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Assembling anisotropic colloidal building blocks

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COLLOIDAL RECYCLING: RECONFIGURATION OF RANDOM AGGREGATES INTO PATCHY PARTICLES

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* Vera Meester, Ruben W. Verweij, Casper van der Wel, Daniela J. Kraft, *Colloidal Recycling: Reconfiguration of Random Aggregates into Patchy Particles*, *ACS Nano*, 2016, 10(4), 4322-4329, DOI: 10.1021/acsnano.5b07901.

Abstract

The key ingredients to the successful bottom-up construction of complex materials are believed to be colloids with anisotropic shapes and directional, or patchy, interactions. We present an approach for creating such anisotropic patchy particles based on reconfiguring randomly shaped aggregates of colloidal spheres. While colloidal aggregates are often undesirable in colloidal dispersions due to their random shapes, we exploit them as a starting point to synthesize patchy particles. By a deliberate destabilization of the colloidal particles diffusion-limited aggregation is induced which partitions the particles into randomly shaped aggregates with controlled size distribution. We achieve a reconfiguration of the aggregates into uniform structures by swelling the polymer spheres with an apolar solvent. The swelling lowers the attractive van der Waals forces, lubricates the contact area between the spheres and drives the reorganization through minimization of the interfacial energy of the swollen polymer network. This reorganization process yields patchy particles whose patch arrangement is uniform for up to five patches. For particles with more patches, we find that the patch orientation depends on the degree of phase separation between the spheres and the monomer. This enables the synthesis of patchy particles with unprecedented patch arrangements. We demonstrate the broad applicability of this recycling strategy for making patchy particles as well as clusters of spheres by varying the swelling ratio, swelling solvent, surfactant concentration, and swelling time.

3.1 Introduction

Theoretical models and computer simulations have pointed out the tremendous potential of self-assembly for creating functional materials from the bottom up.^{2,77–81} By carefully designing the building blocks' shapes, interactions, and stoichiometry, a wide range of unprecedented structures is expected to become accessible and with it, exciting new physics and concepts.^{78,82,83} For example, simulations on particles with anisotropic shape showed that shape strongly affects the assembly through directional entropic forces.^{84–86} Interaction directionality can also be obtained by defining specific patches of attraction or repulsion on the particle surface, which significantly alters the phase diagram and can lead to liquid states with vanishing density⁸⁷ or the coexistence of a high-density and a low-density liquid phase⁸⁸.

In experiments, a remarkable variety of novel structures has recently been observed even with low-complexity building blocks. Already particles with only one patch arrange into micellar^{29,89–91} and tubular phases⁴⁷ and can form addressable and actuable linear structures, such as ribbons and rings.^{92–97} Particles with two patches on opposing ends assemble into a Kagome lattice⁹⁸, because entropy mechanically stabilizes the open lattice structure. With increasing building block complexity even richer assembly dynamics and equilibrium structures are expected. Hierarchical assembly, for instance, was demonstrated by using particles with two patches of different sizes, which assembled into networks of clusters.⁹⁹ However, there is a shortage in synthetic methods to fabricate suitable, more complex colloidal building blocks. The most important impeding factors are the limitations with respect to the particle material, the yield, and the obtainable particle complexity.¹⁰⁰

Strategies based on 2D functionalization schemes such as angle-dependent vapour deposition or contact printing have an inherently low yield of patchy particles and can only be used to fabricate particles with very few patches and patch locations.¹⁰¹ Bulk strategies for synthesizing anisotropic and patchy particles can achieve high yields but are limited to certain materials and particle properties.

We here present a bulk strategy for fabricating patchy particles based on the reconfiguration of randomly aggregated spheres. The reconfiguration is made possible by depositing droplets in the bond area after swelling with an apolar solvent. Surface tension and geometric constraints determine the shapes of the final patchy particles. We show that our method is able to create particles with chemical differences between the patches and the particle body. Our strategy can employ charge-stabilized polymer spheres for fabricating patchy particles with anisotropic charge distribution, which may be used in self-assembly directed by Coulomb forces or in demixing binary solvents where the wetting properties of the solvent fluctuations are determined by the charge density.^{102,103} This colloidal recycling approach opens up a pathway to produce patchy particles in high yields

upon improving the control over the size distribution of the seed aggregates.

3.2 Experimental Methods

Materials

Styrene ($\geq 99\%$, contains 4-tert-butylcatechol as stabilizer) was obtained from Sigma Aldrich and used after passing through an inhibitor remover column (Sigma Aldrich). Divinylbenzene (DVB, technical grade 55%), sodium dodecyl sulfate (SDS, $\geq 98.5\%$), hydroquinone (HQ, $\geq 99.5\%$), poly(vinyl alcohol)(PVA, Mw 13,000–23,000, 98% hydrolysed), methylmethacrylate (MM, 99%, contains ≤ 30 ppm mono ethyl hydroquinone as inhibitor), ethylene glycol dimethacrylate(EGDM, 98%, contains 90–110 ppm mono ethyl hydroquinone as inhibitor) and azobisisobutyronitril (AIBN, $\geq 98\%$) were purchased from Sigma Aldrich and used as received. Potassium chloride ($>99\%$, p.a.) and methacrylic acid(MA, 99.5%, extra pure, stabilized) were obtained from Acros Organics. The potassium peroxydisulfate ($\geq 99.0\%$, p.a.) and the poly(vinyl pyrrolidone) (PVP, K30, Mw 40,000) were purchased from Fluka, Germany. All solutions were prepared from deionized water with $18.2\text{M}\Omega$ resistivity, using a Millipore Filtration System (Milli-Q® Gradient A10), unless stated otherwise. RITC-dyed polystyrene colloids crosslinked with 5% divinylbenzene and with a diameter of $1.06\mu\text{m}$ (polydispersity 5.3%) were purchased from Magsphere Inc.

Methods

Carboxylic acid functionalized particle synthesis Linear polystyrene spheres were synthesized by a single step surfactant free emulsion polymerization.¹⁰⁴ The obtained carboxylic acid functionalized colloids were $1.05 \pm 0.02 \mu\text{m}$ in diameter (as measured from SEM micrographs) and had a zeta potential ϵ of -60 mV as measured by a Malvern Zetasizer Nano ZS. The colloids were filtered with glass wool and washed 3 times with Millipore filtered water at 2000g for 90 minutes. The colloids were stored in water.

To crosslink the particles, 1.7 mL swelling solution containing styrene, 2% w/w AIBN and 1.5% v/v DVB was added to 2.5 mL linear polystyrene spheres (12.4% w/w). To this mixture 10 mL SDS (0.5% w/v) and 1.0 mL HQ (0.03% w/w) dissolved in water were added. The spheres were swollen for approximately 24 hours while tumbling at 20 rpm in the dark. The swollen colloids were polymerized for 24 hours in a 70°C oil bath while rotating under an angle of 45° at 100 rpm. The colloids were washed three times and stored in water. The resulting carboxylic acid functionalized crosslinked spheres were $1.40 \pm 0.06 \mu\text{m}$ in diameter (see Figure 3.1A)

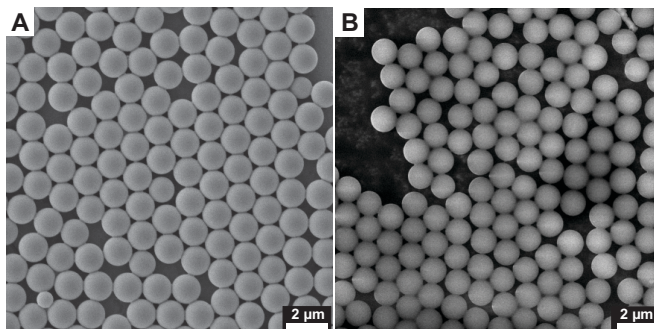


FIGURE 3.1: SEM micrographs of crosslinked polystyrene spheres synthesized by an emulsion polymerization procedure which were used as seed particles. A) Carboxylic acid functionalized spheres of $1.40 \pm 0.06 \mu\text{m}$ in diameter. B) Sulfate functionalized spheres of $1.38 \pm 0.03 \mu\text{m}$ in diameter.

Surfate functionalized particle synthesis Linear polystyrene spheres were synthesized by a surfactant free emulsion polymerization procedure. Here, a solution of 112.85 mg KPS in 112.5 mL water was flushed with nitrogen and heated to 70 C in an oil bath. Under magnetic stirring 22.5 mL of inhibitor-free styrene was quickly added and the reaction mixture was stirred for 24 h.

The resulting linear particles were crosslinked by adding a mixture of 2.6 mL swelling solution (styrene with 1.5% v/v DVB and 2% w/w AIBN), 2 mL of a 0.03% w/w hydroquinone solution and 23 mL of a 5% w/w PVA (Mw 13,000-23,000, 98% hydrolysed) to 5 mL of the obtained linear particle dispersion. The added mixture was emulsified at 8000 rpm for 2 min using an IKA T 18D Ultra Turrax homogenizer before it was quickly added to the linear particle dispersion. The reaction mixture was flushed with nitrogen and tumbled for 12h at 25 rpm to allow for swelling of the particles. Polymerization was performed in a 70°C oil bath for 24h while rotating at 60 rpm under an angle of 45°. The resulting sulfate functionalized crosslinked spheres were $1.38 \pm 0.03 \mu\text{m}$ in diameter (see Figure 3.1B)

Formation of random aggregates Diffusion-limited aggregates of cross-linked polystyrene colloids were obtained using a salting-out quenching method.¹⁰⁵ Here, 200 μL of a 2 M potassium chloride solution was added to 200 μL of 2% w/w cross-linked polystyrene particles in a 40 mL graduated flask. The solution was gently swirled twice, and after an aggregation time, t_a of 1, 2, 4, or 10 min, the suspension was quenched with 30 mL water.

Formation of well-defined patchy particles To 5 mL of the random cluster dispersion various amounts (10-200 μL) of a 10% w/v SDS or PVP in water solution was added followed by a swelling solution consisting of styrene with 1% v/v DVB or 49:1 MM:MA with 1.5% v/v EGDM. We define the degree of swelling by the swelling ratio S , that is, the mass of monomer divided by the mass of the polystyrene colloids. We employed swelling ratios of 1 to 80. Immediately after the addition of the swelling solution the mixture was placed on a magnetic stirrer for 20-24 hours at 200 rpm. After swelling, the clusters were transferred to a preheated 80°C oil bath and magnetically stirred at 270 rpm. After 10-120 min a solution of 0.4 mg AIBN in 20 μL monomer was added and the particles were polymerized for 20-24 hours. The clusters were washed three times and stored in water. Additionally, carboxylic acid functionalized polystyrene seeds swollen with 49:1 MM:MA with 1.5% v/v EGDM were selectively functionalized at the polystyrene surface areas with Neutravidin according to a method described by van der Wel *et al.*¹⁰⁶, where the carboxylic acid groups were used as reactive sites.

Formation of colloidal clusters To 5 mL of the randomly shaped cluster dispersion, various amounts (10-200 μL) of a 10% w/v SDS in water solution were added followed by toluene of swelling ratios $S=2-16$. Immediately after the addition of toluene the mixture was placed on a magnetic stirrer for 20-24 hours. After swelling, the toluene was evaporated for 4-5 hours in a preheated 80°C oil bath under magnetic stirring at 270 rpm. The obtained colloidal clusters were washed three times with water.

Imaging and analysis The randomly shaped clusters formed by salting-out were imaged using a Nikon Eclipse Ti microscope with an A1R confocal scan head with a 100x oil immersion objective ($\text{NA} = 1.4$). The polymerized particles and clusters were imaged using a FEI nanoSEM 200 scanning electron microscope at 15 kV. The size distribution of the random aggregates and the patchy particles after polymerization was determined by statistical analysis of at least 200 clusters using the cell counter plugin in ImageJ.

3.3 Results and Discussion

3.3.1 Assembly strategy

Stability against aggregation due to van der Waals forces is arguably the most essential requirement for colloidal particles. The first step in our synthesis approach is therefore rather counterintuitive: we deliberately destabilize a colloidal dispersion. See Figure 3.2A. We reduce the colloidal stability of charge-stabilized, crosslinked polymer particles by either adding an excess amount of salt to reduce

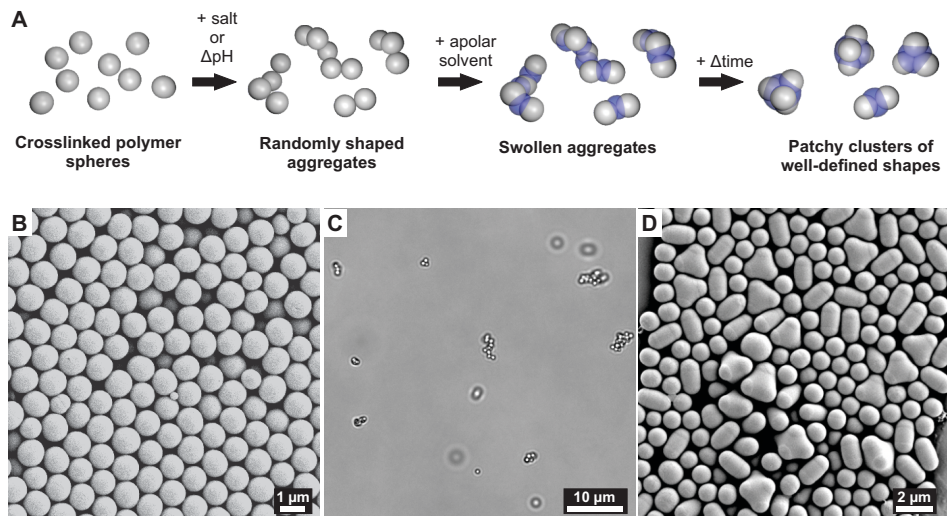


FIGURE 3.2: Colloidal recycling of random aggregates into patchy particles. (A) Schematic of the synthesis strategy. We obtain randomly shaped aggregates by destabilizing colloidal spheres, either by adding an excess amount of salt or by changing the pH to the isoelectric point. In the second step the aggregates are swollen with an apolar solvent. The apolar solvent lubricates the contact area between the spheres and reduces the attractive van der Waals forces such that the individual spheres can reconfigure into uniform patchy particles. (B) SEM micrograph of polystyrene spheres of $1.06 \mu\text{m}$ diameter with 5.3% polydispersity purchased from Magsphere Inc. (C) Bright-field microscopy image of randomly shaped aggregates obtained after increasing the salt concentration to 1.0 M potassium chloride for 2.5 min and followed by quenching with water. (D) SEM micrograph of the reconfigured and polymerized patchy particles obtained by swelling the aggregates with styrene and 1% v/v divinylbenzene at $S=3$.

the Debye-Hückel screening length or by adjusting the pH of the solution to the isoelectric point of the colloidal particles. The destabilization induces diffusion-limited aggregation of the colloids into small clusters^{105,107}, which can be brought to a halt by quenching with an excess amount of water. The resulting aggregates possess a random configuration that is not homogeneous for each cluster size as can be seen in Figure 3.2C. Here, polystyrene spheres of $1.06 \mu\text{m}$ diameter purchased from Magsphere Inc. (5% crosslink density), shown in Figure 3.2B, were aggregated by adjusting the salt concentration to 1.0M using potassium chloride. Similar random aggregates were obtained by aggregating carboxylic acid functionalized polystyrene spheres of $1.40 \mu\text{m}$ diameter (Figure 3.1A) by lowering the pH to 0 using hydrochloric acid or alternatively, increasing the salt concentration to 1.0 M (see Appendix Figure 3.8). To achieve reconfiguration, we swell the random aggregates with an apolar solvent. We define the added mass of ap-

olar solvent, m_{solvent} , divided by the polymer mass of the particles, m_{polymer} , as the swelling ratio S . The actual degree of swelling is strongly dependent on the crosslink density of the particles as well as the exact composition of particle and swelling solvent through the entropy of mixing between the polymer network and the swelling solvent.¹⁰⁸

The swelling serves three purposes: firstly, it swells and softens the polymer spheres resulting in a larger contact area and partial phase separation between the apolar solvent and the polymer network.^{4,7,24,109,110} This liquid-swollen polymer bridge enables particle rearrangement by lubricating the contact area between the spheres and smoothing out any surface inhomogeneity resulting from charges or roughness. The apolar liquid bridge also replaces the solvent between the polymer spheres in the area of closest contact. This change in the dielectric constant of the solvent medium affects the Hamaker constant and thus the van der Waals attraction, which binds the spheres in the randomly shaped aggregate. We can estimate the reduction of the van der Waals attraction by calculating the non-retarded Hamaker constants on the basis of Lifshitz Theory²⁶ for spheres fully immersed in the apolar solvent. For polystyrene spheres, the Hamaker constant reduces by a factor 600 when the aqueous medium is replaced by styrene, and by a factor 17 when replaced by toluene. The significantly lower van der Waals attraction together with the smoothing effect and the lubrication facilitates the rearrangement of the particles.

Secondly, the swelling imposes a driving mechanism to create uniform arrangements of the spheres: to minimize the interfacial energy between the apolar solvent and the water phase the spheres become close-packed. This surface tension driven rearrangement can be further enhanced by heating the dispersion to induce a larger degree of phase separation of the polymer spheres and the hydrophobic solvent, thereby creating droplets of the apolar swelling solvent at the contact points.^{4,7,24,109–112} The interplay between minimization of interfacial area and the geometric constraint imposed by the spheres determines the final structures uniquely for small cluster sizes. For small clusters of N spheres we find the dimer for $N=2$, the triangle for $N=3$, the tetrahedron for $N=4$ and the triangular dipyrmaid for $N=5$ similar to existing droplet based cluster fabrication methods.^{14,113} Finally, swelling with an apolar solvent allows for the fabrication of patchy particles when a monomer is chosen as swelling solvent. Upon heating the dispersion to 80°C, a phase separation occurs between the monomer and the polymer particles^{4,16,110} creating well-defined patches that originate from the seed particles. The number of patches of a patchy particle therefore equals the number of spheres in the random cluster. The addition of a radical initiator such as azobisisobutyronitrile (AIBN) polymerizes the droplet and yields solid patchy particles. We note that the seed particles are not required to be stable in apolar solvents, and that our method for making patchy particles therefore can be applied to purely charge stabilized colloids as well.

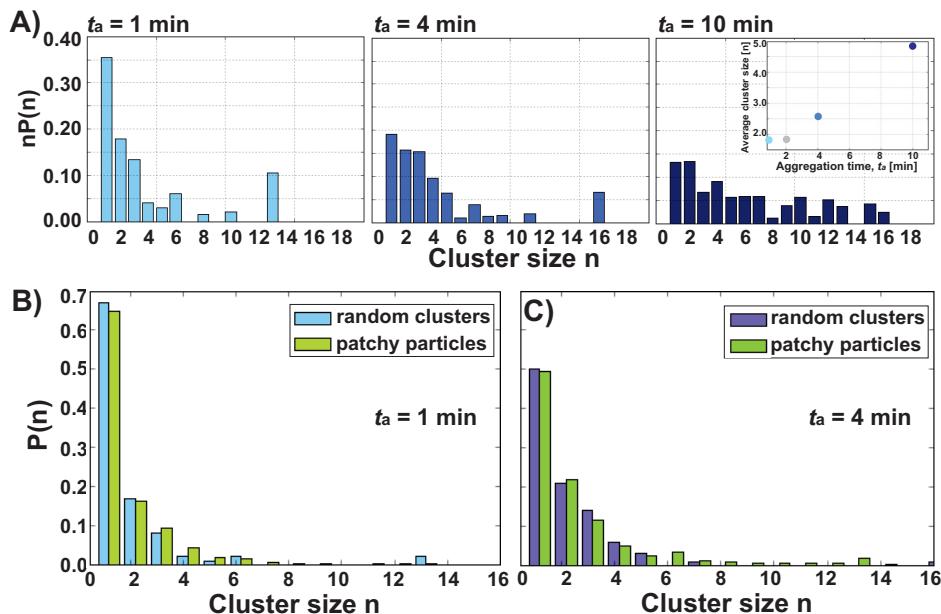


FIGURE 3.3: Tunable cluster size distribution. A) Size distribution of aggregates formed by the addition of salt to charge-stabilized colloids. The cluster size n increased with the aggregation time t_a . A linear relation between the average cluster size and the aggregation time is observed, which points to diffusion-limited aggregation. B) Probability $P(n)$ to find a cluster of n spheres for random aggregates and patchy particles made aggregating $1.06 \mu\text{m}$ polystyrene spheres for $t_a = 1$ min (B) and $t_a = 4$ min (C). The aggregates were subsequently swollen with styrene at $S=7$ to obtain patchy particles. The cluster size distributions of the clusters before and after swelling are in agreement.

To demonstrate the effect of swelling, we added a mixture of styrene and 1% v/v divinylbenzene (DVB) with $S=3$ to the salt-aggregated polystyrene spheres from Magsphere Inc. and allowed the clusters to change their configuration while stirring for a day. To prevent the particles from losing their shape during swelling, we employed crosslinked polymer spheres only. After polymerization with AIBN we imaged the obtained patchy particles using a scanning electron microscope (SEM), see Figure 3.2D. Clearly, all patchy particles of a given size share a uniform shape. For example, all random aggregates consisting of three spheres have turned into triangular clusters with three patches.

3.3.2 Tunable size distribution

By deliberately inducing colloidal aggregation, we can control the cluster size distribution of the random aggregates through an adjustment of the aggregation time, t_a . As expected for diffusion-limited aggregation, longer aggregation times linearly shift the distribution of the random clusters towards larger sizes¹¹⁴, as shown in Figure 3.3A. The size distribution can furthermore be tuned by adjusting the particle volume fraction since the rate of rapid coagulation in the absence of a potential barrier is only limited by the volume fraction and particle size.^{115,116} To confirm that indeed a reshaping of the random aggregates and not further aggregation is the underlying mechanism for the formation of the patchy particles, we compare the size distributions of the clusters before and after reshaping for $t_a=1$ and 4 minutes, see Figure 3.3B and 3.3C respectively. The size distributions of the random and patchy clusters agree very well, supporting the hypothesized reconfiguration mechanism.

3.3.3 Reconfiguration parameters

A successful reconfiguration of the spheres into patchy particles depends on the degree of swelling and the time allocated for rearrangement. In Figure 3.4A bright field images of the reconfiguration of a random aggregate of four polymer spheres of $1.06\ \mu\text{m}$ diameter are displayed. The aggregate has been swollen for 20 minutes at $S=7$ with styrene. Once a sufficient degree of swelling is reached, the cluster changes its configuration from an open structure to a close-packed tetrahedron within several seconds. The spheres within the cluster still fluctuate around the equilibrium position in the tetrahedron structure until the swelling is completed. The polymerized patchy particles show that the final clusters have a fixed geometry.

At swelling ratios $S>2$, the reconfiguration of the random aggregates into uniform patchy particles of well-defined shapes occurs with high fidelity. Lower swelling ratios result in a lower lubrication of the contact area as well as a smaller driving force for rearrangement, similar to particle networks connected by a secondary fluid.¹¹⁷ The reconfiguration of the insufficiently swollen spheres becomes either impossible or is significantly slowed down. For example, $1.40\ \mu\text{m}$ diameter carboxylic acid functionalized polystyrene spheres made through a seeded-growth process show incomplete rearrangement for swelling ratios below $S=2$, as shown in Figure 3.4B, even after 24h swelling. At intermediate swelling ratios between $S=2$ and $S=8$ aggregates of the same colloidal particles reconfigure successfully into patchy particles, see Figure 3.5. A mixture of patchy particles of different sizes is obtained with well-defined structures at fixed cluster sizes (see Appendix Figure 3.9). The configuration of the resulting particles of a given cluster size is independent of the swelling ratio (see Appendix Figure 3.10 for SEM micrographs with systematic variation of S). At even higher swelling ratios, the col-

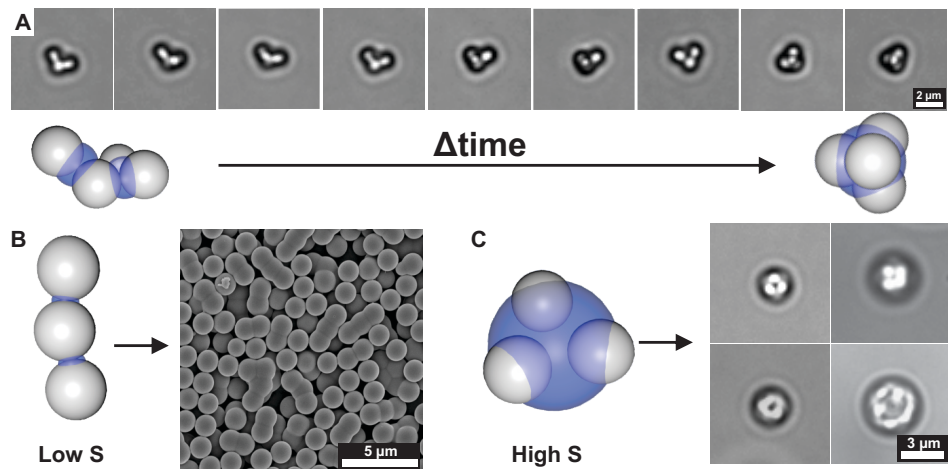


FIGURE 3.4: Reconfiguration of random aggregates into patchy particles. (A) Bright-field images of the reconfiguration process of an open random shape to a close-packed tetrahedron. The duration of the reorganization is 8 s. The aggregate consisted of four $1.06 \mu\text{m}$ in diameter polystyrene spheres and was swollen for 20 min with styrene at $S=7$. (B) Low swelling ratios S deposit insufficient solvent at the contact area and thus do not lead to reconfiguration. SEM micrographs of randomly shaped clusters of $1.40 \mu\text{m}$ carboxylic acid functionalized polystyrene spheres after swelling and polymerization with styrene at $S=1$. (C) At high swelling ratios, phase separation leads to the seed particles being adsorbed to a solvent droplet. Bright-field image of $1.06 \mu\text{m}$ cross-linked polystyrene spheres swollen with 49:1 MM:MA at $S=80$.

loidal particles reconfigure, but in the absence of additional stabilization by a surfactant aggregation of the clusters may occur (see Appendix Figure 3.11). The $1.06 \mu\text{m}$ polystyrene spheres (Figure 3.2B) swollen with 49:1 methylmethacrylate:methacrylic acid (MM:MA) at high swelling ratios ($S=80$) spontaneously underwent a phase separation between the polymer particles and the apolar solvent and formed solvent droplets with the particles attached at the interface, that is, Pickering emulsions. See Figure 3.4C.

Allocating more time for rearrangement may compensate for a slow rearrangement of the spheres in the randomly shaped aggregates. For example, swelling $1.40 \mu\text{m}$ polystyrene particles at a swelling ratio $S=8$ for 3 hours yields non-uniform but swollen aggregates. After 23h rearrangement time, however, the spheres were able to optimize their position in the cluster and now form uniform patchy particles, see Appendix Figure 3.12.

Successful swelling relies on an efficient transport of monomer to the polymer spheres, which we enhance by adding a surfactant, 0.02–0.20% w/v SDS or polyvinylpyrrolidone (PVP), during swelling. The added surfactant also plays

a role in lowering the surface tension of the emerging droplets during phase separation and influences the wetting angle of the droplets with the polymer spheres and the water phase. Therefore, the surfactant concentration controls the patch size, as is shown in Appendix Figure 3.13. Finally, the surfactant may also adsorb onto the particle surface yielding additional stabilization of the particles by steric or ionic repulsion. This additional repulsion can lead to a re-stabilization of the individual spheres after the aggregation and thus to a disintegration of the clusters. We observed this effect for $1.38 \mu\text{m}$ sulfate functionalized polystyrene spheres in the presence of 0.4% w/v SDS, which resulted in snowman shaped particles only. See Appendix Figure 3.14.

3.3.4 Patchy particle configurations

The structures of the clusters resulting from reconfiguring the random aggregates are shown in Figure 3.5. We find that the spheres are closely packed and held together by the apolar solvent with which they were swollen. For polystyrene spheres crosslinked with 5% v/v DVB and swollen with styrene, we observe distinct patches on the particle surface that originate from the seed particles. The body of the patchy particle consists of the coalesced and polymerized styrene droplet. See Figure 3.5A for a schematic, where blue depicts the droplet body and white the spheres and Figure 3.5B for SEM micrographs. The arrangement of the spheres is determined by the constraining droplet. Therefore, the second moment of the mass distribution is minimized, resulting in arrangements in line with emulsion-based sphere packings.^{14,113}

Surprisingly, when we swelled $1.40 \mu\text{m}$ carboxylic acid functionalized colloids with a lower crosslink density (1.5% v/v DVB) with styrene, MM:MA or toluene, other shapes in addition to the second moment minimizing ones are observed (see Figure 3.5D and Appendix Figure 3.8). For clusters up to $N=5$, again the cluster arrangements that minimize the second moment of the mass distribution are obtained, see Figure 3.5D. At $N=6$, however, we find that the polytetrahedron is strongly preferred over the minimal second moment arrangement found in droplet based clusters, the octahedron. For clusters consisting of $N>6$ spheres we found a variety of different compact configurations besides the minimal second moment arrangement (see Appendix Figure 3.15). In earlier experiments on clusters of purely attractive spheres it was found that the octahedron is favoured for long-range attractions, whereas the polytetrahedron is preferred for short-range interactions due to its larger rotational entropy.¹³ Our experimental system features both short-range and long-range organizing principles: on the one hand, a significant degree of swelling and phase separation between the apolar liquid and the polymer spheres leads to droplets that coalesce and impose a cluster spanning droplet that confines and reorders the spheres, which therefore results in arrangements that minimize the second moment of the mass distribution. On the

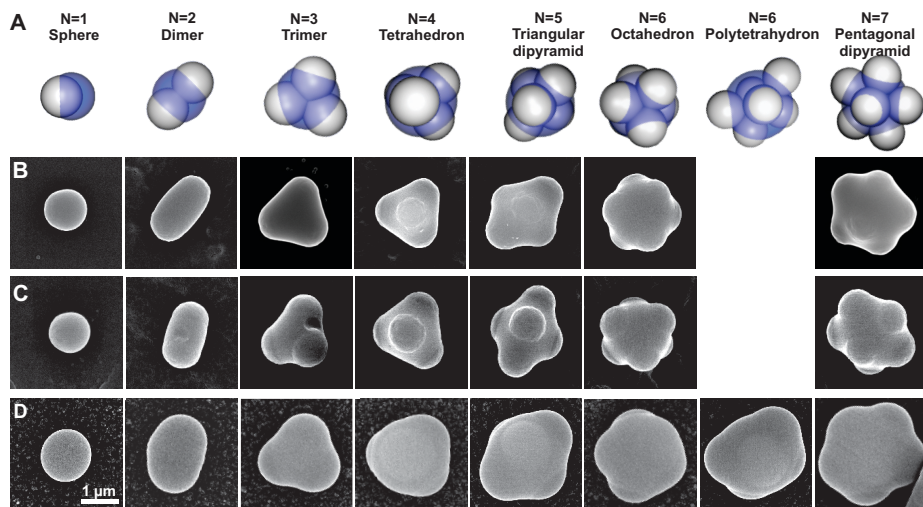


FIGURE 3.5: Reconfigured patchy particles and clusters. (A) Models of the patchy particles consisting of $N=1-7$ spheres. (B-D) SEM micrographs of polymerized reconfigured clusters. Patchy particles obtained from $1.06 \mu\text{m}$ polystyrene spheres (5% v/v cross-link density), purchased from Magsphere Inc. (Figure 3.2B), obtained after swelling random aggregates (B) with styrene at $S=5$ and (C) with 49:1 MM:MA at $S=80$. (D) Polymerized colloidal clusters of 1.40μ carboxylic acid functionalized polystyrene spheres (1.5% v/v cross-link density), obtained after swelling with toluene at $S=16$

other hand, in the absence of a cluster-spanning droplet, the liquid bridges at the contact points only interact with their nearest neighbours. We therefore hypothesize, that the clusters of particles with a low crosslink density do not feature a cluster-spanning droplet resulting in cluster shapes preferred by entropy.^{13,14} Indeed, it is known that polymer particles with a lower crosslink density also show a smaller degree of phase separation.⁴ In addition, these particles are made by a seeded growth procedure where not all polymers are covalently linked to the polymer network.^{4,118} Swelling the particles with a good solvent leads to migration of some polymer chains to the centre, see Figure 3.5D, possibly lowering the interfacial tension of the apolar solvent and the water phase. Excitingly, the resulting patchy particles therefore have anisotropic shapes and patch arrangements that have not been accessible by other fabrication methods until now.

The simplicity of this reconfiguration method allows it to be applied to a variety of polymer colloids and swelling solvents. The patches can be rendered functional by designing a chemical or physical difference between the polymer spheres and the swelling solvent. We demonstrate this flexibility by employing a 49:1 mixture of MM:MA as swelling monomer of the $1.06 \mu\text{m}$ diameter, 5%

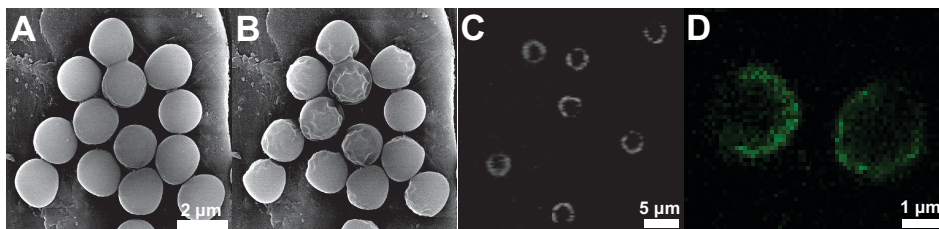


FIGURE 3.6: Functionalization of patchy particles. A-B) SEM micrographs of Janus particles with a polystyrene and a pMMA side. After severe exposure of the electron beam the pMMA crumpled (B). Confocal microscopy images of partly fluorescent particles, where the fluorescence stems from the polystyrene side of the particle originating from C) fluorescein amine and D) Neutraavidin, by reaction with the carboxylic acid groups on the polystyrene surface.

crosslinked polystyrene spheres. After swelling, reconfiguration, and polymerization we obtain patchy particles possessing a pMMA body and polystyrene patches, as shown in Figure 3.5C. The resulting patchy particles have shapes that minimize the second moment of the mass distribution and show particle spanning droplets. The pMMA and polystyrene areas on the particles could be distinguished by SEM since the electron beam induced crumpling of the pMMA, see Figure 3.6A and 3.6B. Addition of fluorescein amine to the particles resulted in fluorescent polystyrene and non-fluorescent pMMA (Figure 3.6C). This indicated that the carboxylic acid groups of the polystyrene seed particles reacted with the amine groups and did not migrate on the particle surface with the pMMA during phase separation. The carboxylic acid groups could also be replaced by Neutraavidin (Figure 3.6D), which can easily be used to selectively bind to biotinylated surfaces such as membranes.^{106,119}

Making use of a volatile swelling solvent, toluene, we can also obtain compact clusters of spheres without patches. After heating and reconfiguration, we selectively evaporate the toluene from the swollen clusters by stirring the open sample flask in an 80°C oil bath. The resulting particles are therefore not patchy particles, but clusters of spheres, although we often find that some of the non-crosslinked polymers migrate towards the centre of the cluster.¹⁰⁹ When employing aggregates of the Magsphere colloids, we find clusters that minimize the second moment of the mass distribution similar to the styrene and MM:MA swollen clusters (see Appendix Figure 3.16).

In all cases, a mixture of clusters or patchy particles with well-defined geometries and low polydispersity is obtained. To quantify the uniformity of the particle arrangements, we measured the polydispersity of the distance of the seed spheres in a polymerized trimer patchy particles made from aggregates of 1.06

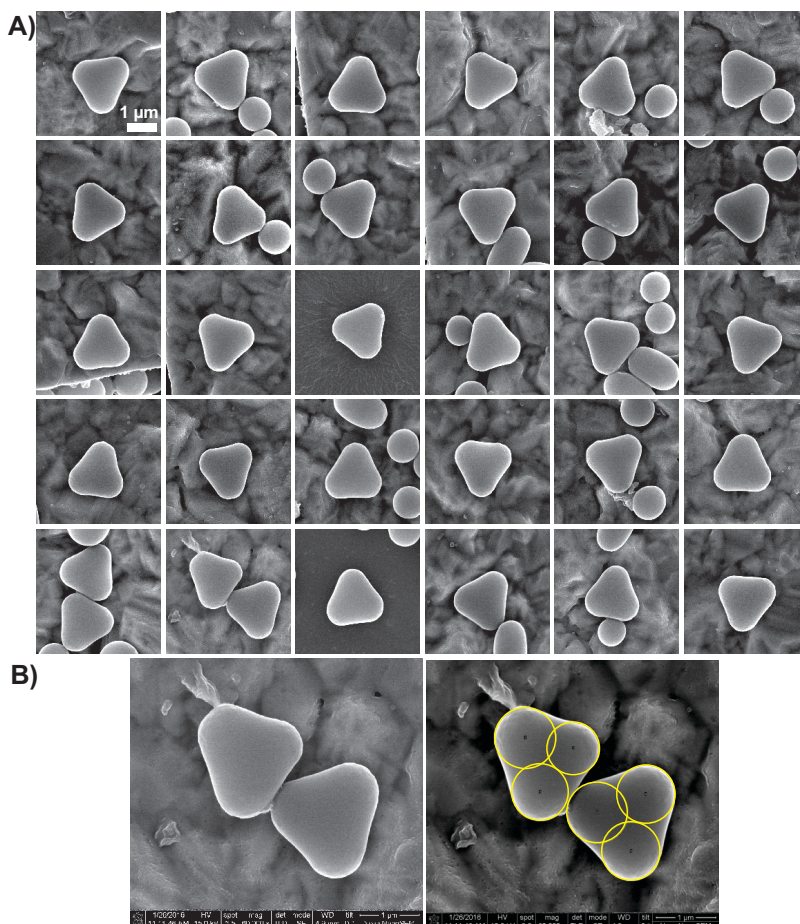


FIGURE 3.7: Patchy particle shape analysis. A) SEM micrographs of trimer patchy particles consisting of three seed particles obtained after reconfiguring aggregates of $1.06 \mu\text{m}$ polystyrene spheres (Magsphere Inc.) with styrene at $S=7$. B) To obtain information on the polydispersity of the clusters the center-to-center distances of the reconstructed seeds was measured using high resolution SEM micrographs of trimer particles. From the original SEM micrographs (left) the position and size of the seed particles was reconstructed by fitting a circle at the patches using ImageJ (right). The center-to-center distance in 33 trimers was measured, where an average distance of $0.95 \mu\text{m}$ was found with a polydispersity of 5.8%. This distance is slightly shorter compared to the diameter of the seed particles due to capillary forces acting on the particles during reconfiguration which can deform the polymer spheres. The polydispersity of the trimers is consistent with the 5.3% polydispersity of the seed particles.

μm polystyrene particles with styrene at swelling ratio $S=7$. We found the polydispersity to be 5.8%, which is comparable to the polydispersity of 5.3% for the seed particles (see Figure 3.7). The sphere arrangements are not affected by polymerization (see Appendix Figure 3.17) and the uniformity for particles with $N < 6$ spheres indicates that these are the most stable configurations, which in principle can be stored even in the swollen state if sufficiently stabilized against further coalescence¹¹³.

Similar to existing cluster preparation methods, a post-processing step is required to separate the different cluster sizes. Although techniques such as density gradient centrifugation are suitable for separation¹⁴, we emphasize the need for cluster preparation methods with narrow size distributions. Our reconfiguration method provides an opportunity for achieving this, since it only requires randomly aggregates as a starting point. Therefore, any method that provides a sharply peaked size distribution of random aggregates may be used to make uniform patchy particles in high yield.

Besides the fundamentally different reconfiguration approach, our strategy distinguishes itself from existing patchy particle preparation methods by combining the arrangement of spheres into uniform structures and the formation of patchy particles into a single step. Emulsion-based strategies first require the preparation of well-defined colloidal clusters²⁵, before patchy particles can be formed by the addition of a swelling agent or polymerizable liquid. Because our approach combines the two steps, it does not require the seed particles to be stable in apolar solvents nor to be able to form well-defined protrusions upon swelling^{16,113}. Therefore, the reconfiguration approach for making patchy particles can also be applied to purely charge stabilized colloids and colloids with a wider range of crosslink density and surface hydrophilicity. The non-toxic, aqueous environment makes our “recycling” method a user-friendly and cost-effective process that can easily be scaled up to yield large quantities of patchy particles and clusters.

Finally, we note that while we are exploiting the swelling of crosslinked polymer spheres to deposit droplets at the contact points of the spheres, the reconfiguration mechanism should be extendable to other non-polymeric colloidal systems if an alternative droplet deposition method, for example by nucleation from solution³ or mechanical mixing¹²⁰, is employed. The generality of the principle that enables reconfiguration of particles attached by van der Waals forces by simple droplet lubrication may also offer the opportunity to create microscopic hinges that can be applied in nano-robotics, actuators, or switchable structures.

3.4 Conclusions

We presented a general method to reconfigure particle aggregates and synthesize complex patchy particles of well-defined shape. Our starting point is randomly

aggregated particles, which we obtain by deliberately destabilizing spherical colloids using an excess amount of salt or by changing the pH to the isoelectric point. The size distribution of these aggregates can be tuned by changing the aggregation time. We showed that these randomly shaped clusters can be recycled into uniform patchy particles by swelling and depositing apolar solvent at the particle contact area. These droplets significantly reduce the attractive van der Waals forces, lubricate the contact area and induce a reconfiguration of the spheres in order to minimize the interfacial energy. The resulting particles are anisotropic in size and shape, and uniform for small cluster sizes. For clusters consisting of six spheres or more, particles with a high crosslink density rearrange into structures that minimize the second moment of the mass distribution. At low crosslink density, structures with higher entropy are preferred; for example, we find that the polytetrahedron is strongly favoured over the octahedron for clusters of six spheres. We show that besides patchy particles, colloidal clusters can be formed as well using a volatile apolar solvent. Furthermore we discussed and demonstrated the broad applicability of this strategy by tuning the swelling ratio, swelling agent, surfactant concentration, and colloidal material. We believe that the principle of bond lubrication that underlies the reconfiguration is general in nature and can be transferred to other systems as well.

3.5 Appendices

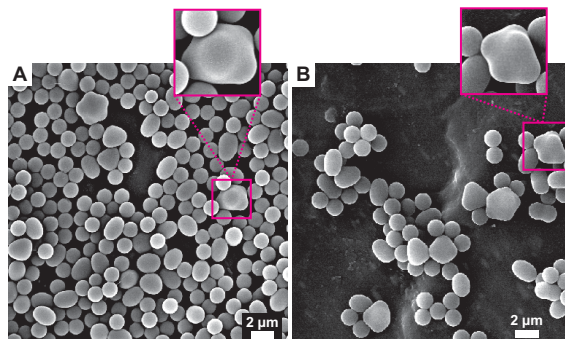


FIGURE 3.8: Different aggregation pathways give similar patchy particle shapes. SEM micrographs of polymerized patchy particles obtained by aggregating $1.40\ \mu\text{m}$ carboxylic acid functionalized polystyrene spheres with 1.5% v/v crosslink density. A) in a 1M potassium chloride solution for 1.5 min B) in a 1M HCl solution for 2 min. Both samples were swollen with styrene at $S=4$ for 24 hours, followed by polymerization. The resulting patchy particles have similar shapes independent of the aggregation method. Furthermore, the polytetrahedral shape for clusters consisting of six spheres is observed in both samples.

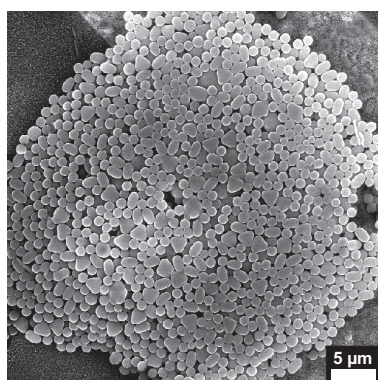


FIGURE 3.9: Large field of view by SEM of polymerized patchy particles of different sizes obtained by swelling colloidal aggregates of $1.06\ \mu\text{m}$ polystyrene spheres with styrene at $S=5$. For each cluster size, a well-defined arrangement is obtained.

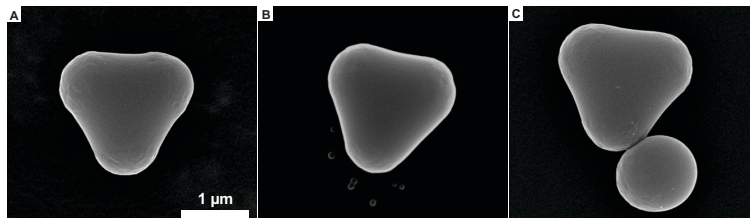


FIGURE 3.10: The shape and arrangement of the patchy particles are independent of the swelling ratio S . Colloidal aggregates of $1.06 \mu\text{m}$ polystyrene spheres were swollen with styrene at different swelling ratios. The SEM micrographs of typical trimer patchy particles obtained at A) $S=2$ B) $S=5$ C) $S=8$ show that at fixed sizes similar shapes and arrangements are observed, independent of the swelling ratio used.

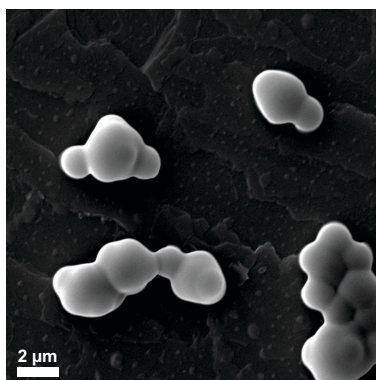


FIGURE 3.11: Patchy particles destabilize when the SDS concentration is insufficient. SEM micrograph of aggregates of patchy particles obtained by swelling aggregates of $1.40 \mu\text{m}$ polystyrene spheres with styrene at $S=8$. Clustering of the patchy particles was observed at this swelling ratio, since the concentration of surfactant was insufficient to stabilize the swollen patchy particles. This problem can be resolved by addition of surfactant shortly after the swelling has been initiated.

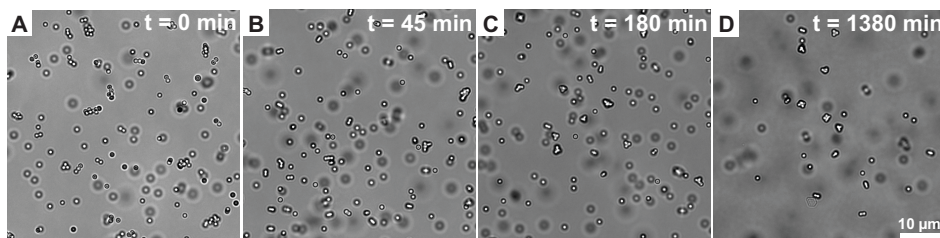


FIGURE 3.12: Swelling process of $1.40 \mu\text{m}$ carboxylic acid functionalized polystyrene aggregates with styrene at $S=4$ and 0.02% w/v SDS imaged with bright field microscopy over time A) After salting out for 4 min in a 1M potassium chloride solution randomly shaped aggregates were observed B) After 45 minutes of swelling the aggregates had swollen slightly, but mainly random shapes were observed C) After 3 hours of swelling part of the aggregates reconfigured into compact shapes. D) After 23 hours of swelling all swollen aggregates reconfigured into compact well-defined shapes.

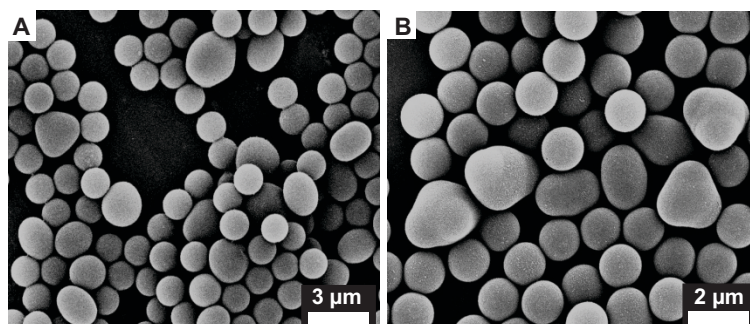


FIGURE 3.13: The concentration and timing of the addition of SDS influences the final particle shape. Colloidal aggregates of $1.40 \mu\text{m}$ polystyrene spheres were swollen with styrene at $S=4$ with A) 0.04% w/v SDS and B) 0.04% w/v SDS + an additional 0.04% w/v SDS added after a few hours of swelling. The additional amount of SDS leads to an increase in the transport rate of styrene to the aggregates and an increase in stability of the clusters. It also changes the surface tensions present in the system and therefore the wetting angle of the monomer with the particle. This results in patchy particles with more clearly defined patches(B).

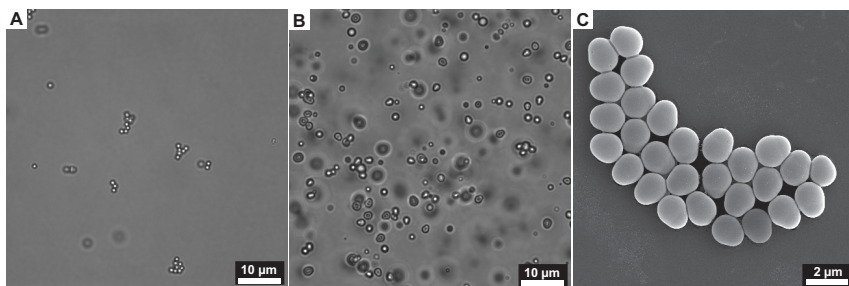


FIGURE 3.14: SDS can re-stabilize individual spheres breaking up the aggregates. Swelling of $1.38 \mu\text{m}$ sulfate functionalized polystyrene spheres A) Bright field microscopy image of aggregates formed after aggregation with salt B) Bright field microscopy image after 2 hours of swelling with styrene. The particles have non-spherical shapes and are clearly swollen C) SEM micrograph of the polymerized patchy particles. Well-defined protrusions are formed on the seed particles, displaying snowman-like shapes.

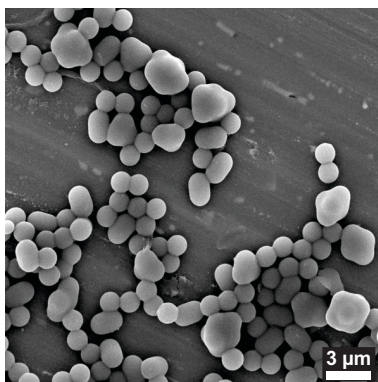


FIGURE 3.15: Large clusters shaped from low crosslink density seed particles have various shapes. SEM micrograph of patchy particles of $1.40 \mu\text{m}$ carboxylic acid functionalized polystyrene spheres with 1.5% v/v crosslink density. The patchy particles were obtained by swelling the aggregates at $S=40$ with MM:MA at a ratio of 49:1. Various shapes for clusters of $N>5$ spheres were formed.

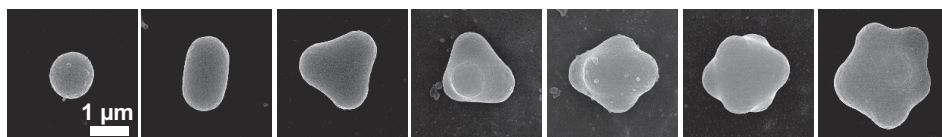


FIGURE 3.16: Colloidal clusters can be obtained by using toluene as swelling agent. SEM micrographs of colloidal clusters consisting of 1-7 spheres from left to right respectively. The colloidal clusters are obtained by swelling aggregates of $1.06 \mu\text{m}$ polystyrene spheres for 24 hours with toluene at $S=8$. After evaporation of the toluene well-defined colloidal clusters shapes are observed. The seed particles are slightly deformed during the process since the uptake of toluene softened the particles, leading to migration of linear polystyrene polymer out of the seed particles during the evaporation process to reduce the surface tension of the cluster.

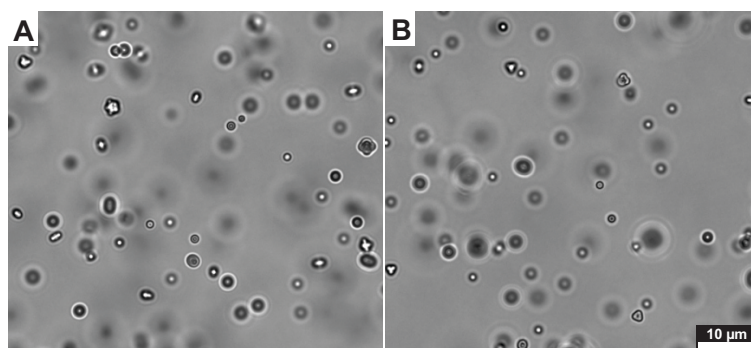


FIGURE 3.17: Comparison between swollen, unpolymerized (A) and polymerized (B) re-configured patchy particles. A) Bright field microscopy images of patchy particles obtained from salted-out $1.40 \mu\text{m}$ polystyrene spheres ($t_d=2$ min, 1M potassium chloride solution) after 18 hours of swelling with styrene at $S=5$ B) The cluster arrangements are maintained during polymerization for 24 hours at 80°C .

