Colloidal molecules with well-controlled bond angles

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We present a straightforward technique for the synthesis of asymmetric colloidal molecules with uniform and well-controlled bond angles. The new method makes use of coalescence of liquid protrusions on polystyrene spheres. The bond angle between the seed particles and central sphere can be chosen as desired by adjusting the size of the liquid protrusion. The surprising uniformity of the colloidal molecules comprised of small numbers of seed particles is proven by comparison with 3D models. Considering different origins for this uniformity we conclude that the asymmetric and unique shape is induced by aggregation inside the liquid droplets upon polymerization. This technique offers a new and simple way to make a wide variety of asymmetric colloidal molecules in a reproducible and controlled fashion.

The prospect of using colloidal particles as building blocks for colloid and material science has been a driving force in extending colloidal syntheses to a variety of shapes and materials. Colloidal particles with rationally designed topologies may lead to precise control over the macroscopic assemblies of the particles. Specifically, colloidal particles with shapes resembling space-filling models of molecules are expected to exhibit complex behavior similarly to molecules or even beyond. Taking the analogy between colloidal spheres and atoms further, such colloids are termed colloidal molecules. Simulations have predicted that these are likely candidates for forming intriguing new fluid and crystal phases as well as finite superstructures such as rings, shells and chains. These crystals may form a new category of materials with novel properties, such as optical band gaps.

Several methods have been proposed to create highly symmetric colloidal molecules as well as simple asymmetric shapes such as snowman particles. To date only few methods either based on emulsification or aggregation have been reported to produce more complex asymmetric arrangements. Due to the lack in control over the size and composition of particle containing emulsion droplets it is still prohibitively difficult to obtain uniform clusters from emulsification methods. Snyder et al. recently obtained colloidal trimers from different materials by a multi-step method of aggregation and partial polymer coating.

In this Communication we introduce a new one-step technique for producing uniform, asymmetric colloidal molecules such as colloidal water and ammonia by coalescence of liquid protrusions attached to polystyrene particles.

Raising the temperature of monomer-swollen crosslinked polymer particles causes phase separation of the monomer from the polymer seed in form of a liquid protrusion. Subsequently, the seed colloids can bind by fusion of the attached liquid protrusions to form colloidal molecules (Fig. 1a). The wetting angle between the seed particles and the monomer phase as well as the extent of the swelling provides precise control over the shape and size of the protrusions and hence, the final topologies of the colloidal molecules. In previous experiments the volume of the liquid protrusions was small, restricting the movement of the seed particles inside the fused protrusions. This resulted in highly symmetric clusters as well as large droplets with many attached seed particles.

In our present work we chose a high degree of swelling which induced liquid protrusions larger than the original seed particles (see N = 1, Fig. 1b). Fusion of such protrusions leads to large droplets with attached seed particles that are expected to move freely over the surface. Surprisingly, we observed well-defined seed particle positions for assemblies of small numbers of seed particles after polymerization. For each assembly of N seed particles we found one type of asymmetric colloidal molecule with a unique bond angle. Representative examples of the obtained colloids from cross-linked polystyrene spheres (CPS) are shown in Fig. 1b. Clusters comprised of two CPS

![Fig. 1](https://www.rsc.org/softmatter/softmatter_2009/5/3823-3826/3823)

(a) Crosslinked polystyrene colloids (CPS) with liquid protrusions self-assemble into colloidal molecules by fusion of the liquid protrusions. The process is driven by minimization of the surface energy between the protrusions and the water phase. If the seed particles are not restricted inside the fused protrusions, they are expected to be randomly distributed over the surface. (b) After polymerization we observe colloidal molecules with a controlled bond angle by scanning electron microscopy. Assemblies consisting of two and three seed particles resemble water (N = 2) and ammonia-like (N = 3) molecules, respectively.
seed particles resembled water molecules, whereas three seed particles formed colloids resembling ammonia molecules.

To elucidate that the obtained colloidal particles are exhibiting a single, unique shape we employed separation of the assemblies by density gradient centrifugation (DGC) and imaged the obtained fractions by scanning electron microscopy (SEM). The fraction containing dimers is shown in Fig. 2a (further images, see Fig. S1–S4, ESI†). We modeled the shape of the water-like arrangements as shown in Fig. 3a. By only rotating this model, that means changing the viewpoint, we could reproduce all colloids observed within one DGC band, convincing us that the obtained colloidal particles are exhibiting an unique shape (Fig. 2b).

The 3D models were constructed according to the wetting angle, $\theta$, and the radius of the seed particles, $r$, and the droplet, $R$ (Fig. 3c). Agreement between model and experiment required slightly interpenetrating seed particles as shown in Fig. 3a. Similarly, for trimer clusters the seed particles partially overlapped inside the center (Fig. 3b) forming a unilateral triangle immersed in the protrusion body. In both cases the particles interpenetrated by about 18% of their original size. This ‘soft’ behavior can be understood considering that the polymer network of the seeds was only cross-linked by 3% w/w divinylbenzene. The bond angle $\alpha$ of a particle with two seeds can be calculated, via $\sin\alpha = \sin^{-1}(r/c) = \sin^{-1}(r/(r^2 + R^2 - 2rr\cos\theta))$, as seen in Fig. 3c. $r$ is half the distance between two seed centers and $c$ the distance between any seed center and the center of the fused protrusion droplet. In analogy, we define a bond angle $\beta$ for colloidal molecules with three seeds as the angle between the center of the coalesced protrusions and any two seed particles. As shown in Fig. S2 and S3 (ESI†) all colloidal arrangements consisting of two and three seed particles could be described well with those models.

Variation of the amount of styrene allows for adjustment of the volume of the protrusions and therefore the radius of the central body of the colloidal molecules. We define the swelling ratio as the volume of the fused protrusions over the volume of one seed particle. Since the particles were always found to be overlapping inside the center an increased liquid volume changes the angle $\alpha$ (Fig. 3c) between the centers of the seed particles and the center of the liquid droplet. As shown in Fig. 4, increasing the actual swelling ratio, $S$, (volume of the protrusion per volume of seed particle) from $S = 0.52$ (top row) to $S = 1.70$ (bottom row) changes the dimer angle from $\alpha = 180^\circ$ to $\alpha = 100^\circ$. Similarly, for trimer particles the angle between any two seed particles and the liquid center changes from $\beta = 180^\circ$ to $\beta = 80^\circ$ (Fig. 4, right columns). As only one unique angle is found within each batch of particles this procedure provides a unique opportunity to create colloidal “water” (dimer) and colloidal “ammonia” (trimer) at any desired angle. The smallest obtainable angle is only restricted by the maximum volume of monomer that can be taken up by the seed particles.

To demonstrate that the shape can further be influenced by the wetting angle between the seeds and the fused protrusions, we used CPS with a wetting angle of $\theta = 30^\circ$ as shown in the last row of Fig. 4. All other pictures show CPS seeds with a wetting angle of $\theta = 23^\circ$. The larger wetting angle clearly increases the extent to which the seed

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**Fig. 2** (a) Scanning electron micrograph of water-like colloids in the second band after density gradient centrifugation. (b) Turning a 3D model constructed from the EM image reproduces all observed views of the colloidal particles in the SEM image indicating that the assembly produces uniform colloidal particles with a fixed bond angle of 139°.

**Fig. 3** Transparent 3D models of the (a) dimers and (b) trimers showing that the white seed particles are interpenetrating each other by 18% inside the protrusion body (depicted in grey). (c) A schematic representation of a dimer. The bond angle $\alpha$ can be calculated from the wetting angle $\theta$ and the seed and center radius, $r$ and $R$, respectively.

**Fig. 4** Increasing the volume of the liquid protrusions with respect to the seed volume in the system decreases the bond angle between the seed particles and the center. For a swelling ratio of 0.52 (top row) we find bond angles of $\alpha = 180^\circ$ and $\beta = 180^\circ$ for assemblies comprising two and three seed particles, respectively. For a swelling ratio of 1.7 (bottom row) the bond angles change to $\alpha = 100^\circ$ for assemblies of two and $\beta = 80^\circ$ for assemblies of three seed particles.
particles protrude from the droplet, yielding an even richer variety in shapes. At larger wetting angles, asymmetric assemblies can be obtained even with small protrusions, as long as the seed particles are not restricted to move inside the droplet. The particles with a higher wetting angle were interpenetrating by only 11% compared to 18% for the ones with a low wetting angle.

To elucidate the underlying physical mechanism of local attraction between the seed particles we consider different possible contributions. Charged polystyrene particles adsorbed at a styrene water interface are accompanied by an asymmetric ion cloud that forms a dipole moment perpendicular to the interface.19 Straightforward calculations reveal that two dipoles attached to a spherical surface have minimum repulsive interaction energy at maximum separation. Experimental observations do not agree with this seed arrangement and we therefore conclude that dipole–dipole interactions are not playing a major role.

If van der Waals forces caused attraction between the particles, aggregation is expected to occur upon transfer from water to styrene. We washed a small quantity of vinyl acetate coated polystyrene particles twice with ethanol and styrene. Immediately after preparation the sample looked macroscopically stable and remained so for over three months without precipitation. Transmission electron micrographs of dried samples do not show aggregation in three dimensions but two-dimensional layers of seed particles (ESI†, Fig. S4). Dynamic light scattering measurements yielded a size of $R = 195 \pm 32\,\text{nm}$, and proved furthermore that only swelling, but not aggregation occurred in styrene. Steric stabilization provided by vinyl-acetate polymers grafted to the interface could explain this behavior. Van der Waals forces are thus not responsible for the observed attraction between seed particles.

Another possible candidate is depletion interaction. Upon polymerization polymers are formed inside the droplet which could induce attractive interactions by depletion forces. This mechanism has been seen in other systems such as Pickering emulsions18 and requires that diffusion of colloids on the droplet surface happens on a much faster time scale than polymerization of the whole droplet. To get an estimate of the time it takes a particle to diffuse from one side of the droplet to the other, we simplify the system in the following way: the seed particle can diffuse on a two dimensional spherical surface of radius $R$ with a diffusion coefficient assumed to be given by $D = k_B T/(6\pi \eta R)$. Here, $\eta = 3.75 \times 10^{-4}\,\text{Pa}\,s$ is the viscosity of styrene at $80^\circ\text{C}$ as the seeds are mainly immersed into styrene. $k_B$ is the Boltzmann constant and $T$ the temperature during synthesis. We then obtain for the diffusion time from one side of the sphere to the other: $t_d = \sqrt{2}(4D) = 3(\pi R^2 \eta \eta / (2k_B T))$. For dimer and trimer particles as shown in the third row of Fig. 4, this yields diffusion times of $t_d(R = 250\,\text{nm}) = 68\,\text{ms}$ and $t_d(R = 320\,\text{nm}) = 0.11\,\text{s}$. However, for large droplets with tens to hundreds of adsorbed seed particles, we find that the seed particles aggregate locally, but do not maximize the number of contacts on a global length scale (Fig. 5). This indicates that the seed particles can indeed move freely over the droplet surface before polymerization. However, diffusion across such a droplet takes an estimated $t_d(R = 2\,\mu\text{m}) = 4.36\,\text{s}$ and may explain why it is not possible for the seed particles to rearrange quickly enough upon polymerization (for intermediate droplet sizes, see Fig. S6, ESI†). Polymerization thus happens on the timescale on the order of seconds: too fast for rearrangement of the spheres on large droplets, but slow enough for the seeds in small assemblies to respond to depletion attraction induced by the formation of polymers.

In conclusion, we have presented a new and facile synthesis method for preparing colloidal molecules with well-controlled bond angles. The choice of the size of the liquid protrusion and the wetting angle allows for uniform particles with a bond-angle “made to order”. Utilizing polymerization induced depletion interaction we find reproducible shapes for small assemblies. The technique can be easily extended to other seed polymers or swelling monomers due to its underlying generality,10,11,13 providing a simple method to produce asymmetric colloidal molecules for studying collective behavior as well as self-assembly.

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