Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Synthesis of Non-spherical Patchy Particles at Fluid-Fluid Interfaces via Differential Deformation and their Self-Assembly

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1. Contact angle of PS particles at various decane-aqueous suspension containing positively charged silica nanoparticles.

Figure S1 shows the SEM images that are used to measure contact angle of PS particles at water-decane interface based on a recently developed method by us.[1] In this method, position of negatively charged PS particles at decane-water interface is visualized by exploiting hetero-aggregation of PS particles with oppositely charged silica nanoparticles in the bulk. The attachment of silica particles on the PS particles exposed to water side leaves a distinct contact line, which can be used to quantify the contact angle of particles at fluid-fluid interfaces. By measuring two dimensional projection of diameter of the contact line (d) and diameter of the particles (D), we found the contact angle to be 63 ± 2˚. For this study, we use a dilute (1 % by weight) aqueous dispersion of positively charged silica (Ludox CL-30) nanoparticles of 15 nm diameter, as sub-phase. The zeta potential of silica nano particles for CL-30 is +60 ± 1 mV at 1 mM NaCl electrolyte solution. After spreading PS particles at decane-water interface, an equilibration period of 60 min is allowed such that the CL nanoparticles have sufficient time to deposit on the surface of the PS particles exposed to the aqueous phase. The positively charged silica CL nanoparticles electrostatically bind over negatively charged PS particles. Figure 1 shows a circular region (marked by an arrow line) where there is nanoparticle deposition, and a distinct contact line. The contact angle is estimated by the geometric relation: $\theta = \sin^{-1}(d/D)$ ------- (1). Alternatively, the qualitative evidence of equilibrium position can also be visualized by following the deforming contact line at the interface during heating. As described in the manuscript in experimental section, the particles heated upto 10 min are imaged using high resolution scanning electron microscope (HRSEM). Figure S1 B reveals the thin deforming interface line after 10 min of heating. At this time of heating, although particles slightly deform and leave a distinct line of protrusion at the contact line, yet it retains a spherical shape but the deformation begin to grow over time. The deformation line can be easily tracked to visualize the equilibrium position of the particles. The visual appearance shown by Figure S1 B is in agreement with the contact line measured from Figure S1A.

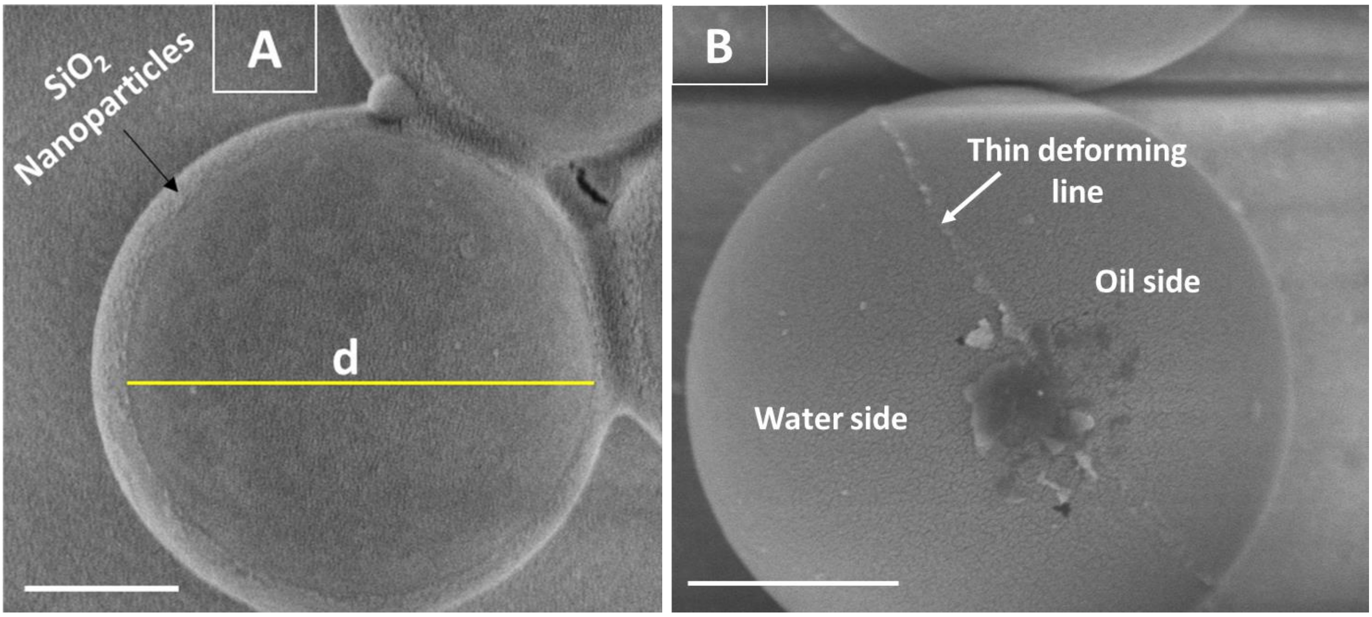

Figure S1. A) Visualization of equilibrium position of particles at the decane-water interface by depositing Ludox-CL nanoparticles on the part exposed to water side, B) qualitative evident for visualizing equilibrium position by tracing deformed contact line due to differential deformation. The scale bar corresponds to 1 µm.

2. Contact angle of PS particles at decane-aqueous solution containing negatively charged SDS surfactants.

Measurement of contact angle of particles spread at aqueous surfactant solution-decane interface is done by visualizing the deformed line formed at the interface as similar as the one shown in Figure S1 B. From Figure S2, it appears that the contact angle of particles is close to 90˚. However, when emulsifying decane and aqueous suspension containing SDS and PS particles, we find that the particles stabilize preferentially oil-in-water type emulsion. This observation suggests that the contact angle could be slightly lesser than 90˚.

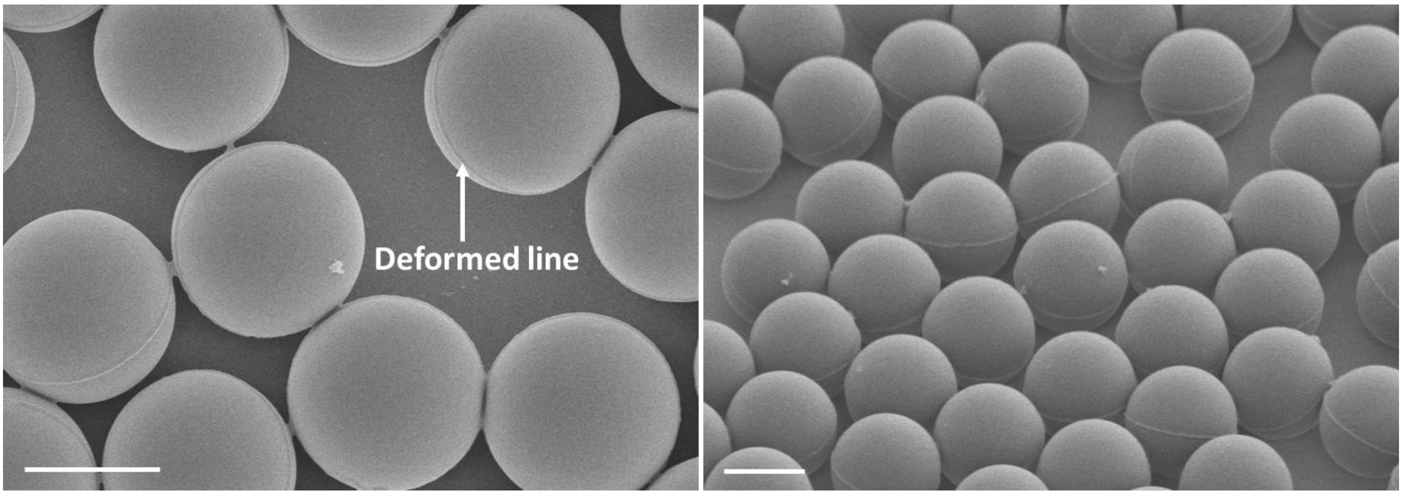

Figure S2. HRSEM images at different regions of deposition of particles showing distinct demarcation line when imaged A) from top and B) by tilting the substrate upto the observation angle of 50˚ using tilted mode of operation. The scale bar corresponds to 2 µm.

3. Contact angle of PS particles at decane-aqueous solution containing positively charged CTAB surfactants.

Measurement of contact angle of particles spread at aqueous CTAB solution-decane interface is done by emulsifying aqueous solution containing CTAB and PS-decane. The type of emulsion formed is an indication of particle wettability. From Figure S3, we find that water-in-oil (W/O) emulsion is formed by synergistic stabilization of CTAB and the PS particles. It appears that the contact angle of particles is more than 90˚, in accordance with well accepted rule that the hydrophobic particles stabilize water-in-oil emulsions. Figure S3 D-E reveals the deforming contact line at the interface. Thus, the thin and distinct contact line showing demarcation of deforming boundary line between water and oil interface reaffirms the trend of wettability or contact angle of PS particles found in emulsion based system. The demarcation made by thin deforming line suggests that the contact angle is higher than 90˚, $\theta > 90^\circ$.

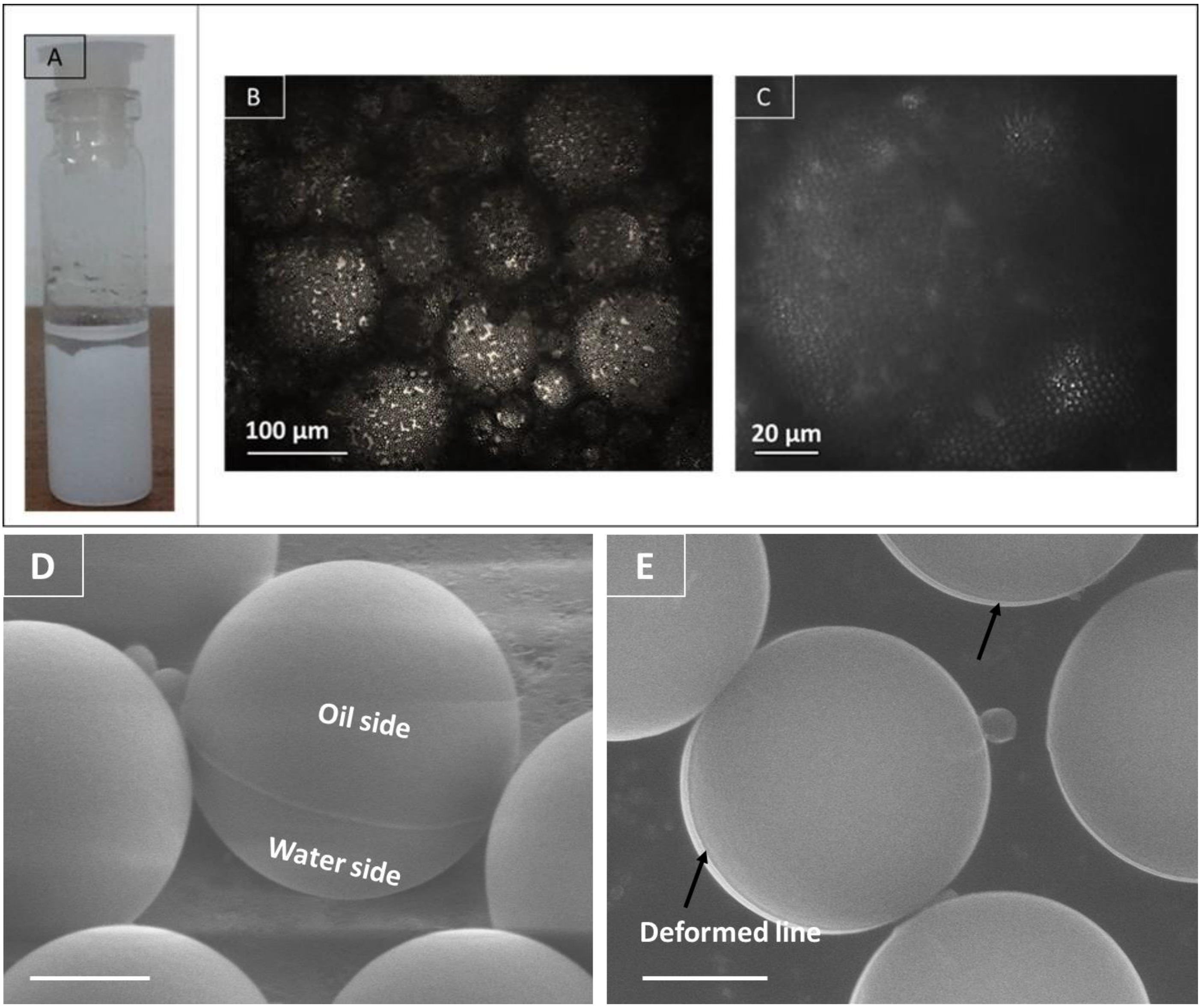

Figure S3. A qualitative assessment of contact angle of particles using emulsion route, A) glass vial showing water-in-oil emulsion, B-C) inverted microscope images at different magnification showing water droplets stabilized by particles, D) HRSEM image showing distinct demarcation line when obtained by tilting the particles upto the observation angle of 50˚ using tilted mode of operation, E) HRSEM image showing bottom morphology (bottom part of particles is flipped up by peeling off the particles using carbon tape) of particles with the distinct contact line of interface. The scale bar of Figures D-E correspond to 1 µm.

From Figure S1-S3, it is clear that the initial contact angle of PS particles at the interface of decane and aqueous suspension of silica, SDS and CTAB are 63˚, ≈90˚ and >90˚, respectively.

4. Temperature profile of water and decane medium during heating and cooling cycle

The complete temperature profile of heating and cooling cycle of water-decane interface is given in Figure S4. From Figure S4, it is clear that the total residence time of the particles exposed at a temperature between 50-60 ˚C is ≈ 40 min. The data for cooling cycle is obtained by turning off the heating element and allowing the sample to cool to room temperature without removing the beaker from the heating element.

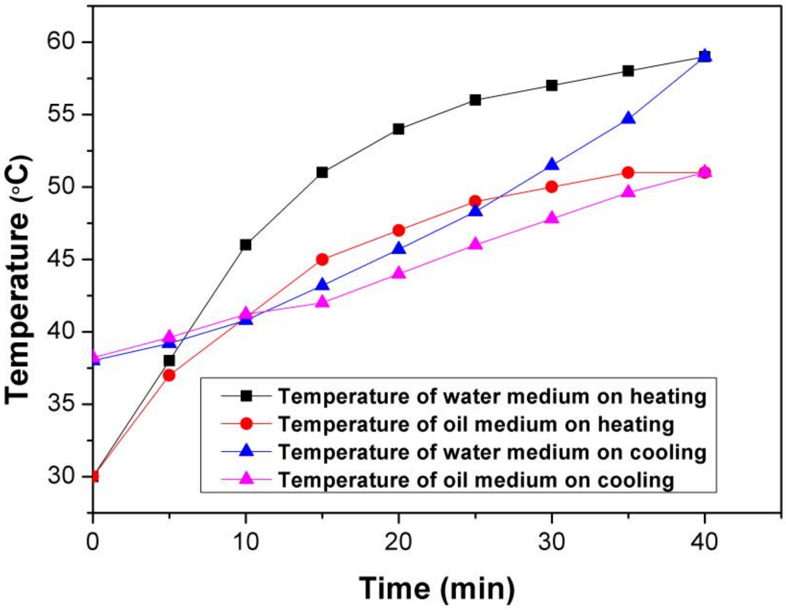

Figure S4. Temperature profile of water and oil medium after creating water-decane interface.

5. Effect of apolar media on the deformation of particles

Figure S5 reveals the intactness of shape when PS particles were heated upto 60˚C for 40 min at water-air and water-octanol interfaces. The structure captured in HRSEM clearly shows the absence of any transformation from spherical to non-spherical shape. The reason for intactness is due to rigidity of the PS particles throughout the experimental time, as the particles are not exposed to temperature close to glass transition temperature when heated at water-air and water-octanol interfaces.

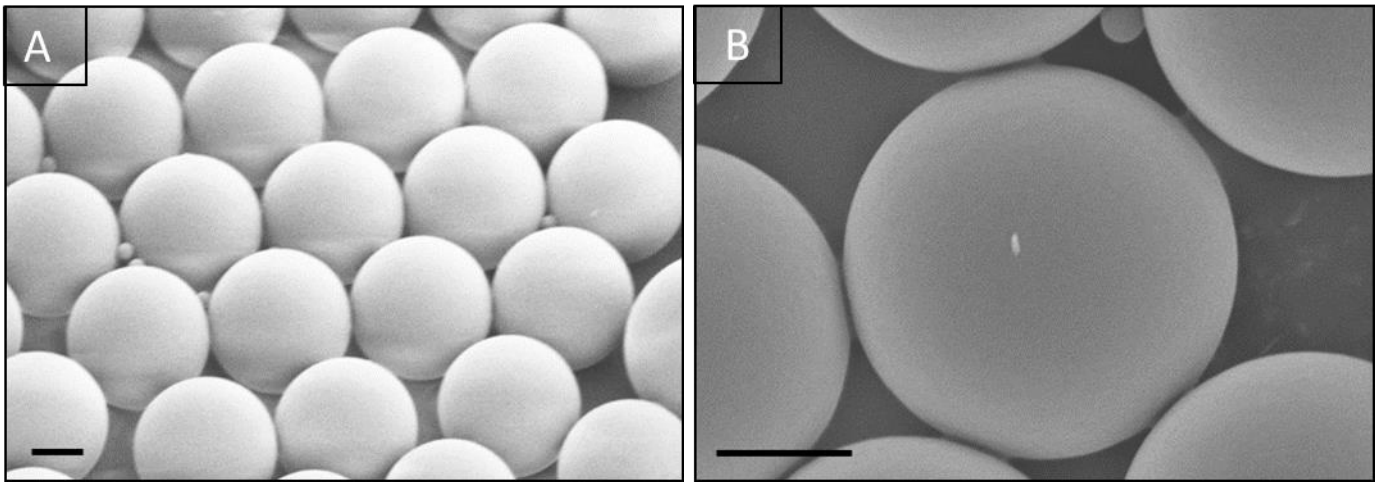

Figure S5. HRSEM images showing the absence of any deformation of the particles when heated upto 60˚C (water temperature) at different interfaces A) water-air and B) water-octanol. Scale bar corresponds to 1 µm.

6. The behaviour of spherical polystyrene (PS) particles of 3μm size dispersed in 0.1mM electrolyte solution.

Figure S6 reveals the behaviour of spherical isotropic PS particles dispersed in 0.1 mM KCl solution. The particles exhibit well dispersed and individually distributed monomer like state due to high repulsive interaction potential experienced by the particles.

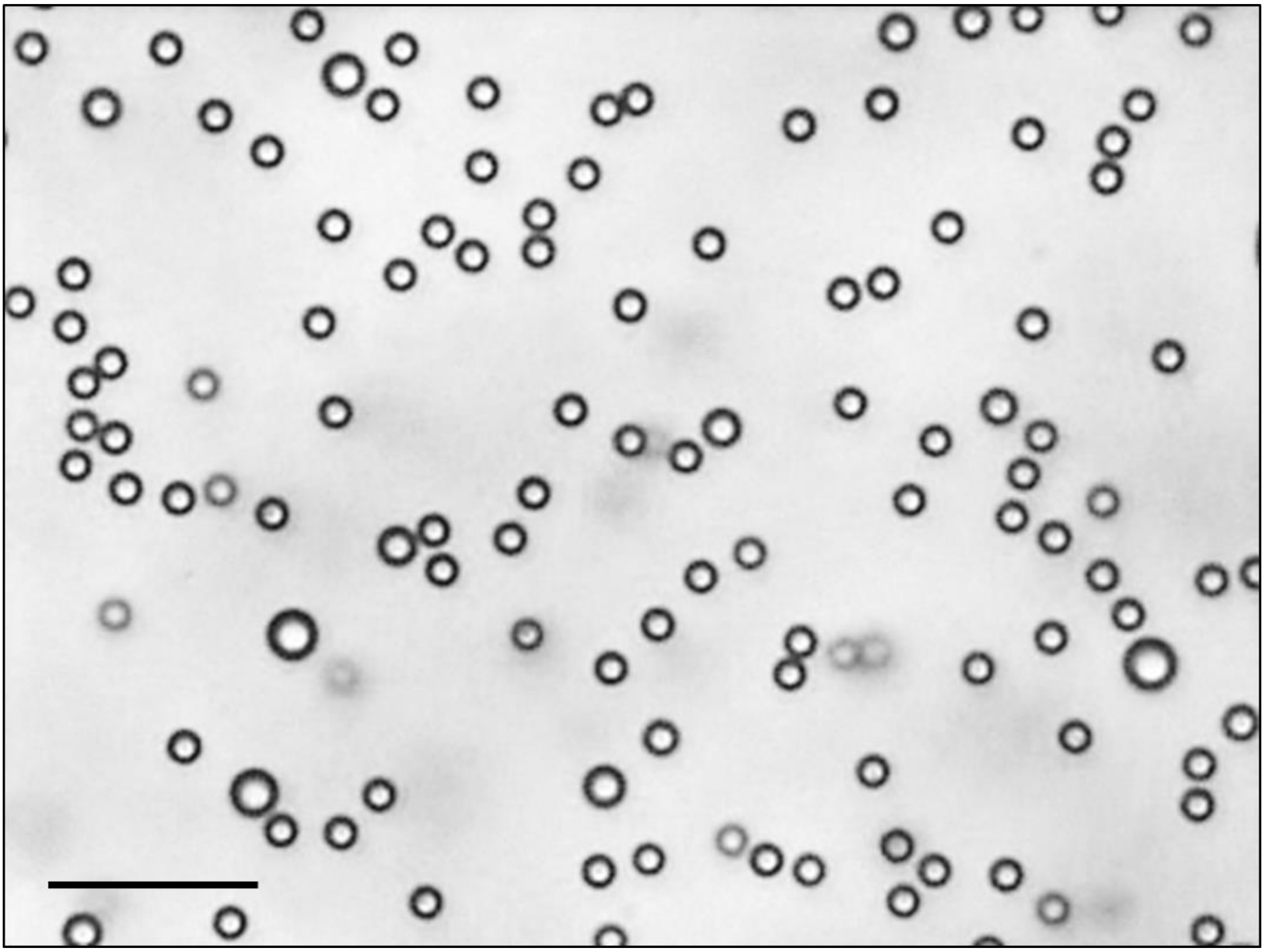

Figure S6. Inverted microscope images showing well-dispersed state of spherical PS particles in 0.1mM KCl solution. The scale bar corresponds to 20 μm.

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Reference:

1. Sabapathy, M.; Kollabattula, V.; Basavaraj, M. G.; Mani, E. *Nanoscale*, **2015**, 7, 13868–13876.