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Reversible assembly of oppositely charged hairy colloids in water

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Supporting information

Synthesis of inimer

The heterobifunctional 2-(2-bromoisobutyryloxy)-ethyl-acrylate, BIEA, is used as an acrylic monomer in radical dispersion polymerization and as an initiator for atom transfer radical polymerization. The synthesis of BIEA, or inimer, is described in detail by Matyjaszewski *et al.*[2]. We follow the same procedure and synthesize 30 g of BIEA. ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.30 (d, 1H, $\mathbf{H}_2C{=}CH$), 6.0 (dd, 1H, $H_2C{=}C\mathbf{H}$), 5.80 (d, 1H, $\mathbf{H}_2C{=}CH$), 4.32 (s, 4H, $C\mathbf{H}_2C\mathbf{H}_2$), 1.85 (d, 6H, $C(C\mathbf{H}_3)_2Br$).

Synthesis of colloids

Monodisperse polystyrene particles are synthesized using dispersion polymerization, following the method desribed by Paine.[3,4] For the 1.1 μm particles, we proceed as follows. We mix 135 mL methanol, 15 mL inhibitor-free styrene (cleaned by washing with neutral alumina) and 7.5 g poly(vinyl pyrrolidone) (PVP-40) in a roundbottom flask. After dissolution of the PVP, we add 150 mg of the radical initiator azobisisobutyronitrile (AIBN) and close the flask tightly. We keep the solution at 0 °C and remove all oxygen by four subsequent cycles of evacuating and refilling with argon, ending under a vacuum atmosphere. To start the free radical polymerization, we quickly heat the mixture to 70 °C causing the AIBN to decompose. The reaction is then left for three hours at 70 °C while continuously rotating under an angle of 30°. During these initial three hours the mixture changes from transparent via blueish transparent to a white opaque suspension. After three hours the reaction mixture is cooled down to 45 °C . We then inject 2.6 g of a 1:1 mixture by weight of inimer and styrene and leave the mixture to react for another twelve hours while rotating.

We end the reaction by cooling down to room temperature. We clean the particles by four cycles of centrifugation (3,500 g), discarding the supernatant, and redispersion in methanol (2x) and water (2x). By weighing the pellet and assuming a random closed packing conformation of the particles in the pellet ($\phi = 64\%$, v/v[5]), we redisperse the particles in the final step to a volume fraction of $\phi = 30\%$.

For the 3.5 μm particles, used as colloidal probes in force spectroscopy measurements, we follow a slightly different protocol. In order to reach a larger particle size we add an additional 7.5 mL styrene and 7.5 mL ethanol to the reaction mixture after three hours. We then leave the reaction mixture for another four hours at 70 °C . After a total of seven hours, we cool down the reaction mixture to 45 °C and follow the protocol described above from there.

We modify the polystyrene particles with either polycation or polyanion chains, which are grown from the surface of the particles using surface-initiated atom transfer radical polymerization, SI-ATRP.[6] BIEA, or inimer, acts as an initiator in this ATRP reaction. Positively charged PTMAEMA-coated particles are synthesized as follows. We mix 1 mL 30% (v/v) polystyrene particle suspension, 2 mL MilliQ water, 6 mL formamide and 1.5 g methacryloyloxy-trimethylammonium chloride (monomer, 80% solution in water) and 90 μL HMTETA together in a 50 mL roundbottom flask. The flask is then sealed with a rubber septum. Argon is purged through the reaction mixture with a syringe for ten minutes. After ten minutes, we add 10 mg Cu(I)Cl and again purge the mixture with argon. The suspension has an intense blue color and is stirred gently at 50 °C for two hours. Negatively charged PSPMA-coated particles are synthesized following a similar protocol. To 1 mL of the 30% (v/v) polystyrene suspension we add 2 mL MilliQ water, 6 mL methanol, 1.2 g potassium sulfopropylmethacrylate (monomer, powder), 20 mg bipyridyl and 4 mg $Cu(II)Cl_2$. After purging with argon, we add 6 mg Cu(I)Cl to start the ATRP reaction. This suspension has a typical brown color and we leave it to react for 45 minutes at room temperature. Both ATRP reactions are stopped by purging with air. We clean the particles again by six cycles of centrifugation (3,500 g), discarding the supernatant, and redispersion in methanol (2x), a 20 mM EDTA solution in water (2x) and water (2x).

We label both types of modified particles by adsorbing two different hydrophobic dyes in their core. In order to get the dye homogeneously distributed in the core of the particles, we equilibrate suspensions of the modified particles with a mini-emulsion of the dye dissolved in CCl_4 (tetra) for one to two days in a closed plastic container. For PTMAEMA-coated particles we use 1 mg pyrromethene-605 (Exciton laser dyes) in 1.5 mL tetra and mix this with 10 mg CTAB in 10 mL water using a tip sonicator. For PSPMA-coated particles we use 1 mg pyrromethene-546 (Exciton laser dyes) in 1.5 mL tetra and mix this with 72 mg SDS in 10 mL water using a tip sonicator. After equilibration, we open the container and stir the suspension gently for six hours to evaporate all tetra. We clean the particles again by six to eight cycles of centrifugation (1,000 - 3,500 g), discarding the supernatant, and redispersing them in water (6-8x). Finally, the particles are stored in suspension at a concentration of 10% (v/v), which we estimate from a plot of the scattered intensity versus ϕ, taking the suspension of unmodified particles as a reference.

Characterization

Size

Size from confocal image: $2a = 1.1$ μm. Size from SLS fit to Mie theory: $2a = 1.060$ μm, polydispersity = 3-7%. Hydrodynamic diameter from DLS: 1.2 μm. See main text for the plots and details.

Electrophoretic mobility

We have measured the electrophoretic mobility as a function of salt concentration. In 1 we show a plot of μ versus c_{salt} The positively and negatively charged particles show very similar behaviour at opposite sides of the μ-axis. At low salt concentration, we find a constant electrophoretic mobility. A similar trend can be seen in electrophoretic mobility studies of spherical polyelectrolyte brushes by Hoffmann *et al.*[7] They find that trivalent counterions efficiently collapse a polyelectrolyte brush, and the concentrations at which that happens lies approximately at the point where μ changes most strongly with c_{salt}, in 1 approximately 150 mM. For monovalent salt ions a similar brush transition is known from the osmotic to the salted brush regime. The salt concentration at which this transition occurs is roughly equal to the concentration of polymeric charges in the brush. The numerical solutions of the electrokinetic equations for spherical polyelectrolyte-coated colloidal particles presented by Hill[8], also suggest that there might be a region of approximately constant electrophoretic mobility at similar κa for particles with intermediately thick coatings ($L \approx 0.1a$) and polymeric charge densities of more than 0.1 M. Fritz *et al.* have also measured the electrophoretic mobility of polyelectrolyte-coated PS particles.[9] They could fit their results convincingly to Ohshima's theory, which predicts monotonical increasing mobilities when the salt concentration is lowered. However, they never reached salt concentrations lower than 20 mM, so we cannot exclude the presence of a constant mobility region at lower salt also in their system.

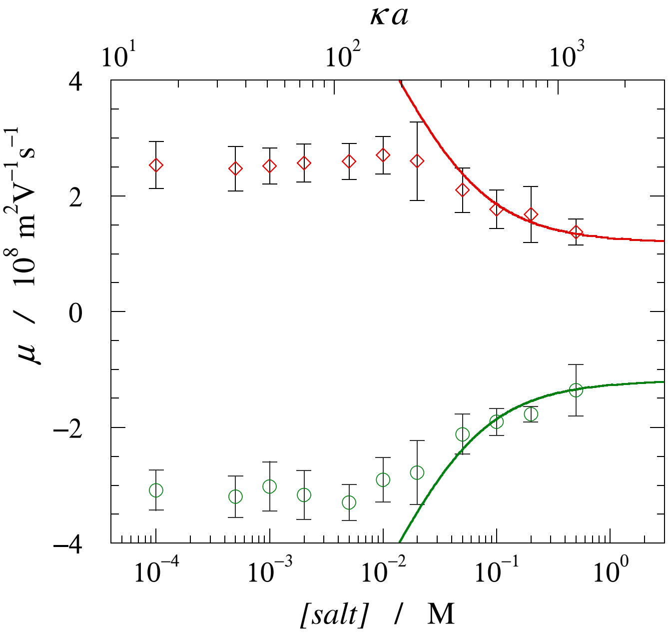

Figure 1: Electrophoretic mobility of hairy colloids as a function of salt concentration: (◇) cationic colloids, (○) anionic colloids. Solid lines are a fit of the data points at high salt concentrations to Ohshima's theory. Dashed lines indicate a plateau of the electrophoretic mobility at low salt concentration, probably caused by counterion condensation inside the polyelectrolyte brushes.

For our PTMAEMA- and PSPMA-coated particles, we also find that the mobility at high salt concentration (¿ 20 mM) follows the prediction by Ohshima.[10] This theory is suited for particles with a soft outside layer in which the charges are located. As a result, the mobility is expected to go to a nonzero limiting value at high salt concentration. Like Fritz *et al.* , we fitted our mobility measurements at high salt concentration to Ohshima's theory, using a density of polymeric charges of 0.15 M and a softness parameter λ of 0.9 nm^{-1}.

Brush thickness

The polyelectrolyte brush thickness follows from AFM force measurements of the PTMAEMA- and PSPMA-coated particles against bare silica in MilliQ water. For PSPMA-coated particles we find a repulsion from about 50 nm. For PTMAEMA-coated particles we find an attraction upon approach from about 50 nm. This is an indication that both particles have a 50 nm thick polyelectrolyte coating.

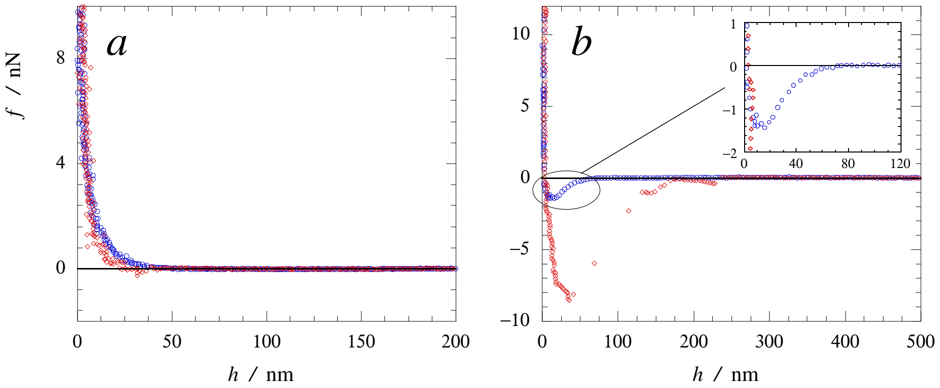

Figure 2: AFM force measurements with a colloidal probe of a 3.5 μm PS particle with (a) an anionic PSPMA brush and (b) a cationic PTMAEMA brush grafted to its surface, against bare silica in MilliQ water. Shown are both approach (○) and retract (◇) curves.

The swollen thickness of the PSPMA brush used to keep oppositely charged colloidal particles attached to a flat surface follows from AFM force measurements as well. In MilliQ water the swollen brush thickness is roughly 200 nm.

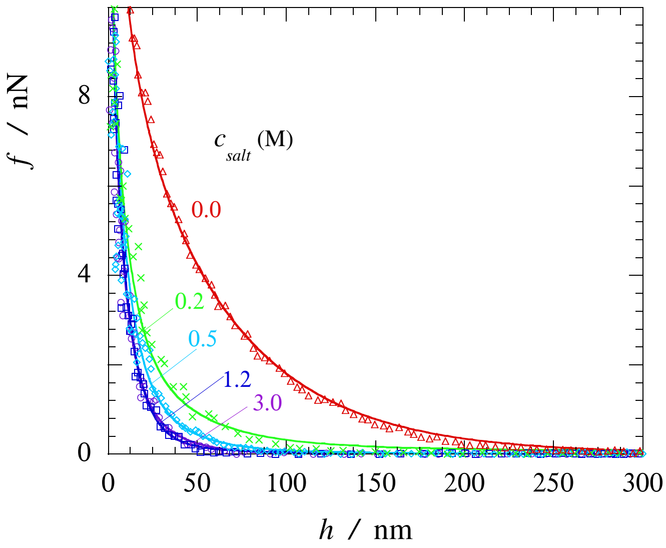

Figure 3: AFM force measurements with a colloidal probe of a 3.5 μm PS particle with an anionic PSPMA brush against a PSPMA brush on silica, grown by SI-ATRP, in various salt concentrations, as indicated in the figure.

Grafting density

To estimate the grafting density of the polyelectrolyte brush surrounding the particles, we assume a Alexander-de Gennes brush model (σ denotes the grafting density, L the brush height, b the Kuhn length, ξ the correlation length in the brush layer, g the number of monomers per correlation volume, N the total number of Kuhn monomers and ν the Flory scaling exponent).

$$\phi \approx b^3 g/\xi^3 \approx \left(\sigma b^2\right)^{(3\nu-1)/(2\nu)} \tag{1}$$

$$g \approx \left(\frac{\xi}{b}\right)^{1/\nu} \approx \sigma^{-1/(2\nu)} b^{-1/\nu} \tag{2}$$

$$L \approx N\xi/g \tag{3}$$

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Once the number of Kuhn monomers is known, the number of chemical monomers (N_m) can be estimated using a measure for the monomer volume (v_m)

$$Nb \approx N_m v_m^{1/3} \tag{4}$$

Critical salt concentration

Measurement of critical salt concentration for 3.5 μm colloids by light scattering. The plot for 1.1 μm colloids can be found in the main text.

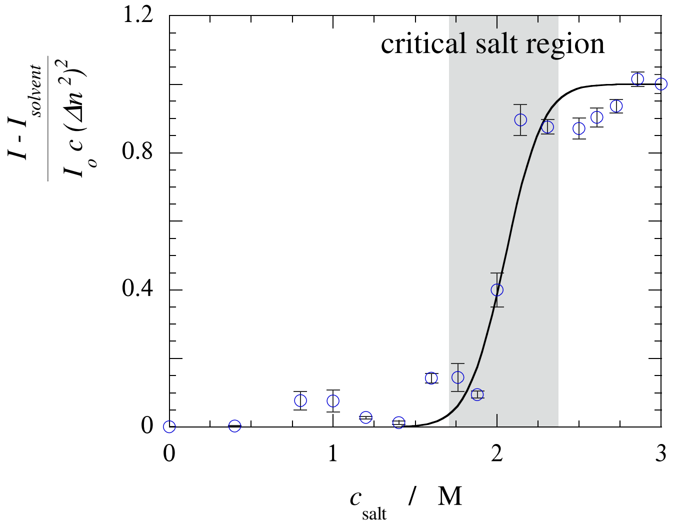

Figure 4: Critical salt concentration of aggregation of hairy colloidal particles of 3.5 μm diameter with either an anionic PSPMA or a cationic PT-MAEMA polyelectrolyte brush grafted to their surface.

AFM force measurements

We check the presence of the colloidal probe on the AFM tips after glueing by confocal microscopy. The other surface consists of a relatively thick (200 nm) polyelectrolyte brush, to which oppositely charged colloids are adsorbed, as shown by optical microscopy (6). The image shows that the chance of measuring an interaction oppositely charged colloids is quite low. This is indeed what we find in experiments: we scan the surface until we start measuring an attraction. In roughly 90% of the positions, we find no attraction. Once, an attraction is measured, we record several hundreds of force-distance curves, while varying the contact time step-wise. We then average force curves with an identical contact time. Examples of the raw force-distance curves are shown in 7. The variation between individual curves is quite large, which we attribute to the low grafting density of chains on the surface of the particles. After averaging a smooth curve is obtained, which resembles part of the schematic pair potential in the paper. We clearly see that the interaction becomes stronger for lower salt concentrations.

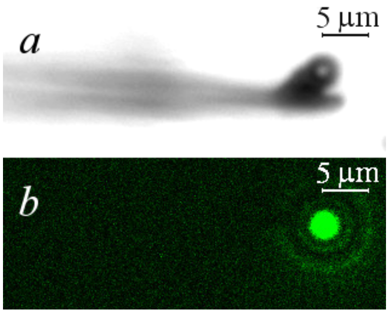

Figure 5: Optical microscopic image and fluorescence image of an AFM tip with a 3.5 μm colloidal probe glued to it. The colloidal probe is a PS colloid, with an anionic PSPMA brush grafted from its surface. The PS core of the colloid is stained with a pyrromethene-546 laser dye by adsorption in methanol/water (1/1, v/v).

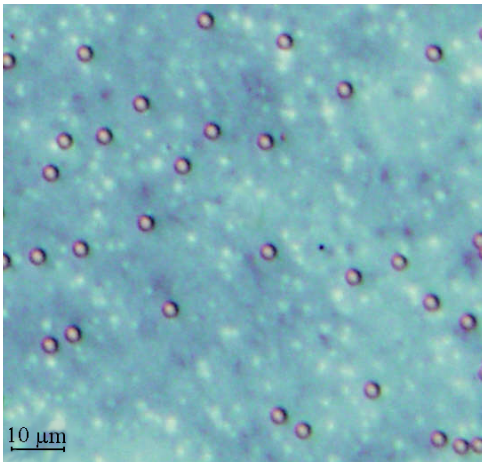

Figure 6: Optical microscopic image of cationic 3.5 μm colloids adsorbed to an anionic PSPMA brush on silica with a thickness of ∼100 nm. The colloids have a PS core and a cationic PTMAEMA brush grafted from their surface.

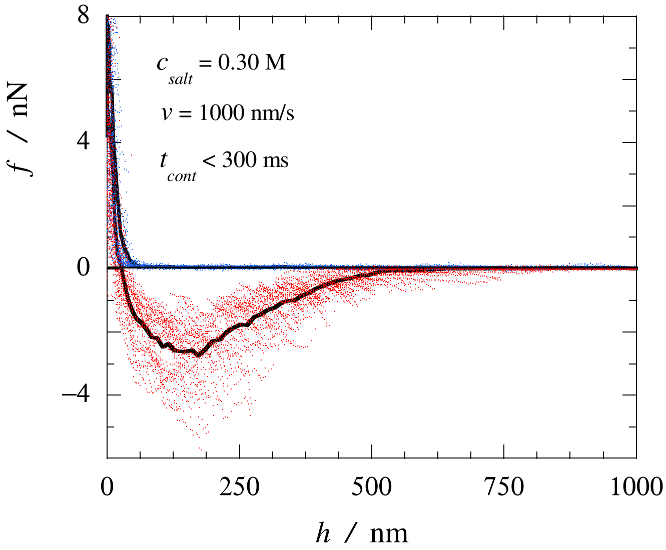

Figure 7: AFM force measurements with a colloidal probe of a 3.5 μm PS particle with an anionic PSPMA brush grafted to its surface, against similar colloids with a cationic PTMAEMA brush grafted to their surface. For these curves the contact time varies from 100 ms to 300 ms. Salt concentration is 0.30 M KCl, 100 force curves plotted.

Particle detection

Particle positions are detected using Image J, particle detection and tracking plugin.[11] The following image shows an example for the image that was used to generate the partial radial distribution functions in the manuscript.

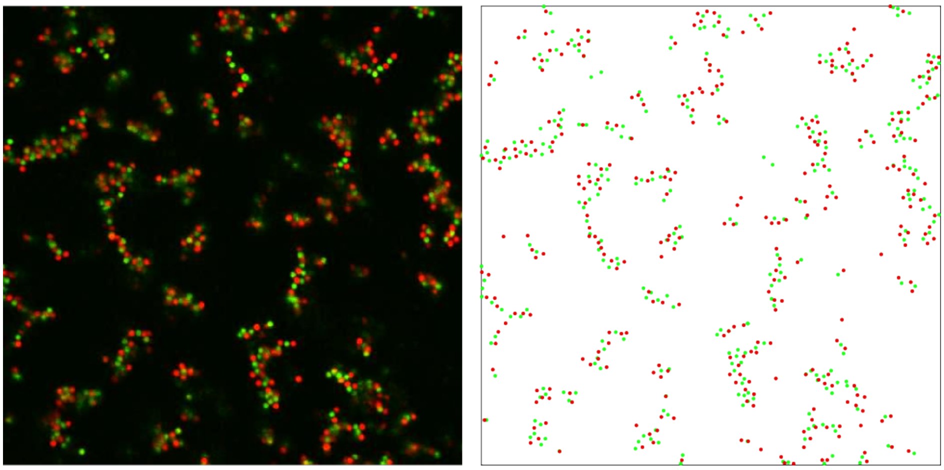

Figure 8: Confocal image and detected particles by Image J.

Rheometry

Rheological measurements are carried out on an Anton Paar MCR301 stress controlled rheometer, using a Couette geometry with $R = 5$ mm, $L = 15$ mm and a gap width, d, of 0.42 mm. We characterize the following four samples with different overall volume fractions (1:1 ratio) and different salt concentration: (A) $\phi = 1\%$, $c_{\mathrm{salt}} = 0.85$ M; (B) $\phi = 3\%$, $c_{\mathrm{salt}} = 0.85$ M; (C) $\phi = 3\%$, $c_{\mathrm{salt}} = 3.0$ M and (D) $\phi = 5\%$, $c_{\mathrm{salt}} = 0.85$ M. 9 and 10 show the typical amplitude sweeps, frequency sweeps and strain sweeps, with parameters as indicated in the figures.

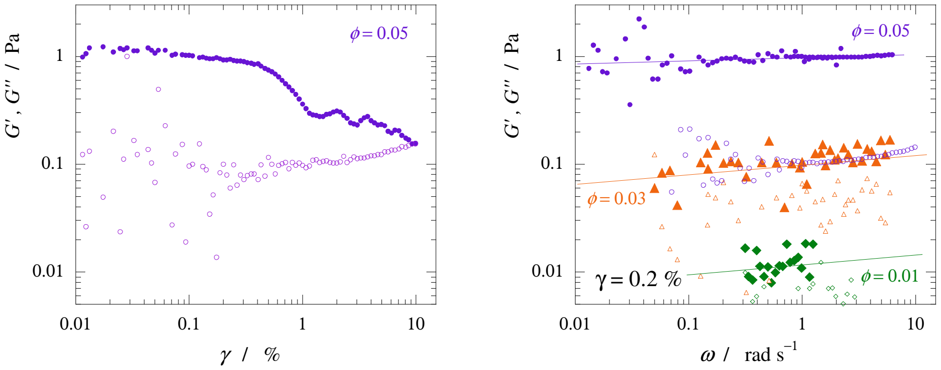

Figure 9: Left: amplitude sweep for sample D at $\omega = 1$ Hz. The regime of linear response is limited to strains of roughly 0.5%. Right: frequency sweeps for samples A, B and D at $\gamma = 0.2\%$. The filled symbols represent storage moduli, the open symbols represent loss moduli. For sample C no modulus could be detected at any frequency.

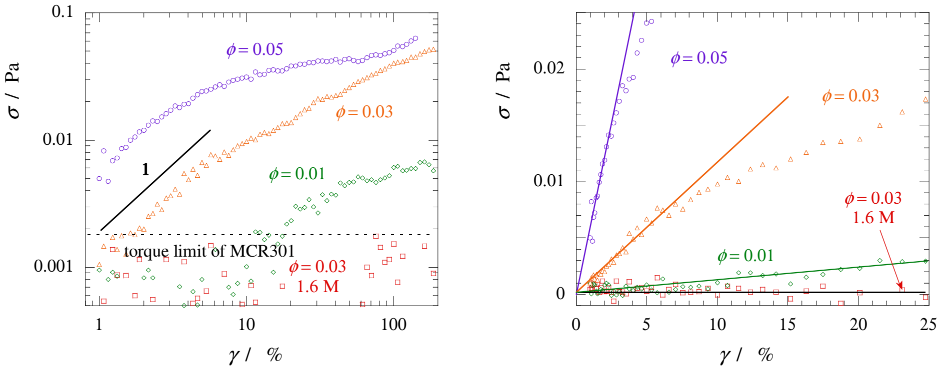

Figure 10: Strain sweeps for samples A-D. Left: double logarithmic scale, right: linear scale.

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