

Self-Assembly of Colloids with Liquid Protrusions

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Abstract: A facile and flexible synthesis for colloidal molecules with well-controlled shape and tunable patchiness is presented. Cross-linked polystyrene spheres with a liquid protrusion were found to assemble into colloidal molecules by coalescence of the liquid protrusions. Similarly, cross-linked poly(methyl methacrylate) particles carrying a wetting layer assembled into colloidal molecules by coalescence of the wetting layer. Driven by surface energy, a liquid droplet on which the solid spheres are attached is formed. Subsequent polymerization of the liquid yields a wide variety of colloidal molecules as well as colloidosomes with tunable patchiness. Precise control over the topology of the particles has been achieved by changing the amount and nature of the swelling monomer as well as the wetting angle between the liquid and the seed particles. The overall cluster size can be controlled by the seed size as well as the swelling ratio. Use of different swelling monomers and/or particles allows for chemical diversity of the patches and the center. For low swelling ratios assemblies of small numbers of seeds resemble clusters that minimize the second moment of the mass distribution. Assemblies comprised of a large number of colloids are similar to colloidosomes exhibiting elastic strain relief by scar formation.

Introduction

Anisotropic particles that resemble molecules or have an integrated patchiness are of great interest in the field of colloid and materials science.^{1–4} They may be used as basic building blocks for hierarchical self-assembly,⁵ which is expected to facilitate and expand the range of possible colloidal structures such as clusters^{1,6,7} and liquid⁸ and crystal⁷ phases. They are likely candidates to succeed in the search for new materials with custom-made properties as they may mimic molecular self-assembly through shape and directional interactions.^{7,9,10}

Different methods are known to create colloidal molecules as well as patchy particles. Colloidal clusters can be made in a controlled way by evaporating toluene droplets in water containing colloids in the oil phase.¹¹ Upon evaporation, the capillary forces pack the colloids into clusters whose topology

only depends on the number of spheres they contain. The cluster structures were found to minimize the second moment of the mass distribution.¹³ Addition of a second type of smaller colloids to the droplets created binary colloidal clusters. The surrounding smaller colloids did not affect the configurations of the larger colloids.¹⁴ However, the number of small colloidal particles per cluster cannot be controlled in the emulsification step, resulting in polydisperse particles. Sonication UV-curable oil drops with adsorbed colloidal particles led to similar clusters with a central body comprised not of colloids but of polymerizable oil.¹⁵ Again, due to the emulsification step this approach does not provide control over the size of the center. The polydisperse shapes are a major drawback for model systems where monodisperse colloids with controlled shape and patchiness are required. Here we take a different approach to make colloidal molecules by starting from colloidal particles with liquid protrusions. This new method provides unique control over the obtained colloidal shapes.

Sheu et al.¹⁶ found that heating monomer-swollen cross-linked polystyrene spheres of a few micrometer causes phase separation of the monomer from the seed particle in the form of an aspherical protrusion from the particle. Covering the seed particle surface with a hydrophilic layer of vinyl acetate or

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acrylic acid allowed Mock et al.¹⁷ to extend this technique to smaller colloids of about 250 nm.

Here, we show that delaying the polymerization of the liquid protrusions leads to coalescence of the droplets upon collision, thereby creating colloidal molecules as well as colloidosomes in a simple one-step synthesis. Our new technique allows for tuning the topology from colloidal clusters to patchy particles via adjustment of the swelling ratio and hydrophilicity of the particle surface. This uniquely provides precise control over the shape and patchiness of the resulting particles. We demonstrate the generality of the method by conducting the synthesis both for polystyrene and for poly(methyl methacrylate) and by using different swelling monomers.

Synthesis of Colloidal Molecules

Cross-linked seed particles of different materials and sizes were synthesized as follows (for details see the Supporting Information): Monodisperse cross-linked (3%, w/w, divinylbenzene) polystyrene spheres (CPSs) were prepared using an emulsion polymerization procedure described previously.¹⁷ The resulting colloidal CPS had a size of 113 nm in radius (measured by transmission electron microscopy (TEM)) at a weight fraction of 7% (w/w) in aqueous solution. A part of the CPS suspension was consequently coated with vinyl acetate (surface coverage 3.56×10^{-21} g/nm²) to increase the hydrophilicity of the surface. The obtained CPS particles of 111 nm radius (measured by TEM) had a polydispersity of 2.5% and weight fraction of 2.6% (w/w) in aqueous solution. Further, monodisperse cross-linked (1%, w/w, ethylene glycol dimethacrylate (EGDMA)) poly(methyl methacrylate) (PMMA) spheres were prepared using a surfactant-free emulsion polymerization procedure according to a modified procedure of Paquet et al.¹⁸ The PMMA spheres were made from a mixture of methyl methacrylate (MM) and methacrylic acid (MA) in varying weight ratios where 90:10 proved to be the optimal ratio for formation of colloidal molecules. The resulting seed particles measured 220 nm in radius by scanning electron microscopy (SEM). Furthermore, commercially available sulfated 1.88 μ m polystyrene spheres, cross-linked with 5% divinylbenzene, were ordered from Magsphere Co. and used at 3% (w/w) concentrations for synthesis of colloidal molecules as well.

For each of the experiments with CPS seeds varying volumes of the seed suspensions were added to a glass flask equipped with a magnetic PTFE-coated stir bar. We define the amount of monomer, m_{monomer} , added to the suspension divided by the polymer mass present in the seed solution as the swelling ratio $S = m_{\text{monomer}}/m_{\text{seed polymer}}$. Additionally, 1% (w/w) SDS was added to the 1.88 μ m CPS samples. All samples were stirred vigorously during swelling for about 1–2 days and subsequently placed in an 80 °C oil bath. Heating causes phase separation of the monomer taken up by the cross-linked polymer network, resulting in the formation of a droplet on the colloidal surface.^{17,19,20} The hydrophilicity of the surface determines the wetting angle between the monomer and the colloidal surface. The less favorable it is for the monomer to wet the surface, the more aspherical the protrusion is to, ultimately, the extent of forming a separate droplet.

For CPS seed particles 222 nm in size we have never observed more than one protrusion on the particles. For the larger colloidal particles of 1.88 μ m we sometimes found secondary protrusions, which are significantly smaller than the primary protrusion. However, they were only present if polymerization was induced

after short coalescence times. The formation of more than one protrusion is an unfavorable state in terms of surface energy, and protrusions on the surface of one seed particle coalesce over time. We expect that coalescence of protrusions on larger seed particles takes place on a longer time scale compared to that of the smaller particles due to their larger diameter.

After the formation of a droplet on the colloid surface the samples were taken out of the oil bath and allowed to stir for several days. During this period colloidal molecules were formed. Subsequent polymerization was carried out at 80 °C by addition of hydroquinone (0.75 mM, 99% purity, Riedel), a water-soluble inhibitor, and azobisisobutyronitrile (0.94 mg of AIBN dissolved in 0.046 mL of styrene/mL of seed suspension) after heating for about 1 h. Polymerization was allowed to continue for 24 h. The syntheses typically yielded about 10% dimers and another 12% higher multimers after a coalescence time of 24 h.

For the formation of PMMA colloidal molecules a similar procedure was followed with a shorter clustering time. A 250 mL round-bottom flask equipped with a PTFE-coated stir bar and a reflux condenser was used. A 60 mL volume of a diluted (2.5%, v/v) and washed seed dispersion in water was added to the flask along with 0.01 g of AIBN. The flask was put in a thermostated oil bath at 80 °C and allowed to reach the bath temperature in 30 min. Then a 24.44 g MM/MA mixture (10%, w/w, MA), 0.1123 g of EGDMA, 71.1 μ L of DDM, and 0.1805 g of AIBN were added dropwise at a rate of 1 drop every 3 s under vigorous stirring. When the monomer addition was complete (typically 30 min), the reaction was allowed to proceed for another 2 h. The coagulum that formed was removed, and the remaining particles were cleaned by centrifugation and redispersion in deionized water.

In the case of PMMA seed particle protrusions were not observed, but the particles grew from a 220 to 335 nm radius. Small clusters formed if the monomer was a mixture of MM and MA containing at least 5% MA. The number as well as the size of the clusters increased with the MA percentage. Also a higher percentage of MA in the seed particles favored cluster formation. We found that 10% MA in both the seed and the swelling monomer was a suitable value to obtain clusters in good yield: about 16% dimers and 16% higher multimers were found.

From the formation mechanism it is expected that the distribution of multimers shifts to higher cluster sizes, N , the longer the coalescence is allowed to continue. This means that there is no unique distribution of clusters as it depends on the rate of formation. In the beginning mainly monomers, dimers, and trimers are expected, whereas at later stages larger clusters should prevail.

Polymerized samples were imaged using a scanning electron microscope (SEM XL FEG 30). The PS and PMMA particles were sputter coated with platinum/palladium and gold, respectively, prior to imaging. Light microscopy was performed with a Zeiss Axioplan using an oil immersion lens (NA = 1.4, 100 \times magnification). Pictures were captured with a Basler scout camera.

Results and Discussion

Topology of the Clusters. Each batch of colloidal particles made by this method contained a distinct variety of colloidal molecules comprised of different numbers of seed spheres. They are formed by merging of the liquid droplet upon collision as is shown schematically in Figure 1. The size of the protrusion can be chosen by the wetting properties of the seeds and by the swelling ratio, yielding colloidal molecules that ranged from clusterlike particles to patchy spheres. A representative example of colloidal molecules ($N = 1-9$) made from vinyl acetate-coated CPSs swollen with styrene ($S = 3.4$) is shown in Figure 2. In this case a distinct protrusion was present as can be seen for the case $N = 1$. Also, each cluster of N seeds has a unique central body with a volume roughly equal to N times the protrusion volume. In the case of PMMA seeds, a protrusion or a central droplet was not observed while the particles had

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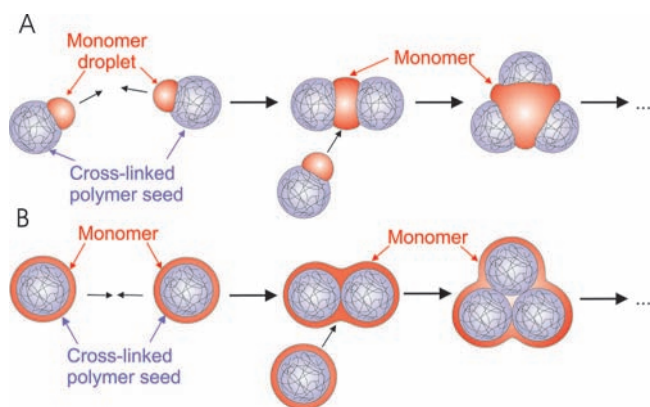


Figure 1. Schematic of merging of (A) liquid protrusions or (B) wetting layers, yielding colloidal molecules.

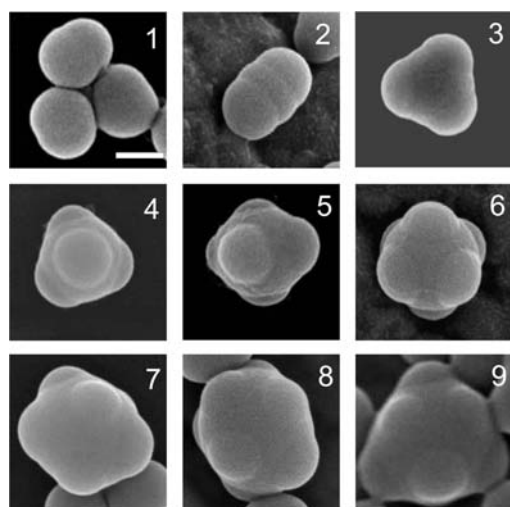


Figure 2. Scanning electron micrographs of colloidal molecules for $N = 1$ to $N = 9$ created by merging of liquid protrusions (vinyl acetate-coated polystyrene spheres with $R_{\text{seed}} = 111$ nm used as seed particles, swelling ratio 3.4, scale bar 200 nm).

grown significantly. Clusters were formed nonetheless as is shown in Figure S2 in the Supporting Information for $N = 1-9$. From these images it is apparent that clusters have become enveloped in an outer skin. Thus, we conclude that the PMMA seeds cluster due to merging of a wetting layer of monomer covering the whole seed surface.

Interestingly, all colloids with a given number of seed particles have identical geometry, supporting the idea of minimization of the second moment of the mass distribution, as will be discussed in the next section. The particles could be separated by density gradient centrifugation (Figure S1, Supporting Information). Spherical clusters containing a large number of spheres on the surface ($N \approx 10^2-10^4$) are known as colloidosomes and were found up to a size of $14 \mu\text{m}$ for high swelling ratios.

The unpolymerized clusters could be observed by light microscopy using larger, $1.88 \mu\text{m}$, styrene-swollen ($S = 3$) and heated polystyrene spheres as shown in Figure 3. They exhibit the same colloidal clusters as CPS seeds 222 nm in size (Figure 2). This further shows that the technique is not restricted to a specific seed size.

Control of Particle Anisotropy via the Swelling Ratio. A facile way to influence the topology of the resulting colloids is the swelling ratio. A higher swelling ratio results in a larger liquid

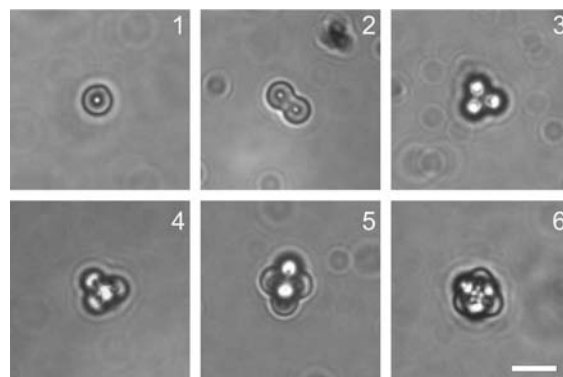


Figure 3. Light microscope images of colloidal molecules for $N = 1$ to $N = 6$ (CPS seeds with a diameter of $1.88 \mu\text{m}$, swelling monomer styrene ($S = 3.2$), scale bar $5 \mu\text{m}$).

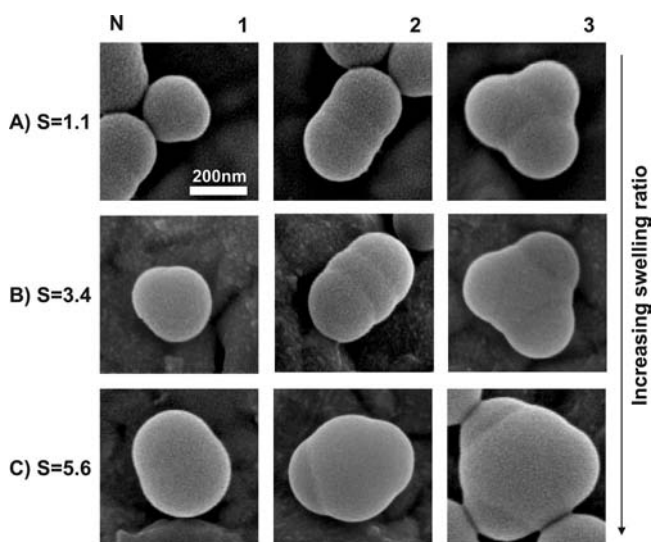


Figure 4. Swelling vinyl acetate-coated polystyrene spheres of $R_{\text{seed}} = 111$ nm with different amounts of styrene changes the geometry of the resulting multimers. SEM pictures show clusters of $N = 1-3$ polystyrene spheres with swelling ratios of 1.1, 3.4, and 5.6. The scale bar is 200 nm.

protrusion after heating as can be seen from the SEM pictures of polymerized colloids for $N = 1$ in Figure 4. Note that for swelling ratios $S = 1.1$ and $S = 3.4$ (Figure 4A,B) the seed particle is larger than the protrusion, whereas for $S = 5.6$ (Figure 4C) the protrusion is larger than the seed sphere. After merging, the protrusion volume determines the size of the liquid center of the resulting colloids (Figure 4, $N = 2, 3$). With an increasing swelling ratio the relative size of the seed particle compared to the droplet shrinks, gradually changing the shape of the colloidal molecules from clusterlike to spheres with patches.

Manoharan et al. created colloidal clusters by evaporating toluene droplets in water with colloids adsorbed to the oil–water interface.^{11,12} Upon evaporation the capillary forces pack the colloids into clusters identical for a given number of spheres and that minimize the second moment of the mass distribution, $M_2 = \sum_{i=1}^N |\vec{r}_i - \vec{r}_0|^2$, where \vec{r}_i is the center coordinate of the i th sphere and \vec{r}_0 is the center of mass of the cluster.¹³ In our colloidal system spheres are attached to an oil–water interface as well. At low swelling ratios interfacial tension compresses the spheres to form clusters partially immersed in a liquid droplet. This may be comparable to the late stage of droplet evaporation. Despite the extra oil contained in the center, this

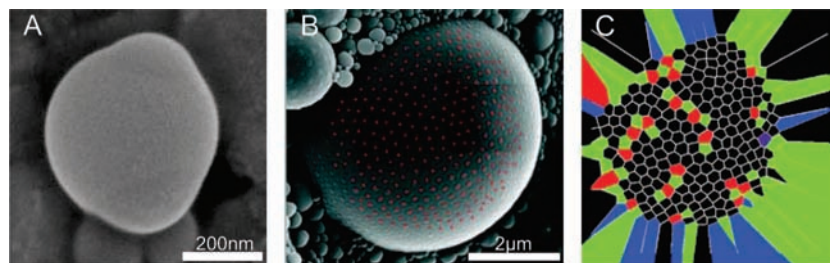


Figure 5. Short-range order is visible at a high swelling ratio. Scanning electron micrographs: (A) dimer for a swelling ratio of $S = 7.9$; (B) colloidosome. (C) Voronoi plot of the seed distribution of the colloidosome in (B). Excess dislocations in chains of 5–7–5–7... defects are visible and known to reduce elastic strain.

explains why we still find the same arrangement of seed spheres inside the liquid center as Manoharan et al.¹¹ Defining the center of the sphere as a vertex of a polyhedron, we find the following for the lowest order configurations (Figure 2): line segment ($N = 2$), triangle ($N = 3$), tetrahedron ($N = 4$), triangular dipyramid ($N = 5$), octahedron ($N = 6$), pentagonal dipyramid ($N = 7$), snub diphennoid ($N = 8$), and triaugmented triangular prism ($N = 9$).

Seed Arrangement on the Interface. For high swelling ratios the seed spheres are not constrained inside the liquid droplet. It is therefore expected that the seed spheres do not pack in a way as to minimize the second moment. Instead surface packing constraints as well as screened electrostatic repulsion between the charge-stabilized spheres determine the arrangement. For example, in dimers at a high swelling ratio ($S = 7.9$) the seeds are not aligned in a straight line but form an angle with respect to the center of the colloid (Figure 5A), which resembles colloidal water.²¹ It is currently being investigated whether the angle comprised by the seed particles is unique for a specific swelling ratio and fixed number of seeds. Similarly, colloidosomes exhibit short, but no long-range order as shown in Figure 5B,C). Short-range order can be quantified by determining the seed positions on the interface. The nearest neighbor angle distribution of the spheres in the center of the 2D projection clearly shows six peaks with an average distance of $60 \pm 3.6^\circ$ (see Figure S3, Supporting Information). Furthermore, besides single 5-fold disclinations, there are chains of excess dislocations in the form of 5–7–5–7–...–5 defects visible in the Voronoi plots as is expected for systems with $R_{\text{cluster}}/(\text{interparticle spacing}) > 5$ (Figure 5C).²³ These scars are known to relieve elastic strain on the surface by forming high-angle grain boundaries.²²

Colloidosome Size. Furthermore, qualitative observations were made with respect to the maximum size of the colloidal clusters. Small liquid volumes limit the number of seed particles that can attach to the interface. For low swelling ratios mainly monomers, dimers, and trimers were found. On the other hand, large liquid protrusions can form colloidosomes comprised of many seeds. Even though no upper limit in size could yet be uniquely determined, we expect this process to be self-sharpening. Considering that the bare surface created by the addition of a seed particle to an existing cluster decreases for large N , the system cannot grow beyond a critical size, N_{max} . The maximum number of seeds at which no additional seeds

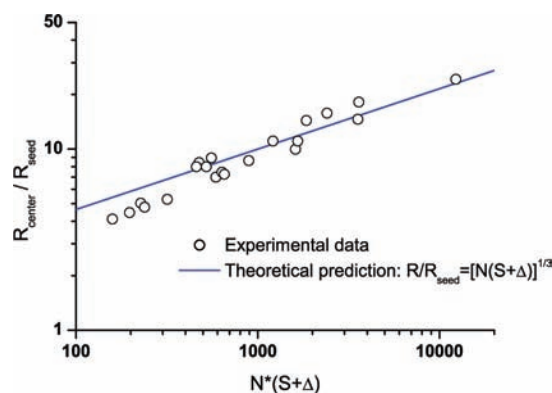


Figure 6. The colloidosome size can be described as a function of the swelling ratio, S , and the number of swollen seeds, N , by $R_{\text{center}}/R_{\text{seed}} = [N(S + \Delta)]^{1/3}$, where $\Delta = 1/4(2 - z)(1 + z)^2$. Experimental data shown are for colloidosomes of vinyl acetate-coated polystyrene spheres of $R_{\text{seed}} = 111$ nm and $z = 0.16$.

can be integrated is given by $N_{\text{max}} = 4\sigma^3(z^2 - 1)^{-3}(2 + 4S - 3z + z^3)^2$, where σ is the maximum surface coverage, defined as the surface area occupied by seed particles divided by the total surface area, and z is the immersion depth of the seed particles into the liquid droplet normalized to the seed radius, R_{seed} . For large system sizes straightforward geometry yields the radius of the colloidosome as a function of the swelling ratio S and number of integrated seeds, N , to

$$R_{\text{center}} \approx R_{\text{seed}} N^{1/3} \left[S + \frac{1}{4}(2 - z)(1 + z)^2 \right]^{1/3}$$

Experimental data for vinyl acetate-coated CPS colloidosomes ($z = 0.16$) are in good agreement with this simplistic model (Figure 6), despite the fact that the nominal swelling volume calculated from the swelling ratio does not equal the actual volume. However, in the course of the experiment monomer taken up by the liquid center due to diffusion compensates for this. The good quality of the fit is another indication that the colloids form by merging of liquid protrusions.

Control of Particle Anisotropy via the Wetting Angle. The seed particles determine the resulting patch size both by their own diameter and by the wetting angle between the liquid protrusion, the aqueous phase, and the polymer seed particle. Adjustment of either the liquid or the polymer wetting properties therefore affects the shape of the colloidal molecules. This can be done by use of different seed particles, coatings, swelling monomers and different amounts of surfactant. Both acrylic acid and vinyl acetate coatings are known to render polystyrene seeds more hydrophilic, leading to more pronounced protrusions.¹⁷ The same can be observed for the synthesis of colloidal molecules. Uncoated polystyrene spheres exhibit a smaller

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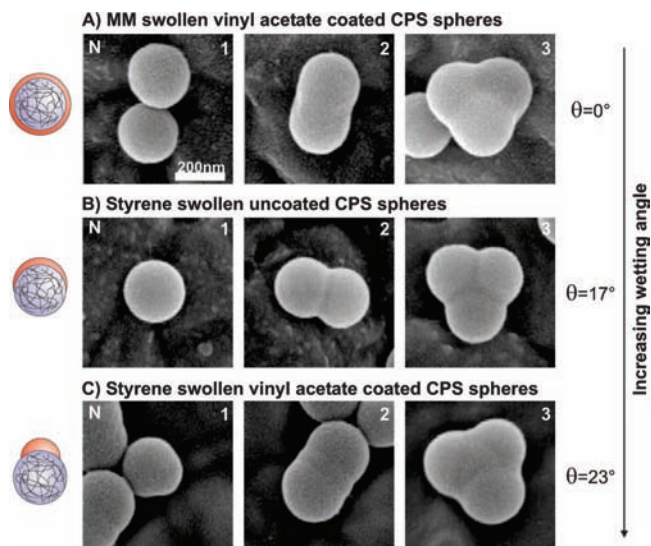


Figure 7. A larger wetting angle creates colloidal molecules with a more pronounced delineation between the liquid center and the seed particles. The wetting angle increases from top to bottom, using a hydrophilic monomer, methyl methacrylate ($S = 3.3$), and styrene on uncoated and vinyl acetate-coated polystyrene spheres ($S = 1.1$). The scale bar is 200 nm.

wetting angle of $\theta = 17 \pm 3^\circ$ (Figure 7B) than vinyl acetate-coated polystyrene spheres when swollen with styrene (Figure 7C), which have a wetting angle of $\theta = 23 \pm 2^\circ$. Even this small difference in wetting angle leads to a clear influence on the shape of the resulting colloidal particles. Different swelling monomers also lead to different wetting angles between the droplet, seed particle, and aqueous phase, as can be seen in Figure 7. Complete wetting, i.e., $\theta = 0^\circ$, of vinyl acetate-coated polystyrene spheres can be achieved by swelling the seeds with a more hydrophilic monomer, methyl methacrylate, leading to poly(methyl methacrylate)-covered CPS clusters (Figure 7A). The latter case leads to clusters that look identical to the one

made from PMMA seeds (Figure S2, Supporting Information), where no protrusions were formed because of a complete wetting of the MM/MA mixture on the PMMA particle.

An advantage of using PMMA as seeds is that those particles can be both refractive index and density matched, which makes them suitable for confocal microscopy studies on concentrated suspensions. Use of different monomers to swell the seed particles may also give rise to different chemical properties of the colloidal body and the patches. This could be used to create spheres with sticky patches.²⁰

Conclusions

We have shown that colloids with liquid protrusions spontaneously merge, forming colloidal molecules that range from clusterlike particles up to the size of colloidosomes. The presented technique uniquely allows for tuning of the colloidal shape via the size of the seed particles, swelling ratio, and hydrophilicity of the polystyrene or poly(methyl methacrylate) surface. Chemical properties can be altered by use of different monomers and subsequent modification. Combining all of the above, a wide variety of colloidal molecules with varying patchiness were obtained. A simple model describes the colloidosome size as a function of the swelling ratio and number of seeds.

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Supporting Information Available: Experimental details and more information on density gradient centrifugation, PMMA colloidal molecules, and seed arrangement on colloidosomes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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