Supporting Information

Colloidal Recycling: Reconfiguration of Random Aggregates into Patchy Particles

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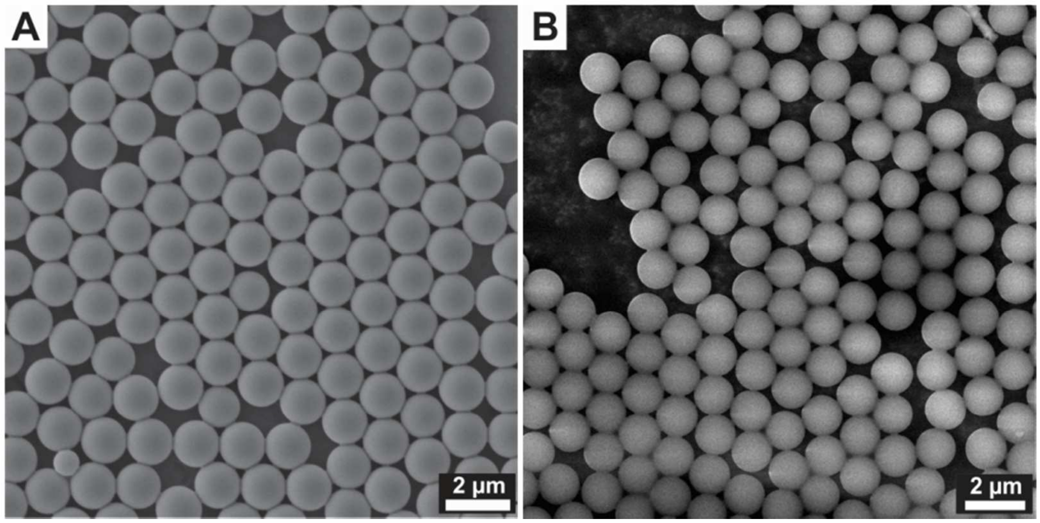

Figure S1: SEM micrographs of crosslinked polystyrene spheres synthesized by an emulsion polymerization procedure which were used as seed particles. A) Carboxylic acid functionalized spheres of 1.40 µm in diameter with a polydispersity of 4.6% B) Sulfate functionalized spheres of 1.38 µm in diameter with a polydispersity of 2.2%.

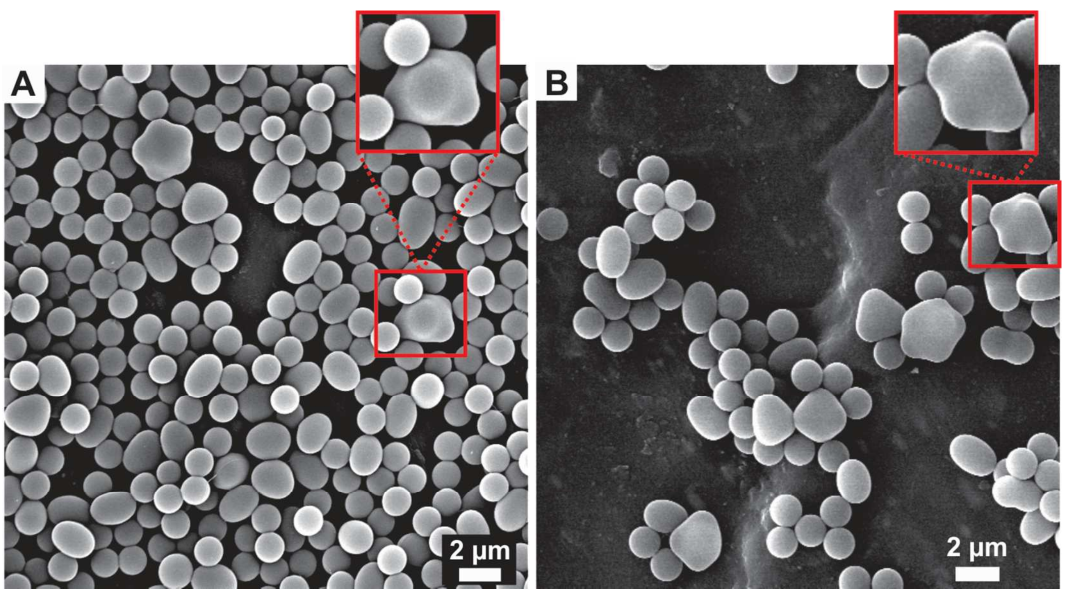

Figure S2: Different aggregation pathways give similar patchy particle shapes. SEM micrographs of polymerized patchy particles obtained by aggregating 1.40 µm carboxylic acid functionalized polystyrene spheres with 1.5% v/v crosslink density A) in a 1M potassium chloride solution for 1.5 min B) in a 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 6 spheres is observed in both samples.

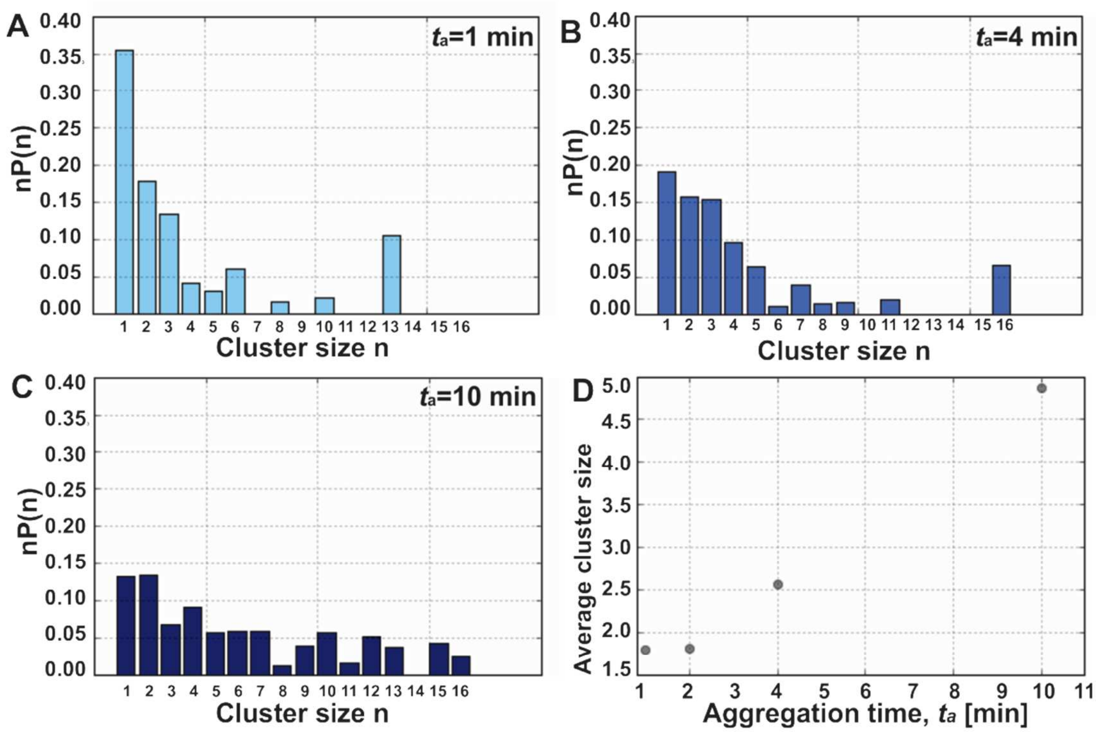

Figure S3: Size distribution of aggregates formed due to diffusion-limited aggregation by the addition of salt at different aggregation times, t_a. A) t_a=1 min, B) t_a=4 min and C) t_a=10 min. D) A plot of the average cluster size *vs* aggregation time shows a linear relation between the average cluster size and the aggregation time, which is in agreement with diffusion-limited aggregation theory.

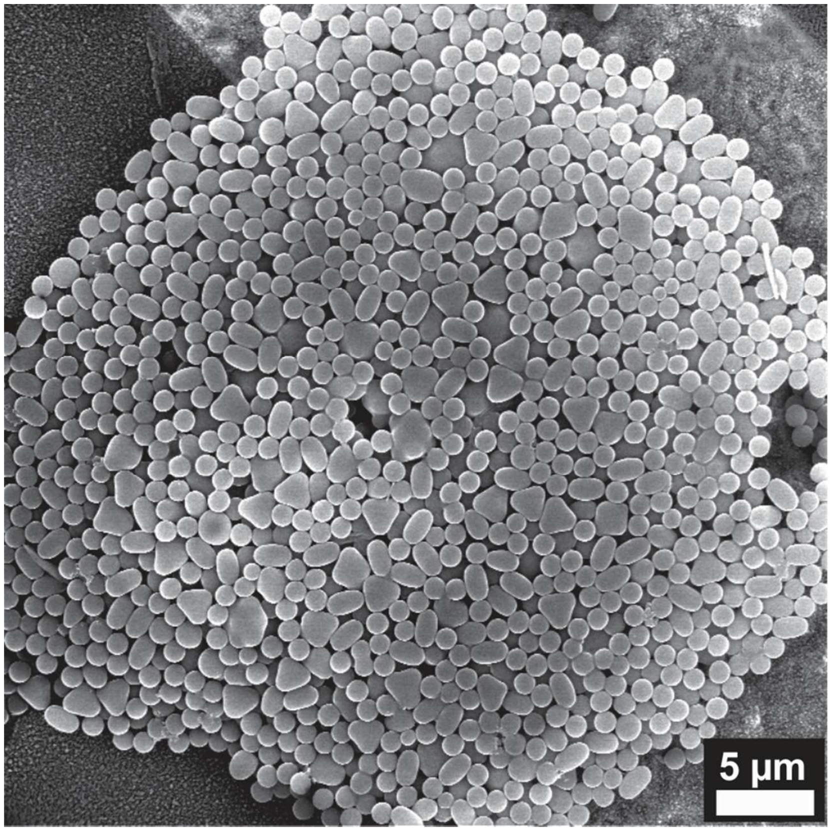

Figure S4. Large field of view by SEM of polymerized patchy particles of different sizes obtained by swelling colloidal aggregates of 1.06 µm polystyrene spheres with styrene at *S*=5. For each cluster size, a well-defined arrangement is obtained.

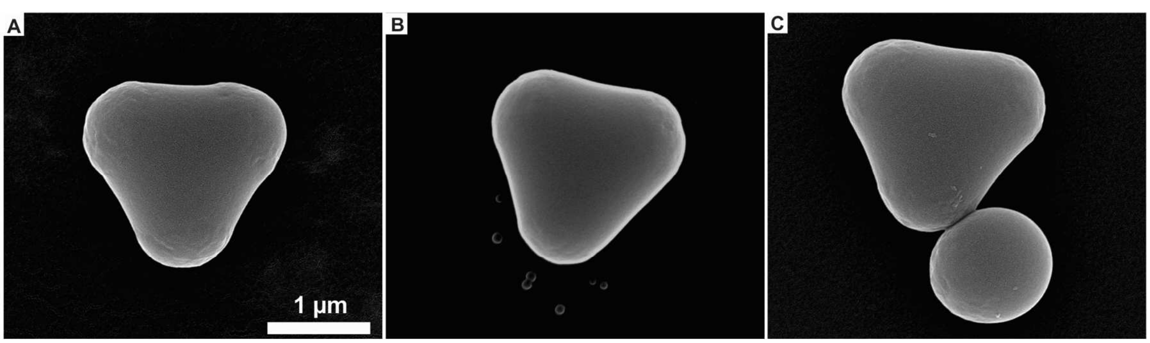

Figure S5. The shape and arrangement of the patchy particles are independent of the swelling ratio *S*. Colloidal aggregates of 1.06 µm polystyrene spheres were swollen with styrene at different swelling ratios. The SEM micrographs of typical trimer patchy particles obtained at A) *S*=2 B) *S*=5 C) *S*=8 show that at fixed sizes similar shapes and arrangements are observed, independent of the swelling ratio used.

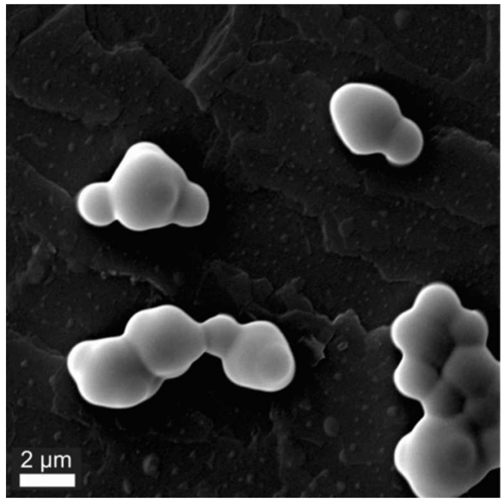

Figure S6: Patchy particles destabilize when the SDS concentration is insufficient. SEM micrograph of aggregates of patchy particles obtained by swelling aggregates of 1.40 µm polystyrene spheres with styrene at *S*=8. Clustering of the patchy particles was observed at this swelling ratio, since the 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.

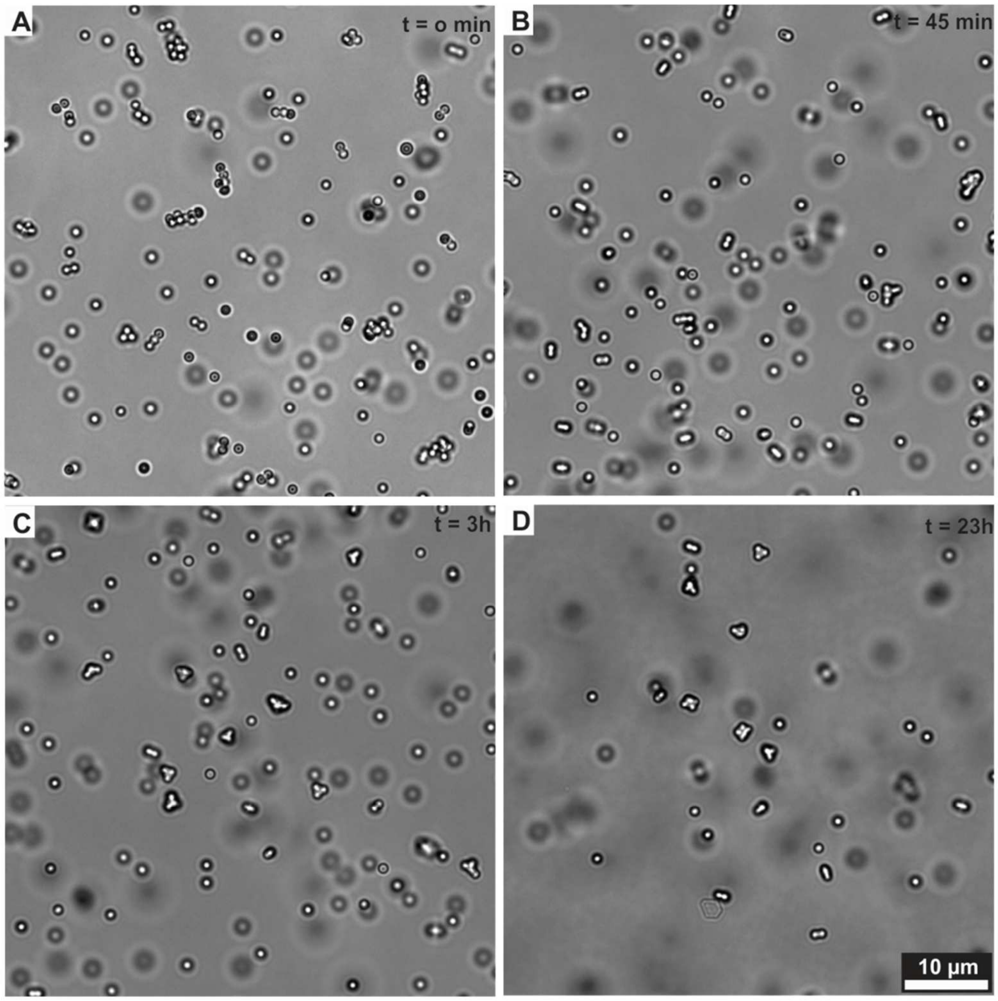

Figure S7: Swelling process of 1.40 µm carboxylic acid functionalized polystyrene aggregates with styrene at *S*=4 and 0.02% w/v SDS imaged with bright field microscopy over time A) After salting out for 4 min in a 1M potassium chloride solution randomly shaped aggregates were observed B) After 45 minutes 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.

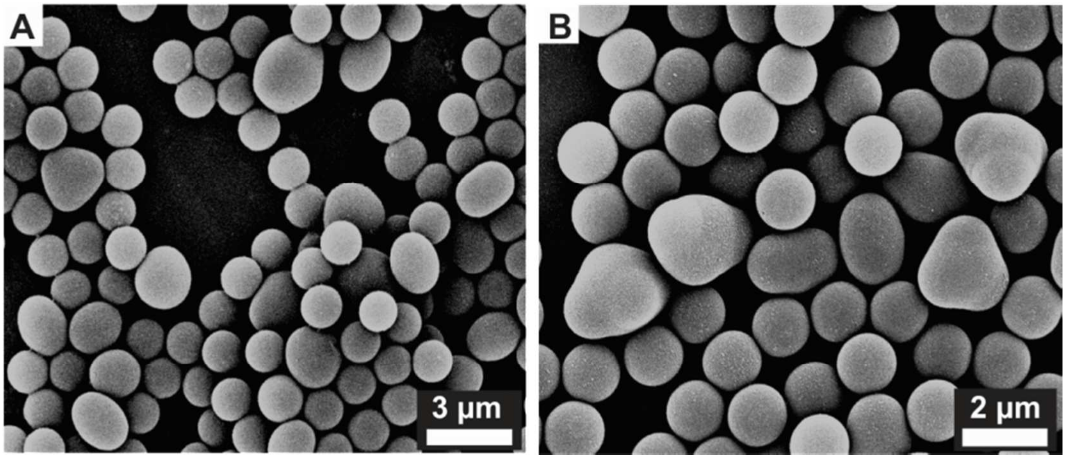

Figure S8: The concentration and timing of the addition of SDS influences the final particle shape. Colloidal aggregates of 1.40 μm polystyrene spheres were swollen with styrene at *S*=4 with A) 0.04% w/v SDS and B) 0.04% w/v SDS + an additional 0.04% w/v SDS added after a few hours of swelling. The 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)

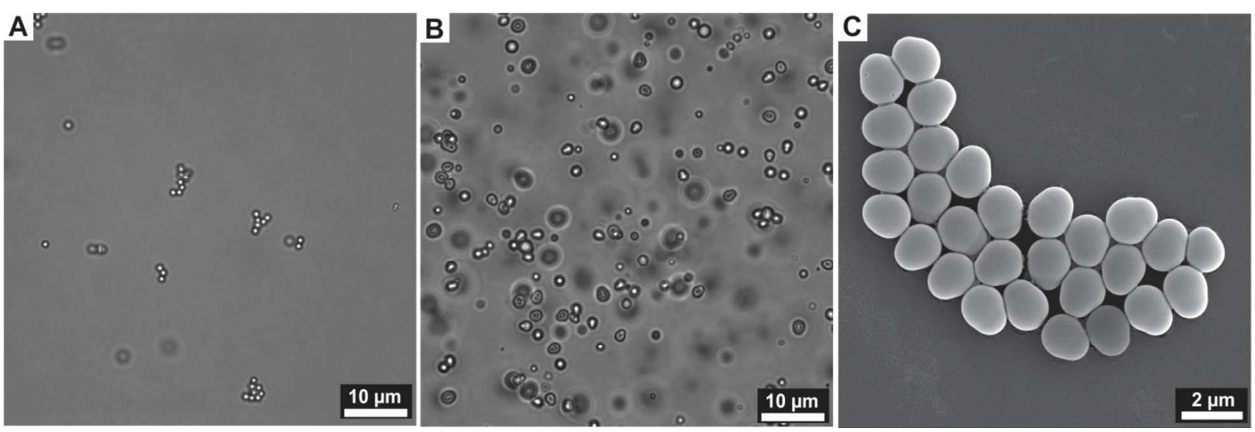

Figure S9. SDS can re-stabilize individual spheres breaking up the aggregates. Swelling of 1.38 μm sulfate functionalized polystyrene spheres A) Bright field microscopy image of aggregates formed after aggregation with salt B) Bright field microscopy image after 2 hours of swelling with styrene. The particles have non-spherical shapes and are clearly swollen C) SEM micrograph of the polymerized patchy particles where clearly defined protrusions are formed on the seed particles, displaying snowman-like shapes.

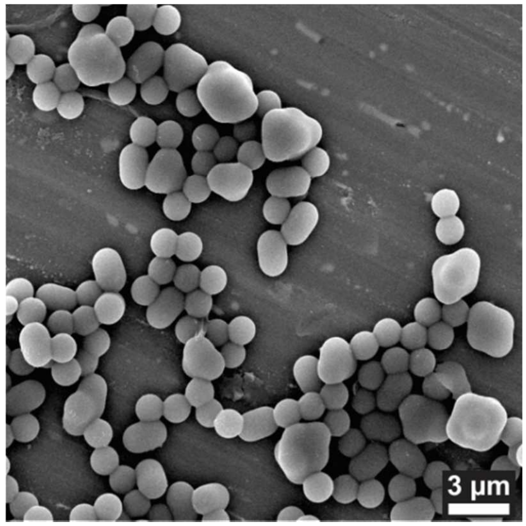

Figure S10. Larger clusters of low crosslink density seed particles have various shapes. SEM micrograph of patchy particles of 1.40 µm carboxylic acid functionalized polystyrene spheres with 1.5% v/v crosslink density. The patchy particles are obtained by swelling the aggregates at *S*=40 with MM:MA at a ratio of 49:1. Various shapes for clusters of N >5 spheres were formed.

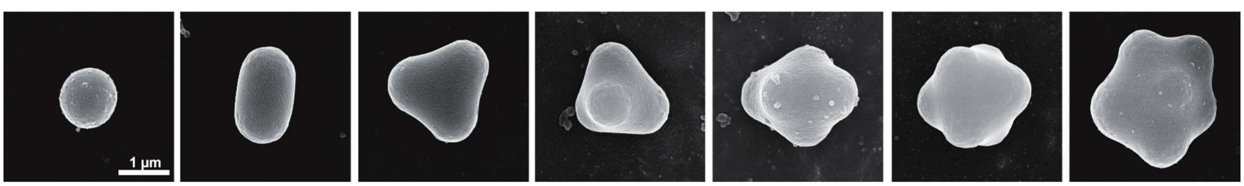

Figure S11: Colloidal clusters can be obtained by using toluene as swelling agent. SEM micrographs of colloidal clusters consisting of 1-7 spheres from left to right respectively. The colloidal clusters are obtained by swelling aggregates of 1.06 µm polystyrene spheres for 24 hours with toluene at *S*=8. 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.

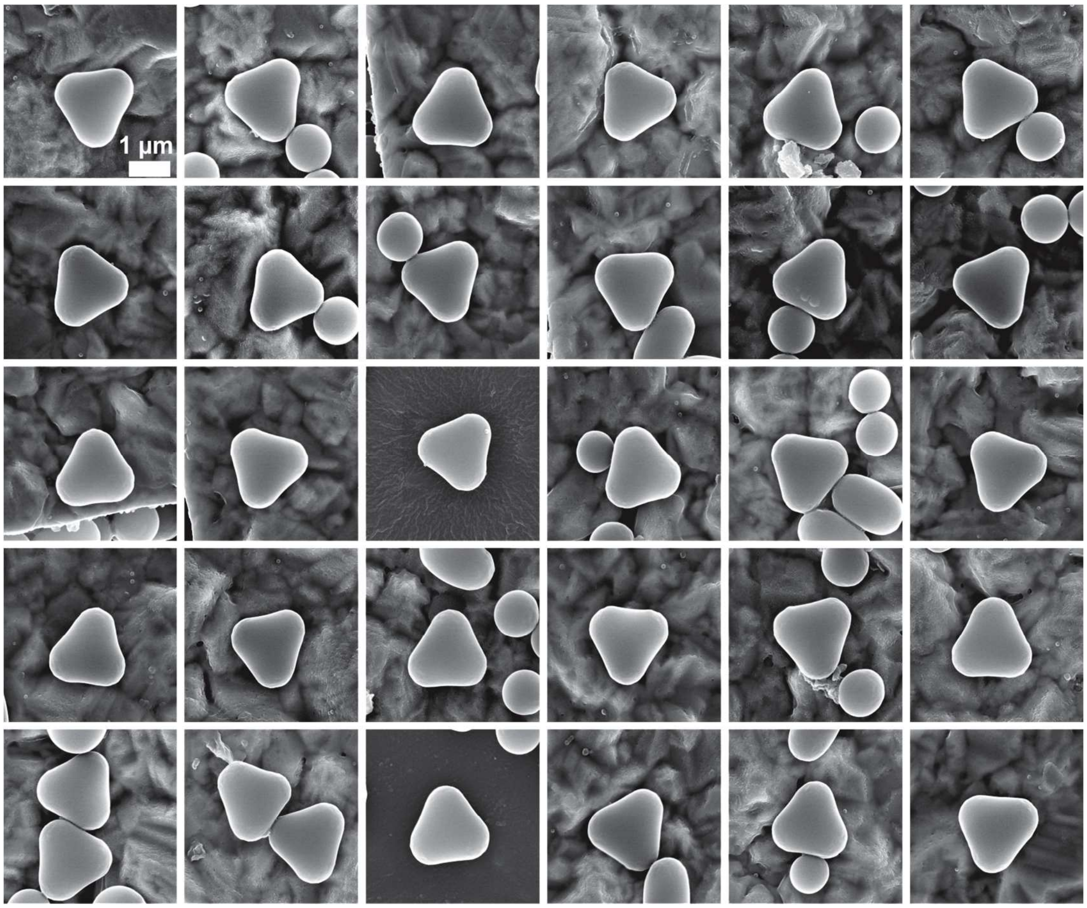

Figure S12: Well-defined shapes and arrangements at fixed cluster sizes. SEM micrographs of trimer patchy particles consisting of three seed particles obtained after swelling aggregates of 1.06 µm polystyrene spheres (Magsphere Inc.) with styrene at *S*=7. A uniform shape and arrangements is observed.

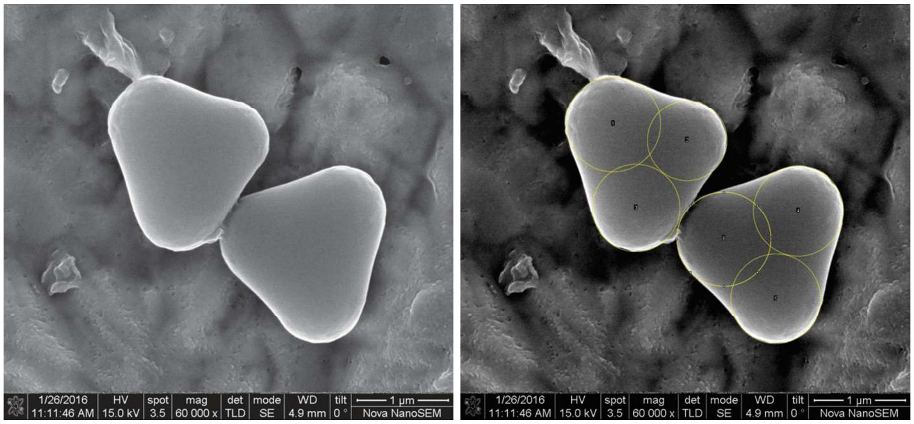

Figure S13: A quantitative analysis of trimer patchy particles. To obtain information on the polydispersity of the clusters the center-to-center distances of reconstructed seed particles was measured using high resolution SEM micrographs of trimer particles. The trimer patchy particles were obtained by swelling aggregates of 1.06 µm polystyrene spheres with styrene at *S*=7. 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 of the reconstructed seed particles is measured for 33 trimers, where an average distance of 0.95 µm was measured with a polydispersity of 5.8%. The size of the seed particles is slightly smaller compared to the seed particles due to capillary forces on the particles during the patchy particle formation. This small deformation is also indicated by the overlapping circles, and is expected since the polymer spheres are softened by the solvent swelling. The polydispersity of the trimers is consistent with the 5.3% polydispersity of the seed particles. We expect the actual polydispersity of the trimers to be even lower, since the measured distances can deviate from the real values due to: 1) slightly tilted particle positions due to roughness of the substrate, 2) imaging aberrations common in scanning electron microscopy, and 3) the approximate nature of fitting circles on the basis of the patches only.

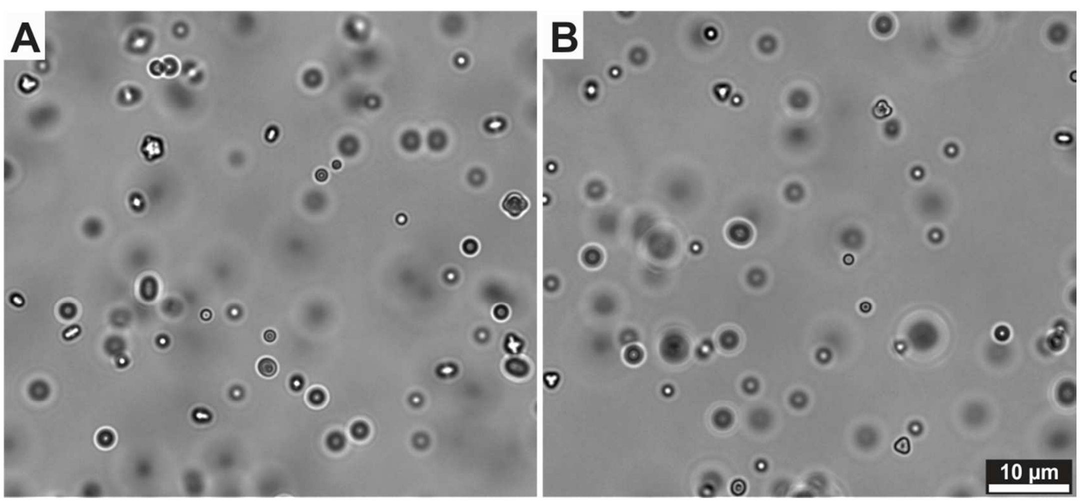

Figure S14: Comparison between swollen, unpolymerized (A) and polymerized (B) reconfigured patchy particles. A) Bright field microscopy images of patchy particles obtained from salted-out 1.40 um polystyrene spheres (t_a=2 min, 1M potassium chloride solution) after 18 hours of swelling with styrene at *S*=5 B) The cluster arrangements are maintained during polymerization for 24 hours at 80 ^{o}C.