Electronic Supplementary Material (ESI) for

Transparent Microparticles in Water/Sucrose

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Supplementary Information 1: Synthesis procedure

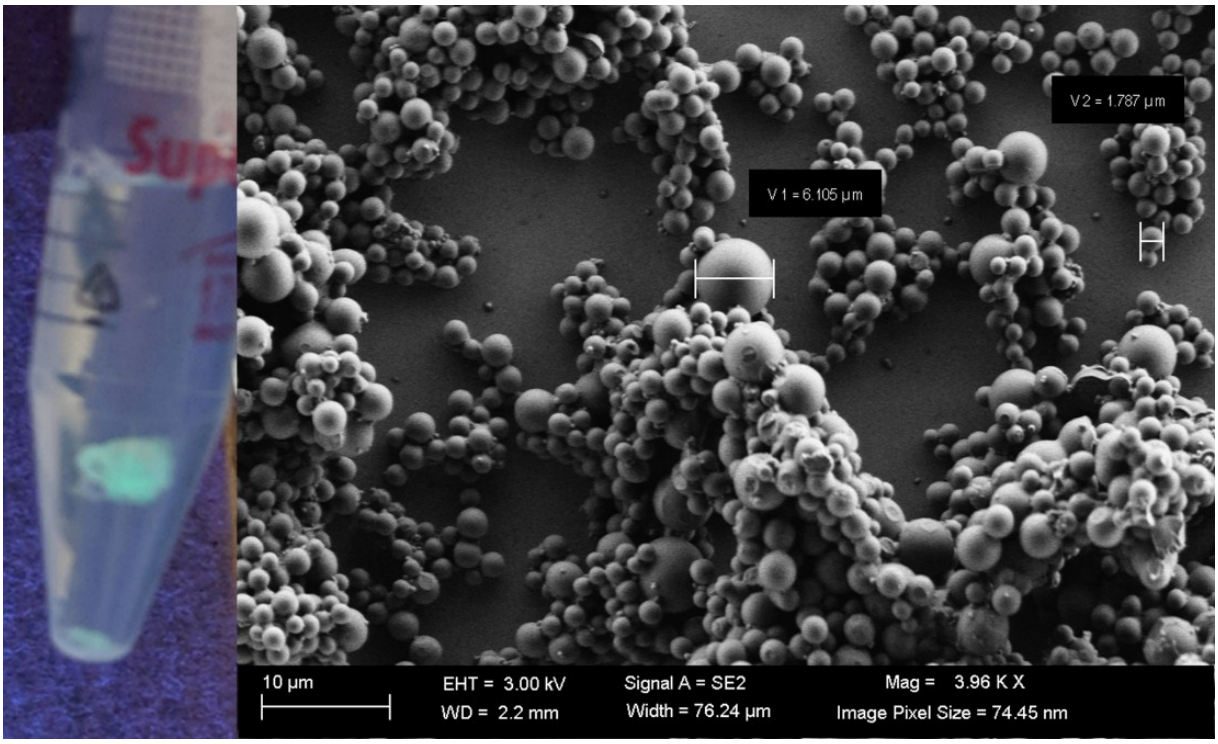
7FBM was purchased from VWR (Matrix Scientific) and all other chemicals from Sigma Aldrich. Monomers and the initiator were used as provided by supplier, without purification.
2 g of polyvinylpyrrolidone (K30 average Mw 40,000) was dissolved in Methanol (45 ml) and water (5 ml). 2.5 ml of the monomer (7FBM) and 0.2 ml of (2-(2-Bromoisobutyryloxy)ethyl methacrylate were added to the mixture. After dissolving 60 mg of 2,2'-Azobis(2-methylpropionitrile, the mixture was bubbled with nitrogen for 20 minutes, sealed with a septum and placed in a 55 °C bath, overnight. The product was cooled to room temperature, filtered and washed through centrifugation at 200 rcf, 3X with water/methanol 1 (vol) : 1 (vol) and 3X with water.
(2-(2-Bromoisobutyryloxy)ethyl methacrylate serves as an initiation site for potential growth of brushes based on ATRP method, which was not performed in this study. The original design of the particle was based on growing a charged brush onto the surface of the particles. But after witnessing the stability of the particles, addition of a charged brush was abandoned while the recipe for making the particles was not changed.

Supplementary Information 2: Why does PVP matter?

To check the effect of the stabilizer on the particles, an additional synthesis was conducted, with a negatively-charged monomer-stabilizer instead of PVP, namely 3-Sulfopropyl methacrylate potassium salt. This resulted in a) a heavily polydisperse sample and b) irreversible aggregation of the particles upon centrifugation (rcf 200 g).

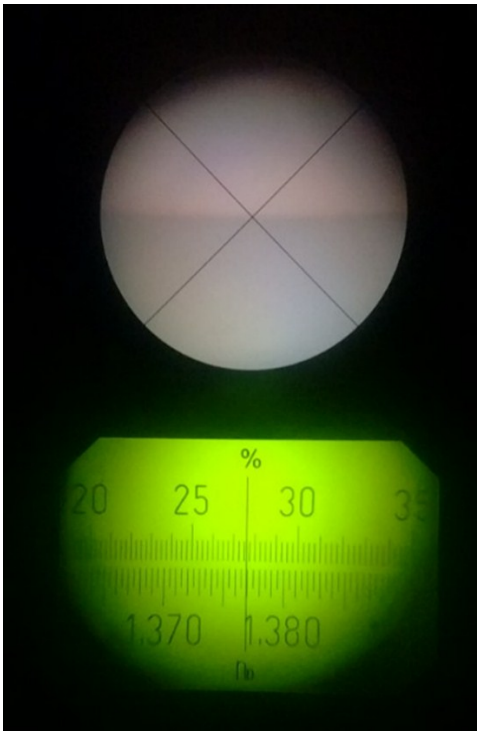
For the synthesis:

13 mg of 3-Sulfopropyl methacrylate potassium salt was dissolved in methanol (7 ml) and water (1.9 ml). Trace amount of Pyrromethene 546 dye (from Exciton) was added from a 1 mg/ml solution in methanol to the reaction mixture. 30 µl of the solution was added to the reaction mixture. Then, 1 ml from 7FBM and 0.163 ml of (2-(2-Bromoisobutyryloxy)ethyl methacrylate) were added and 13 mg of potassium persulfate was dissolved in the mixture. The mixture was placed under reflux at 85 °C for 3 h. The small amount of dispersion obtained after filtering was centrifuged for 10 minutes at 200 rcf which resulted in irreversible aggregation of the particles which had a large size distribution (in the following, see the aggregated chunk and the SEM image of the particles made by the negatively-charged stabilizer).

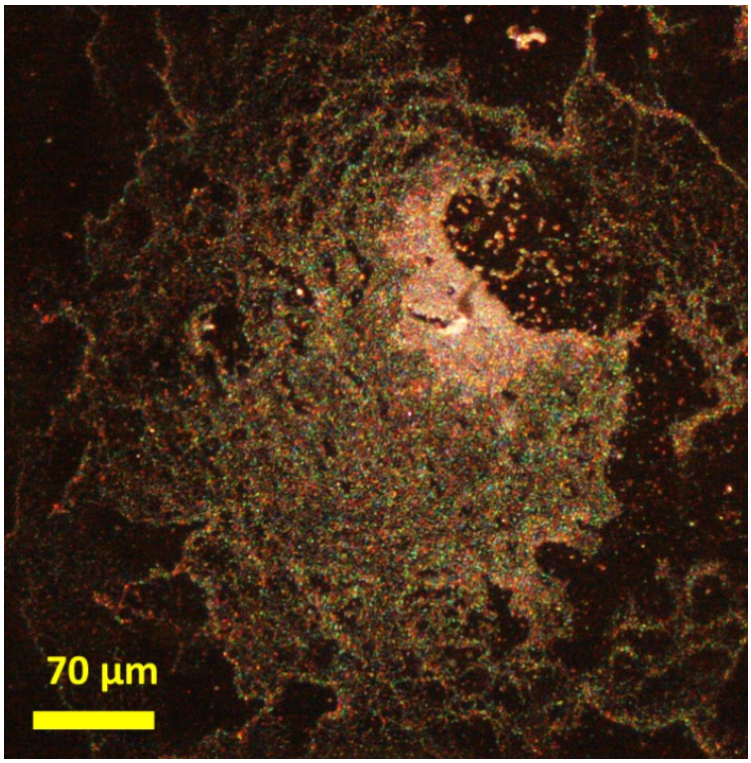


Left: Irreversible aggregation of the particles made by a negatively-charged surfactant upon centrifugation. Right: SEM image of the heavily polydisperse particles

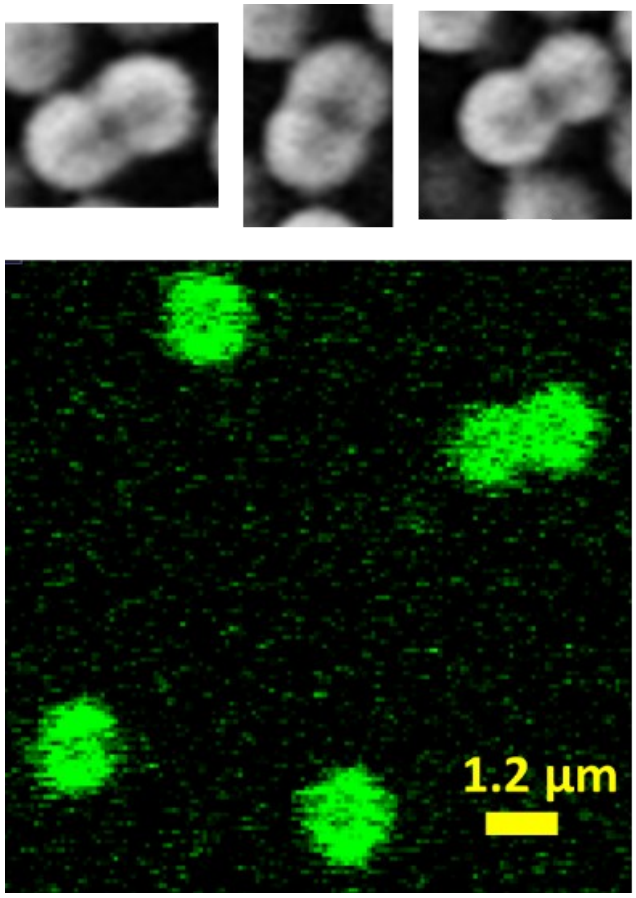
Supplementary Information 3: Refractometry at 24 °C



Supplementary Information 4: Structural color in non-dyed, drop cast sample on silicon wafer



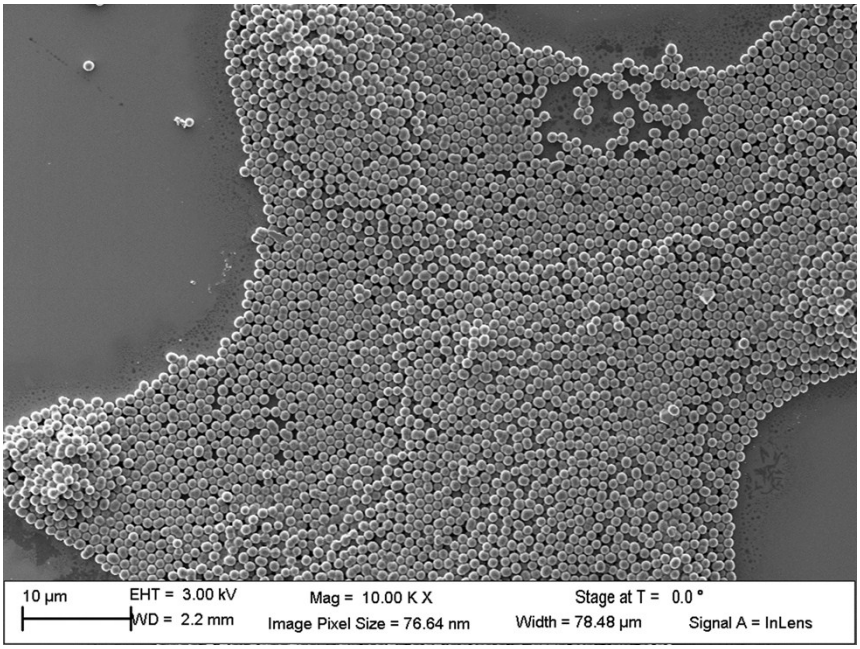
Supplementary Information 5: Doublet particles



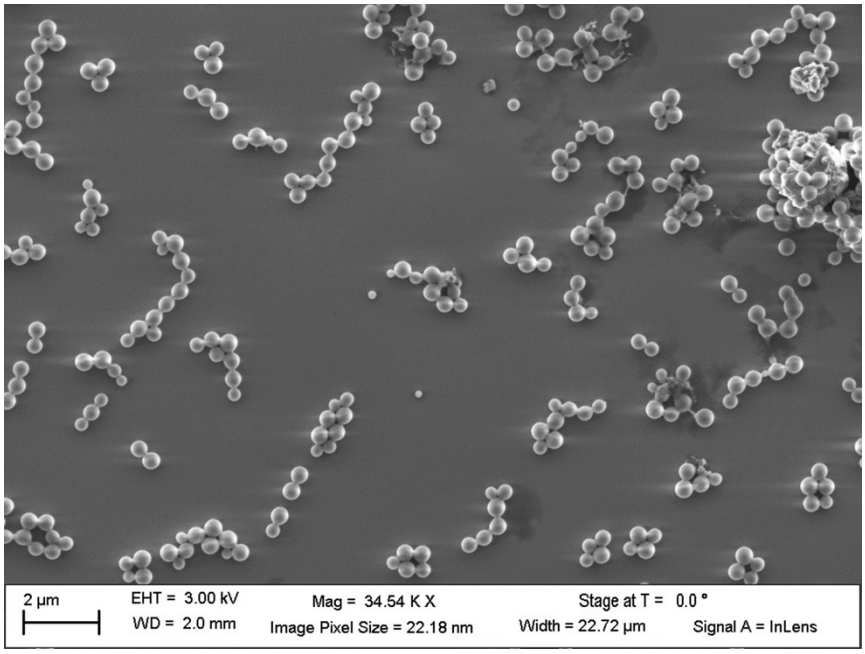
Top: SEM image of doublet particles (not dyed and without a protective conductive layer)
Bottom: Confocal fluorescence microscopy images of dyed particles in water/sucrose with one doublet pair.

Supplementary Information 6: Size and size distribution in other batches

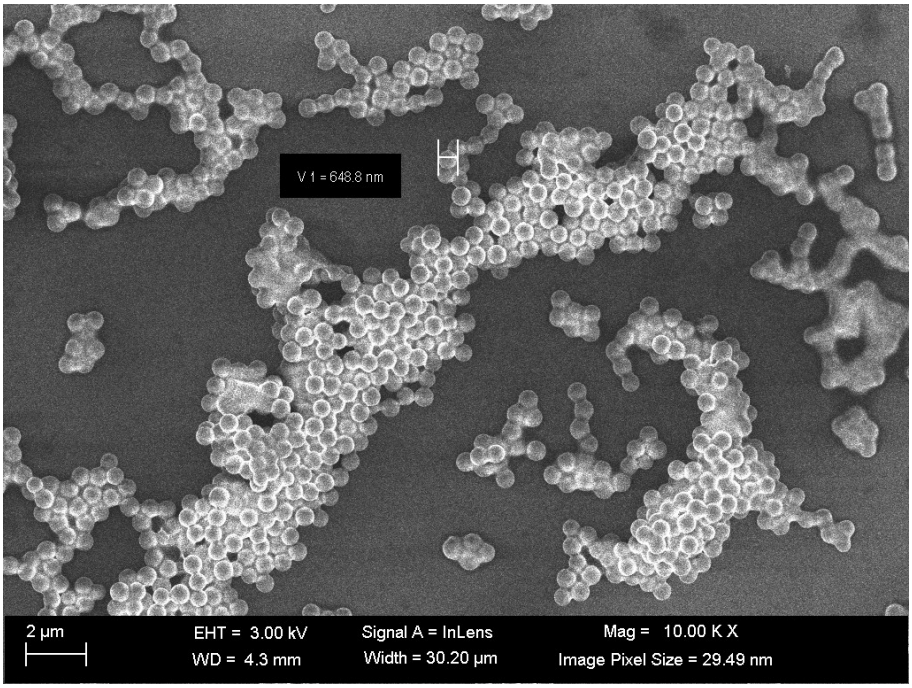
Particles with a size slightly larger than 1 µm and a CV of 8 %, as reported in the paper, is an encounter observed in 1 out of 4 reactions (like the following SEM image at Batch #1). The sensitivity of the nucleation stage can cause similar reactions to provide different size and size distributions (like the following SEM images Batch #2,3 and 4):



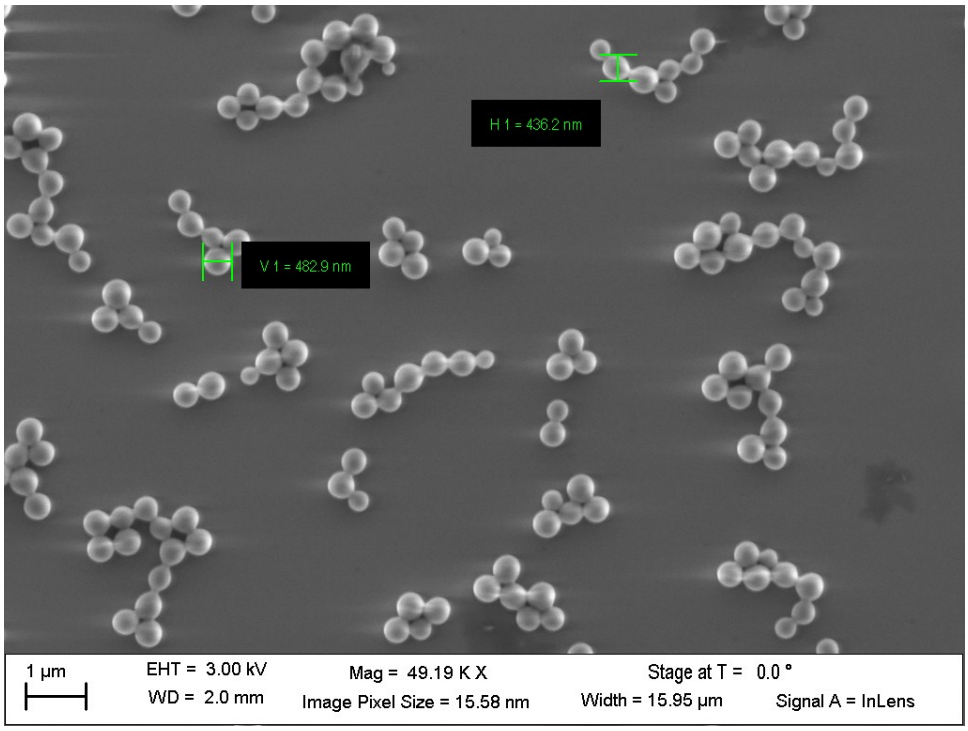
Batch #1: The particles reported in the paper.



Batch #2: Mean particle diameter= 0.411 µm, CV = 13.6 %



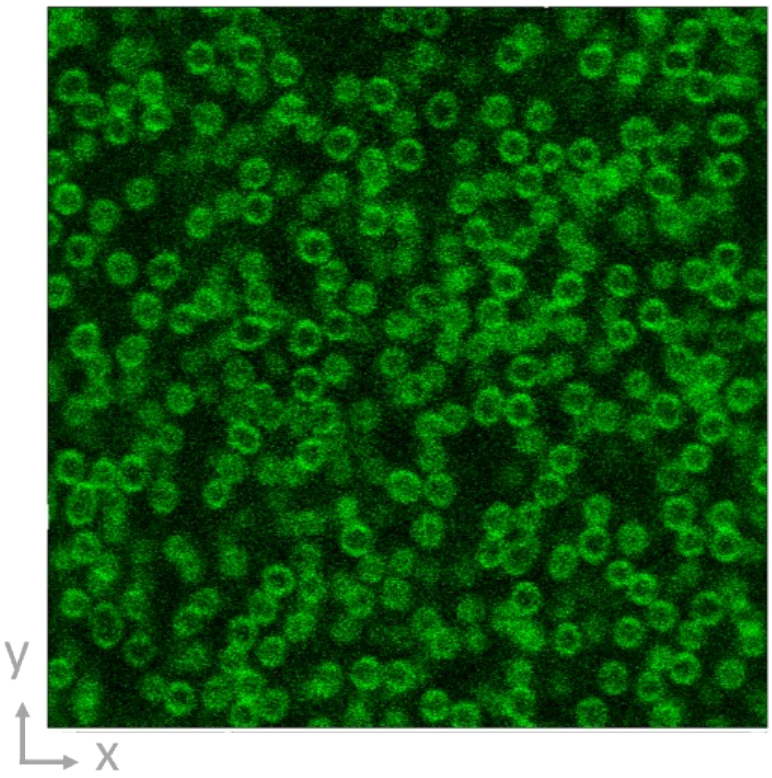
Batch #3: Mean particle diameter= 0.59 µm, CV = 6.11 % (Here, the image quality is reduced due to the presence of unwashed PVP in the sample)



Batch #4: Mean particle diameter= 0.43 µm, CV = 11.5 %

There are two important points to be considered upon dealing with dispersion polymerizations: 1) Dispersion polymerization provides nice control over size and size distribution of the particles. In other words, one can tune the reaction parameters, like the composition of co-solvents (water vs. alcohol) and monomer concentration, such that it will systematically decrease or increase the particle size and size distribution. However, this does not mean that two reactions with experimentally similar parameters will result in equal values of particle size and size distribution. The final particle size in each reaction is dependent–among other parameters–on the number of seeds that are formed in the early phase of the reaction. The number of seeds could be different from one reaction to another, depending on the kinetics of the polymerization and also, the sensitivity of the solubility to the molecular weight of the growing chain or oligomer. That said, dispersion polymerization is an excellent tool to control the range of the particle sizes, but achieving a precise value of size is complicated, especially when a reaction is designed to produce larger particles. 2) Tuning the control parameters in the reaction for the production of larger sizes results in an increase in the particle size distribution. A nice example, showcasing this trend more systematically for polystyrene-based particles could be found at DOI: 10.1016/j.jcis.2009.02.040. As evident from the broad deviation in the size and the size distribution (above SEM images), it is speculated that the nucleation step is very sensitive and heavily batch dependent for the reaction reported here. It should be emphasized that exploring the trend of the resultant particle size according to reaction parameters will be the focus of a future study.

Supplementary Information 7: Dye adsorption onto particles



23.57 µm x 23.57 µm

Supplementary Information 8: Parameters used in confocal fluorescence imaging:

Fluorescence images were recorded with excitation wavelength of 543 nm, read out channel in the range of 553-720 nm. Objective lens was a glycerol immersed Leica HCX PL APO 63x / 1.3 GLYC CORR CS.

Fig 3a:
Pixels: x: 1024, z: 1024
Image size: x: 61.51 µm, z: 61.51 µm
Voxel size: x: 60.13 nm, z: 60.13 nm

Fig 3b:
Pixels: x: 1024, y: 1024, z: 637
Image size: x: 61.51 µm, y: 61.51 µm, z (full range): 80.06 µm
voxel size: x: 60.13 nm, y: 60.13 nm, z: 125.89 nm