

Supporting Information

Self-Assembly of Colloids with Liquid Protrusions

Daniela J. Kraft^{*}, Wessel Vlug[#], Carlos M. van Kats[#], Alfons van Blaaderen[#], Arnout Imhof[#] and Willem K. Kegel^{*}

^{*}*Van't Hoff laboratory, Debye Institute for NanoMaterials Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

[#]*Soft Condensed Matter, Debye Institute for NanoMaterials Science, Utrecht University, Princetonplein 5, 3584 CC, Utrecht, The Netherlands*

Experimental details

Synthesis of monodisperse cross-linked polystyrene spheres

Monodisperse cross-linked polystyrene spheres (CPS) were prepared using an emulsion polymerization procedure described previously¹. All components were used as received.

A 1 liter round bottom flask equipped with a PTFE stir bar was placed in an 80°C oil bath. 400 mL deionized water was charged into the reactor and allowed to reach bath temperature. Then 47 mL (42.3g) styrene (99% purity, Merck) and 0.500g sodium dodecylsulfate (BDH) dissolved in 50.0 mL of deionized water were added, followed by 50 mL of rinse water. To cross-link the latex colloids 1.39 mL (1.27g) of divinylbenzene (DVB, 55% mixture of isomers, tech. grade) was added yielding a cross-linking density of 3% w/w. The ingredients were allowed to mix and reach the temperature of the oil bath for one hour. Addition of 1.55g potassium persulfate dissolved in 75.0 mL deionized water initiated the reaction. Polymerization was allowed to continue for 24h. The resulting colloidal CPS suspension had a weight fraction of 7% w/w. The sphere radius was determined by TEM to 113 nm with a polydispersity of 3.4%.

Vinyl acetate coating of CPS particles

A part of the CPS suspension was consequently coated with vinyl acetate (surface coverage $3.56 \cdot 10^{-21} \text{ g/nm}^2$) in order to increase the hydrophilicity of the surface. For this a round bottom flask equipped with a PTFE stir bar was immersed in an oil bath at 80°C. It was charged with 200 mL of the colloidal polystyrene solution and allowed to reach bath temperature for 1 hour. Addition of vinyl acetate took place in four steps spaced by 15 minutes, each containing 25% of the total mass of 135 mg of vinyl acetate. With the first addition of vinyl acetate 5.05 mL potassium persulfate (1g/150g Millipore water) were charged to the reaction vessel for initiation. Polymerization was allowed to continue for 24h after the last addition. The sample was purified by washing it three times with Millipore water and redispersed by addition of 1.33 g sodiumdodecylsulfate (SDS) in 80 mL water. The final suspension of about 400 mL contained 2.6% w/w polystyrene spheres by weight measurement of 1 mL. The radius was determined to 111.1 nm with a polydispersity of 2.5% by TEM.

Synthesis of monodisperse cross-linked PMMA spheres

Monodisperse cross-linked polymethylmethacrylate (PMMA) spheres were prepared using a surfactant free emulsion polymerization procedure according to a modified procedure of Paquet et al.² A 250 mL round bottom flask equipped with a reflux cooler was filled with 90 mL of deionized water and 0.24 g of potassium persulphate (0.01 M KPS) and magnetically stirred. The flask was put in a thermostatted oil bath at 80.0°C and kept at that temperature for 30 minutes to allow for radical formation of the KPS. A separate vial was filled with 10.0 g of monomer, which consisted of a mixture of methyl methacrylate (MM) and methacrylic acid (MA) in a weight ratio of 90:10, 0.1 g (1%w/w) cross-linking agent ethylene glycol dimethacrylate (EGDMA), and 47.4 μ L of 1-dodecanethiol (DDM). The content of the vial with the monomer mixture was added to the round bottom flask under vigorous stirring. The polymerization was allowed to proceed for 2 hours. The resulting seed particles measured 220 nm in radius by scanning electron microscopy (SEM).

Density gradient centrifugation

Colloidal molecules could be separated into distinct bands by use of density gradient centrifugation. A 12 mL linear gradient ranging from 3% to 9% w/w Ficoll 400 in 1% w/w Pluronic F127/millipore water was prepared with a gradient mixer. Samples were carefully layered on top and centrifuged for 12 minutes at 116,000g and 20°C with a Beckmann Optima L60 Ultracentrifuge yielding up to 10 clearly separated bands (Fig. S1). The bands were taken out with a pipette with a bent tip connected to a peristaltic pump. Each sample was washed three times by centrifugation and redispersion in deionized water.

References:

- (1) Mock, E. B.; De Bruyn, H.; Hawkett, B. S.; Gilbert, R. G.; Zukoski, C. F., *Langmuir* 2006, 22, 4037-4043
- (2) Paquet, C.; Allard, M.; Glédel, G.; Kumacheva, E., *J. Phys. Chem. B* 2006, 110, 1605-1613

Supplementary Figures

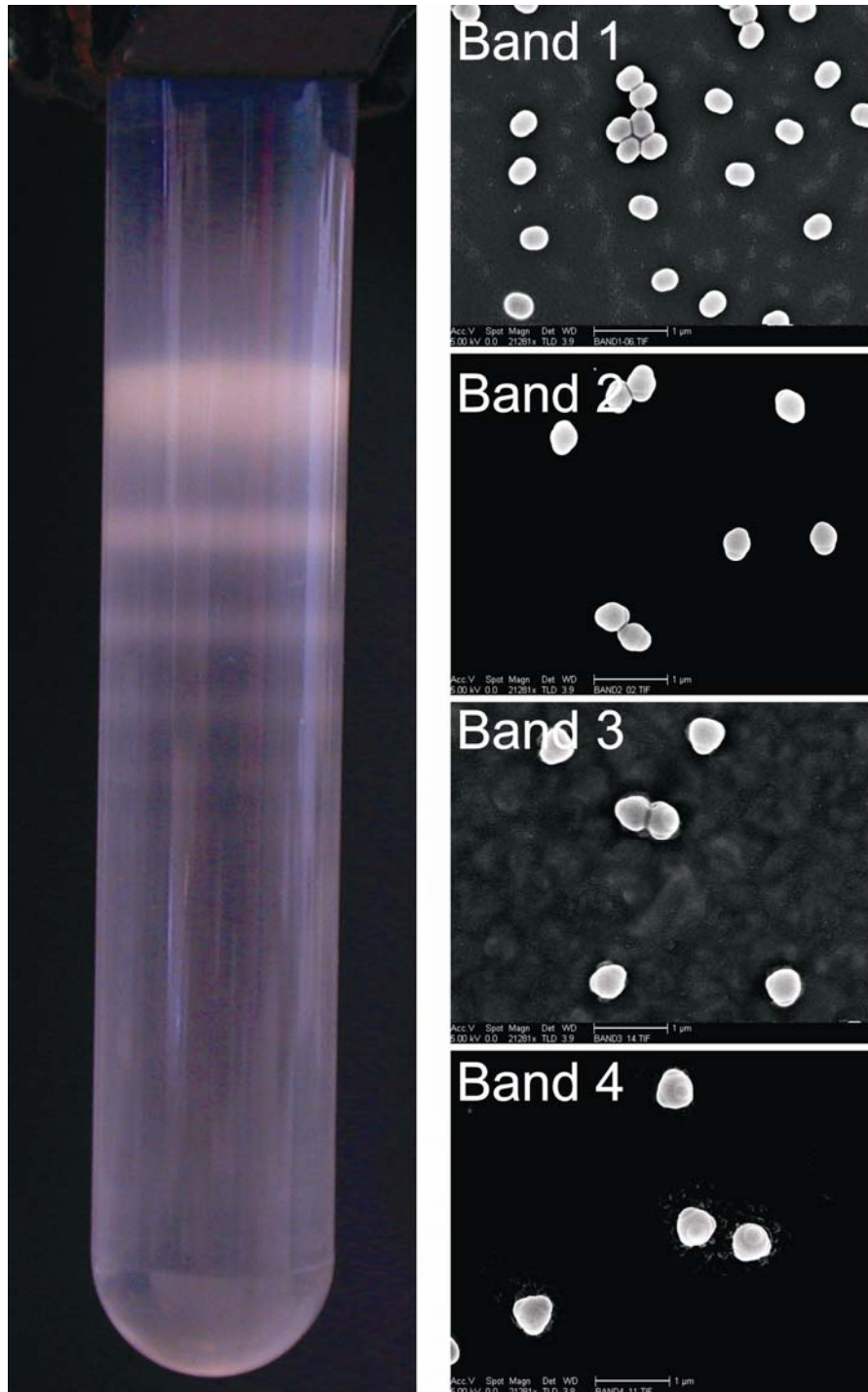


Figure S 1. Density gradient centrifugation in a 3%-9% wt/wt Ficoll 400 in 1% wt/wt Pluronic F127/millipore water yields bands that each contain one type of colloidal molecules. From top to bottom we find monomers, dimers, trimers etc. as shown in the SEM pictures.

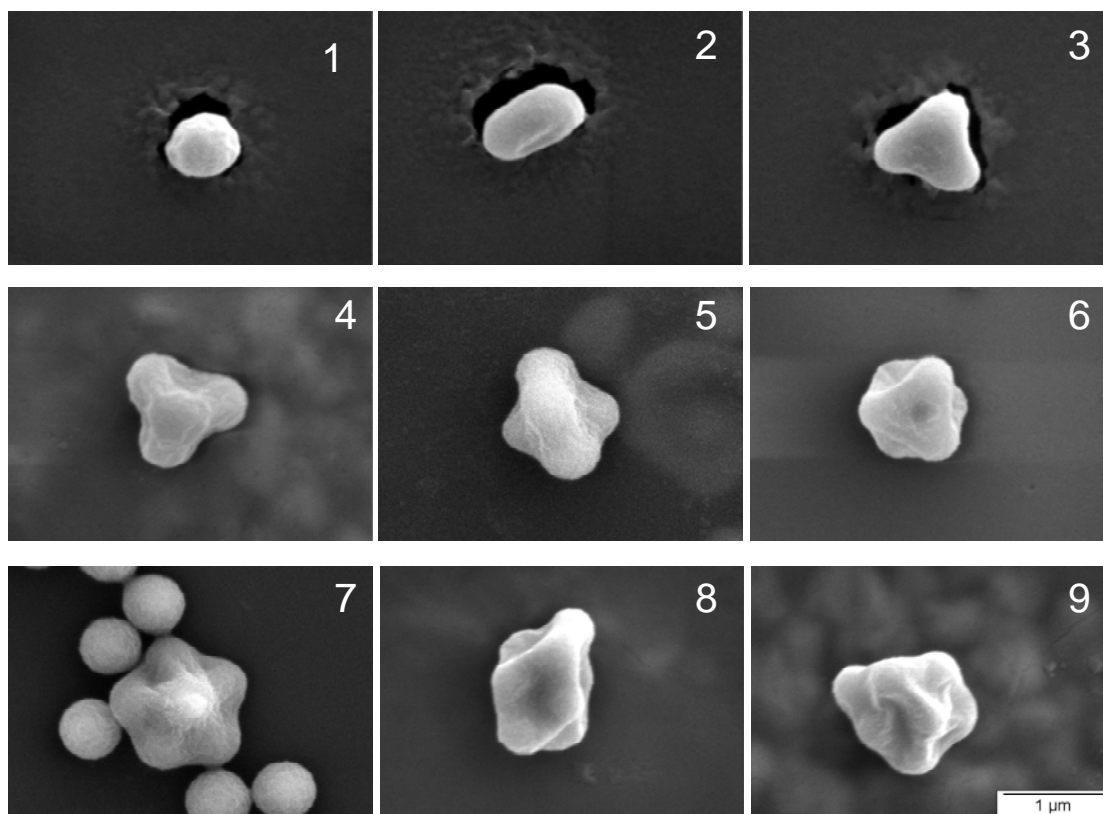


Figure S 2. Scanning electron micrographs of colloidal molecules for $N=1$ to $N=9$ created by merging of liquid wetting layers of methacrylic acid/methyl methacrylate on PMMA seed particles of radius $R_{\text{seed}} = 220$ nm. The scalebar is $1 \mu\text{m}$.

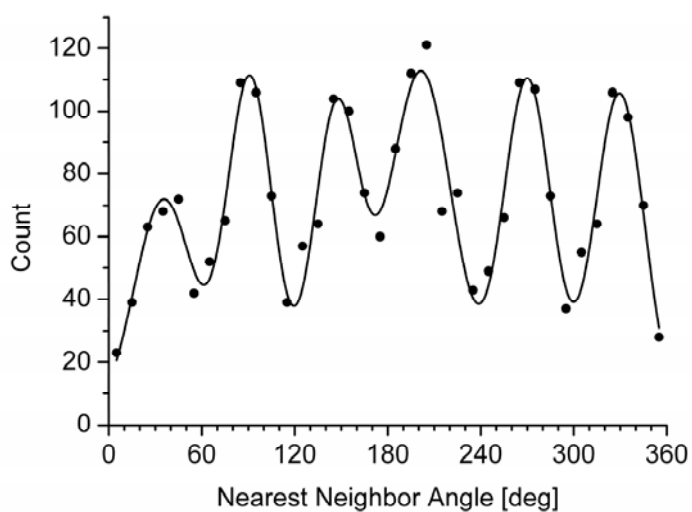


Figure S 3. Nearest neighbor angle distribution of seed particles on the monomer-water interface of colloidosomes consisting of coated polystyrene seeds ($R=111$ nm) swollen with styrene. The average angle obtained from a Multi-Gaussian fit is $60 \pm 3.6^\circ$.