined by statistical analysis of the TEM images (the surface of the circles is proportional to the fraction of the nanoparticles assembled within clusters of similar aggregation number). The blue arrows indicate the average aggregation number \bar{N} calculated without taking into account the clusters with $N > 6$. Assembly experiments were performed with the silica/PS dumbbells of Batch #3 in an ethanol/DMF mixture with DMF fraction of 30 vol. % at 20°C for 20 h with a final centrifugation stage (12,000 g for 10 min).

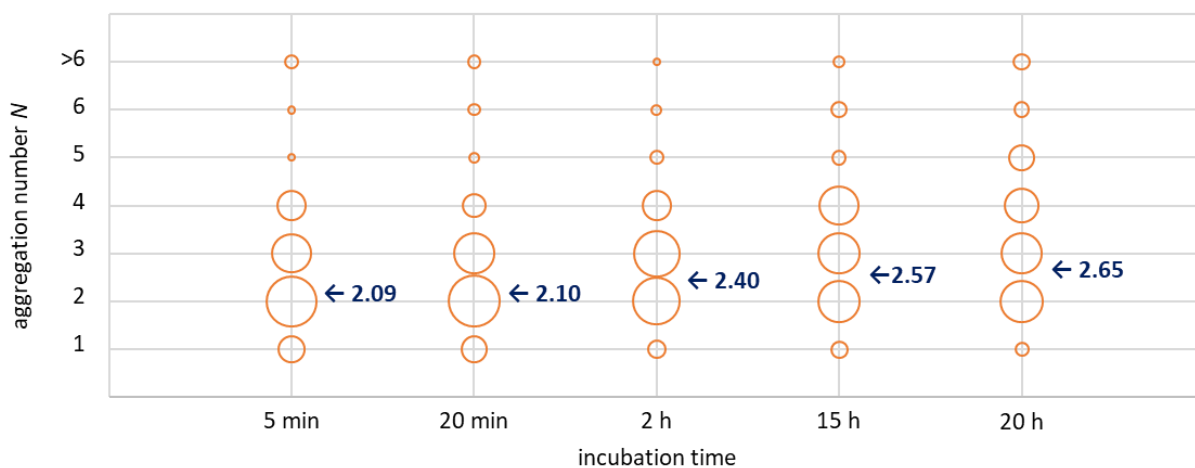


Fig. S6 Distribution of the nanoparticles within the clusters of aggregation number N as a function of the incubation time as determined by statistical analysis of the TEM images (the surface of the circles is proportional to the fraction of the nanoparticles assembled within clusters of similar aggregation number). The blue arrows indicate the average aggregation number \bar{N} calculated without taking into account the clusters with $N > 6$. Assembly experiments were performed with the silica/PS dumbbells of Batch #3 in an ethanol/DMF mixture with DMF fraction of 30 vol. % at 20°C at the concentration of $5.3 \cdot 10^{-14}$ part/L with a final centrifugation stage (12,000 g for 10 min).

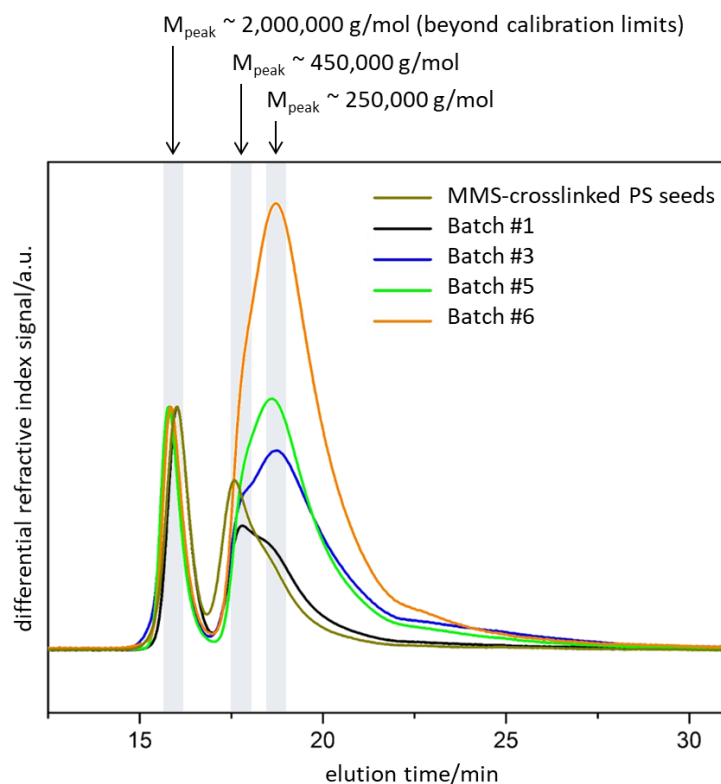


Fig. S7 Molar mass distribution of the PS macromolecules within the different nanoparticles synthesized for this study. Polymer molar masses were determined by size-exclusion chromatography (SEC) using DMF + lithium bromide (LiBr, 1 g/L) as the eluent on an Ultimate 3000 system from Thermo Fisher Scientific equipped differential refractive index detector from Wyatt technology. Macromolecules (5 mg/mL) were separated on Shodex Asahipak gel columns (GF-1G 7B, 7.5*50 mm; GF-310, 7.5*300 mm and GF-510, 7.5*300 mm) at a flowrate of 0.5 mL/min at 50°C. EasiVial kit of PS from Agilent was used as the standard for calibration (\overline{M}_n from 162 to 364,000 g/mol).