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Uniform Nonspherical Colloidal Particles with Tunable Shapes**

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Colloidal particles are ubiquitous for a broad spectrum of applications. Many current applications require nonspherical particles. They have been used for modifying optical properties^[1] and as a building block for self-assembled biomaterials.^[2] They are also beneficial for controlling suspension rheology^[3] and for engineering colloidal composites.^[4] In general, synthesizing uniform nonspherical particles is difficult because surface tension favors spherical shapes in overall length scales. This limitation may be overcome with advanced techniques such as microfluidics^[5,6] and clusterization separations;^[7,8] these precision processes generally produce small yields, severely limiting their utility for practical applications. Recently, several methods that can produce nonspherical particles such as dimers^[9] and higher-order clusters^[10,11] have produced larger yields. These methods all rely on random coagulation of single particles or on the formation of clusters by using emulsification techniques. However, a common limitation of these synthesis techniques is that a single batch contains many particle types, requiring a sorting process to produce homogeneous samples, thus limiting the yield for any given sample type. Thus, there exists a need for flexible and robust techniques to generate nonspherical particles with well-defined shapes and high yields.

One method of controlling particle shapes is to use a controlled phase separation in the seeded polymerization technique. This technique can produce extremely high yields of uniform particles. In the typical technique, seed particles are first swollen with a polymerizable monomer-based solution, and subsequent polymerization induces phase separation.^[12–15] Depending on thermodynamic and kinetic factors, the phase separation results in a variety of particle shapes.^[13–16] Shapes of higher aspect ratio may be obtained by crosslinking the seed particles before the phase separation. The crosslinking makes the seed particles more elastic.^[17] The

elastic forces can impart greater directionality to the formation of the newly polymerizing phase. This suggests that seed particle crosslinking might be used to control the shapes of nonspherical particles.

In this Communication, we introduce a new seeded-polymerization technique that uses the crosslinking forces to synthesize a variety of uniform nonspherical particles in large synthesis scales. Our technique involves controlling the directionality of phase separations in the seeded-polymerization technique by manipulating the crosslinking density gradients of the seed particles. This enables us to generate a variety of particle shapes, including “rod”, “cone”, “triangle”, and “diamond” particles (Fig. 1). The uniform placement of the individual bulbs in nearly all of the particles in each batch is achieved solely by tuning the crosslinking properties of the seed particles.

To illustrate how crosslinking controls particle morphology, we compare the synthesis of two different types of trimer particles: “rods” and “triangles” (Fig. 1a and b, respectively). Rods and triangles both result from the seeded polymerization performed on dimers. The difference is the degree of crosslinking in the two bulbs of the seed dimer. Dimers that contain two bulbs with slightly different degrees of crosslinking become rods when swollen and polymerized. By contrast, dimers that contain two bulbs with equal crosslinking become triangle particles (Fig. 2).

This is demonstrated by a series of experiments in which we synthesized trimers from different types of dimers. First, we synthesized spherical crosslinked polystyrene (PS) particles from linear PS template particles by swelling them with styrene monomers containing a crosslinker, divinylbenzene (DVB). In this swelling step, step a, the concentration of DVB, $[DVB]_a$ was fixed at 1 vol % relative to the total monomers. After polymerizing the spherical particles, we performed another swelling step, step b, to produce dimers. In step b, $[DVB]_b$ was varied from 0.5 to 1.1 vol %. Polymerization after swelling step b resulted in symmetrical phase-separated PS dimers. The size and appearance of the dimers produced were identical for all samples. Finally, in step c, the dimers were again swollen with a similar mixture, and polymerized following the same procedure. This resulted in trimer particles of various shapes. The shape of the trimers depends only on $[DVB]_b$. High values of $[DVB]_b$ produced triangle particles, intermediate values of $[DVB]_b$ produced triple rod particles, and the lowest value of $[DVB]_b$ gave rise to snowman particles.

To understand this behavior, we examine how changing $[DVB]_b$ changes the internal network properties of the seed

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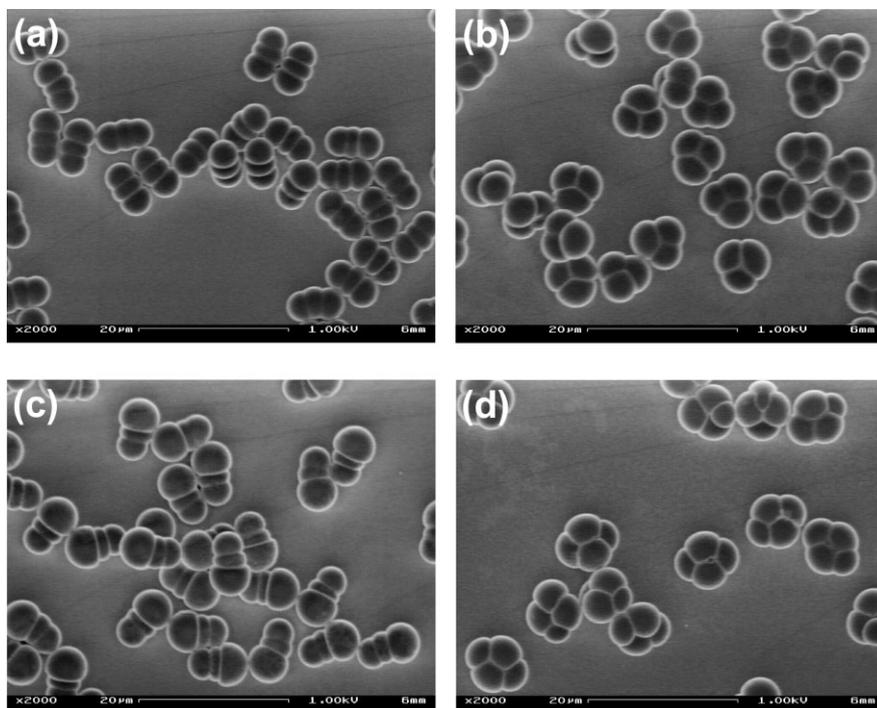


Figure 1. Synthesis of nonspherical particles. Scanning electron microscopy images of a) triple rod particles prepared at $[DVB]_b/[DVB]_a = 0.7$, b) triangle particles at $[DVB]_b/[DVB]_a = 1.1$, c) cone particles at $[DVB]_b/[DVB]_a = 0.7$, and d) diamond particles at $[DVB]_b/[DVB]_a = 1.1$. The diamond particles were made similarly to the triangle particles, but with 20% more total crosslinker.

dimers. We expect that the material added during swelling in step a resides mostly in one of the dimer bulbs, bulb a. The second bulb, bulb b, should contain mostly material added in swelling step b (Fig. 2a). Therefore, we expect the dimers to have crosslinking density gradients when $[DVB]_a \neq [DVB]_b$. Because such gradients are critical to understanding the morphology of the trimers, we confirmed their existence by using dimer-swelling experiments. This was accomplished by transferring the seed dimers to toluene. Because toluene is a good solvent for PS, it causes the polymer chains to uncoil. Thus, the particles swell until they reach an equilibrium size where the solvency of the polymers is balanced by the elastic stretching of the network. Because the elasticity of the network is proportional to its crosslinking density, it is possible to estimate the crosslinking density from the polymer volume fraction, ϕ , the ratio of the unswollen volume to the swollen volume. These principles are formalized by the theory of Flory and Rehner,^[18–20] which, for a perfect network, gives the crosslinking density to be

$$v = \frac{N_A}{V_1} [\ln(1 - \phi) + \phi + \chi\phi^2] / [\phi^{1/3} - \phi/2]$$

where, N_A is Avogadro's number and V_1 is the molar volume of the solvent. The polymer–solvent interaction parameter, χ for the crosslinked PS system can be estimated;^[21] $\chi = 0.431 - 0.311\phi - 0.036\phi^2$. These relations allow us to calculate the crosslinking densities, v_a and v_b of bulbs a and b from

images of the particles taken before and after swelling.

Measured values of v_a and v_b showed that when $[DVB]_b/[DVB]_a < 1$, bulb b is indeed less crosslinked than bulb a. As $[DVB]_b/[DVB]_a$ approaches unity, the crosslinking of bulb b approaches that of bulb a. This demonstrates that the gradient of crosslinking density, $\Delta v = v_a - v_b$ of the PS dimers is precisely tunable by changing the relative concentration of DVB added to form each bulb, as shown in Figure 3. Δv is the critical factor controlling the morphology of the trimers. In the symmetric case where Δv is small, bulb c grows perpendicularly to the line between bulb a and bulb b, finally forming a triangle particle. When Δv is slightly larger (ca. 15 mol m^{-3}), the placement of bulb c breaks symmetry and grows linearly adjacent to bulb b, thus forming a triple rod particle (Fig. 2). Between these critical values we obtain a mixture of the two particle types. For example, at $\Delta v \sim 10 \text{ mol m}^{-3}$, triple rods and triangles are produced simultaneously. When Δv is too large (ca. 37 mol m^{-3}), no

phase separation occurs in the final step because v_b is insufficient for generating the necessary elastic forces. We found that by tuning the synthesis conditions, we were able to cause particles in a given batch to be of one type. These findings demonstrate that we can achieve a high degree of control over the shapes of multibulb particles.

To elucidate the underlying physical mechanisms of this behavior, we performed optical microscopy. Two batches of monomer-swollen PS dimers were polymerized to yield triple rods ($\Delta v \sim 15.3 \text{ mol m}^{-3}$) and triangles ($\Delta v \sim 0.9 \text{ mol m}^{-3}$), while the phase-separation process was recorded with a digital camera (Fig. 4a). The movies revealed a remarkable difference in phase-separation kinetics: the new bulbs of the triple rods formed within ca. 48 s, while the new bulbs of the triangles required ca. 3 h (Fig. 4b). The difference in phase-separation time is likely related to the viscosity difference in swollen dimers. The swollen dimer that forms the triangle should have a higher viscosity due to its higher crosslinking density. Thus, the flow of monomers to form the third bulb is apparently slowed by the existing crosslinked network.

Using the insights gained from studying the formation of triple rod and triangle particles, we were able to produce additional particle shapes, including cones and diamonds, as shown in Figure 1c and d. The cones were produced similarly to triple rods, but with a higher volume of monomers in the final swelling stage. The diamonds were synthesized similarly to the triangle particles, but with higher values of $[DVB]_a$ and $[DVB]_b$ (1.2 and 1.32 vol %, respectively). The stronger elas-

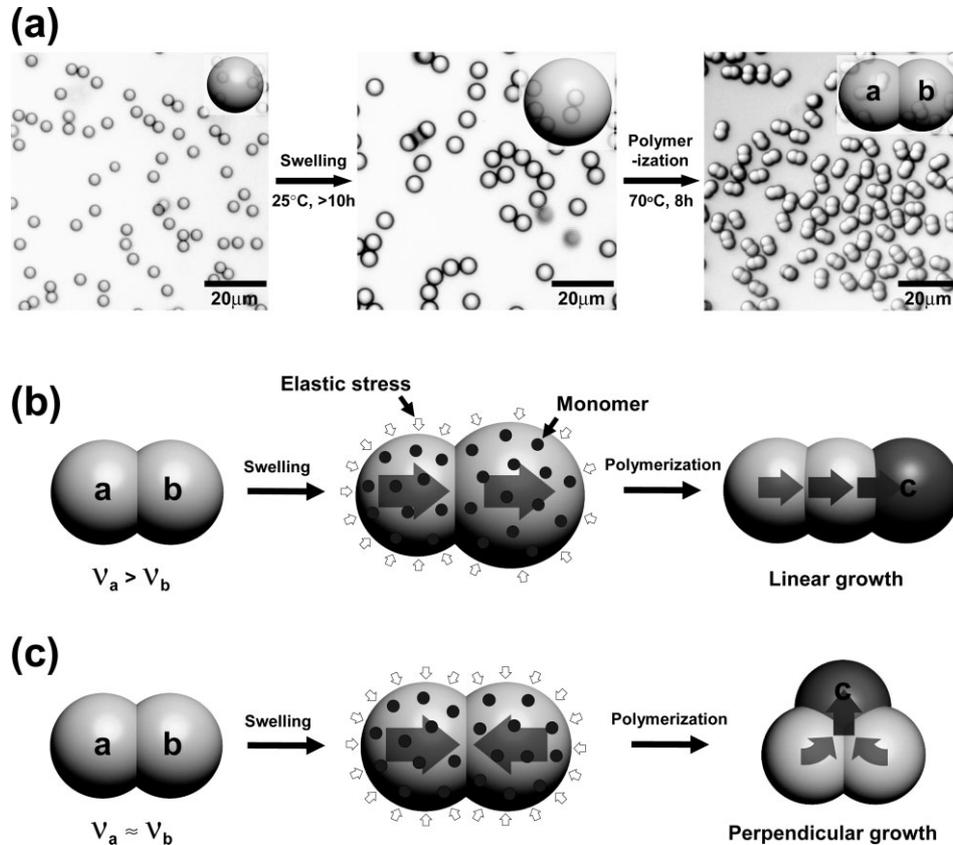


Figure 2. Control of phase-separation directions. a) Synthesis of uniform dimer seed particles by swelling and polymerizing spherical particles. Trimer particles were synthesized by performing an additional monomer-swelling and polymerization step on the dimers. b) Linear growth of bulb c when bulb a has a higher crosslinking density than bulb b. c) Perpendicular growth of bulb c when the crosslinking density of bulb a is equal to that of bulb b.

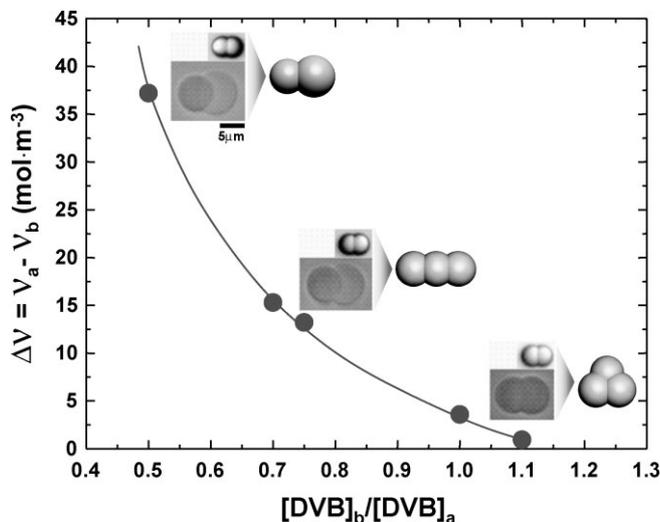


Figure 3. Quantitative measurement of the gradient of crosslinking density. The crosslinking density gradient, Δv can be tuned by changing the concentration of DVB added during each swelling step ($[DVB]_a$ and $[DVB]_b$). Δv were obtained by imaging the dimer particles before and after swelling in toluene. The three insets are the dimer particle images before (upper images) and after (lower images) swellings for $[DVB]_b/[DVB]_a = 1.1, 0.7$, and 0.5 . Although the unswollen dimers appear to be identical, their different network properties account for the dramatic difference in subsequent trimer morphology.

tic contraction gave rise to two new bulbs rather than one new bulb. The two new bulbs appeared opposite each other on the perpendicular axis of the dimer. This illustrates an important feature of our synthesis method: it allows us to synthesize colloid clusters, such as rods and diamonds, that would not be allowed in a drop clusterization process.^[7]

This approach for synthesizing nonspherical particles is not only very reproducible but also produces high yields. After polymerization, typical batches contain ca. 10^{10} particles mL⁻¹. These volumes can be easily scaled up; moreover, because no sorting is required, the yield of this technique is considerably higher than other methods.^[7–11] The ability to produce large quantities of uniform nonspherical particles enables the exploration of many new applications. For example, our synthesis technique allows us to experimentally compare the packing densities of particles of different shape.^[22,23] We carried out simple packing experiments with three particle types: spherical, triple rod, and triangle. The individual particle volumes, overall volume fractions, and dispersion volumes were maintained constant for all particle types (Fig. 5). As the particles sediment, differences in packing densities of the different particle types are readily apparent to the eye. The volume fraction of spherical particles reaches a packing density of $\varphi \approx 0.64$, close to the expected random close-packing value.^[24] Remarkably, however, we observe that the rods and tri-

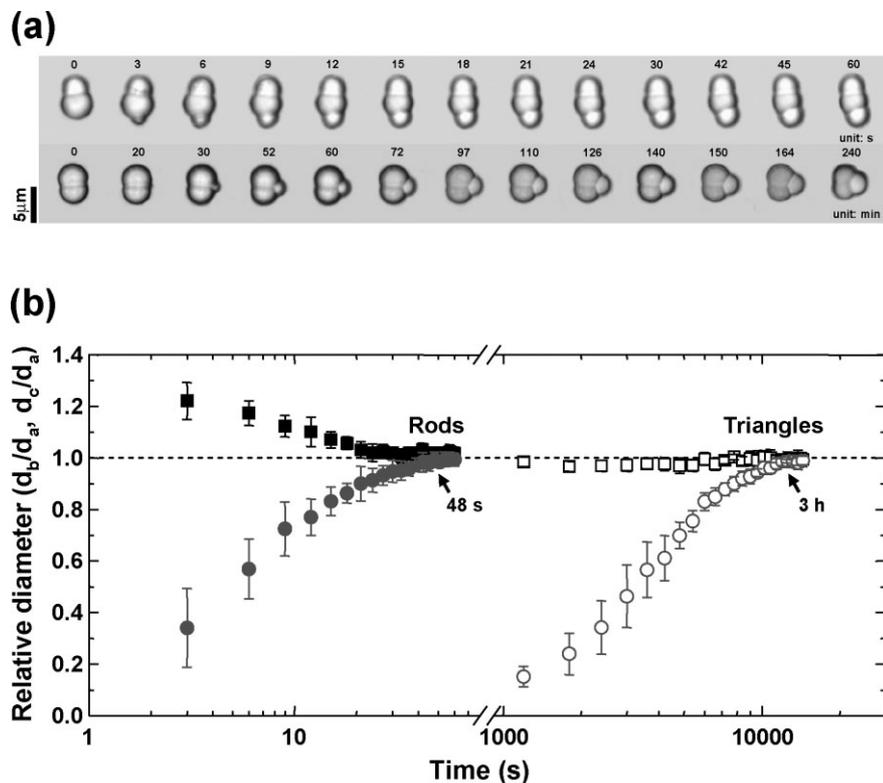


Figure 4. Particle growths depending on the gradient of crosslinking density. a) Time series of micrographs during the polymerization of triple rods (upper) and triangles (lower). b) The changes in the relative diameters of bulbs during polymerization of triple rods (closed symbols) and triangles (open symbols). Squares mark the diameter of bulb b relative to bulb a (d_b/d_a); circles mark the diameter of bulb c relative to bulb a (d_c/d_a). Time = 0 s corresponds to the appearance of the new phase.

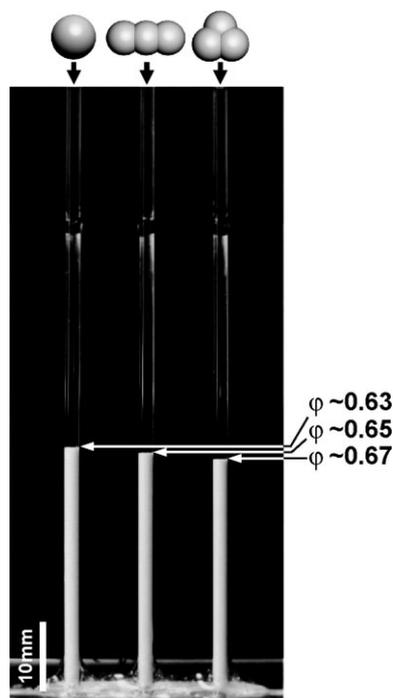


Figure 5. Packings of nonspherical particles. Sedimentation experiments demonstrate that triple rod and triangle particles pack more efficiently than spheres.

angles can pack more densely up to $\phi \approx 0.67$ (Fig. 5). This result is consistent with previous studies showing that nearly spherical ellipsoids pack more efficiently than spheres.^[2,3]

The key to our approach is that crosslinking density gradients can be used to overcome the effect of surface tension and provide reproducible directionality to phase separations. This precise control over phase-separation patterns allows us to obtain novel nonspherical particle shapes, and produces sufficient quantities to allow us to characterize their bulk properties, such as their close-packed volume fractions. Surface tension scales with particle surface area, while the particle crosslinking, or elasticity, scales with particle volume; therefore, the balance of these two effects will be size dependent. Our particles were developed using particles of micrometer-sized scales. To make particles like these at smaller length scales should require a lower particle surface tension so that it does not dominate over the effect of elasticity. Our results illustrate the potential usefulness of first synthesizing nonspherical particles at larger length scales, thereby postponing the more difficult problem of controlling surface tension until the latter stages of particle development.

Experimental

Our particles were produced with a repeated seeded polymerization method [13]. In all swelling and polymerization processes, 20 vol % of seed particles were dispersed in a 1 % w/v PVA (87–89 % hydrolyzed, 8.5×10^4 – 1.24×10^5 g mol⁻¹, Aldrich) aqueous solution. A 20 vol % monomer emulsion was also prepared in a 1 % w/v PVA aqueous solution by homogenizing at 8×10^3 rpm and mixed with the seed particles dispersion. The monomer solution consisted of styrene, DVB (55 % isomer, Aldrich), and initiator (0.5 wt %, V-65B, 2,2'-azodi (2,4'-dimethylvaleronitrile), Wako). The mixture was tumbled at a speed of 40 rpm for more than 10 h at room temperature to allow the seed particles to swell. To minimize the new-particle formation during polymerization, we added 0.05 % w/v hydroquinone in the continuous phase. Polymerization was performed by tumbling again at 100 rpm for 8 h at 70 °C in an oil-filled bath. After the final polymerization, submicrometer-sized particles that might be generated during seeded growth were removed by repeated centrifuges. Then, all unreacted monomers and additives were removed by additional washing with methanol.

In each step of the swelling, the concentration of DVB was varied with respect to the total monomer volume. In the synthesis of spherical crosslinked PS seed particles, a 2.5 mL dispersion of monodisperse PS templating particles (ca. 1.5 μm) produced by using a typical dispersion polymerization technique [25], was swollen by the monomer mixture (2 mL, [DVB]_a = 1 vol % or 1.2 vol %). In the synthesis of di-

mers, a 2.5 mL dispersion of crosslinked PS seed particles was swollen again with the monomer mixture (1.5 mL, $[\text{DVB}]_b = 0.5$ to 1.32 vol %). Finally, the dimers (2.5 mL) were swollen again with the monomer mixture (1.5 mL, $[\text{DVB}]_c = 0.5$ to 1.2 vol %, plus 0.5 mL toluene). Although $[\text{DVB}]_c$ was varied in the experiments reported here, additional experiments confirmed that the trimer particle morphology is essentially independent of $[\text{DVB}]_c$, just as dimer morphology is independent of $[\text{DVB}]_b$. Toluene was added to the monomer mixture in step c to make the phase separation more favorable.

The nonspherical particles were observed with a field emission scanning electron microscope (Leo 982) at an acceleration voltage of 1 kV. Scanning electron microscopy (SEM) samples were prepared by drying 0.1 wt % of purified particles on thin glass and directly examined without further coating of a conductive layer.

In the optical microscopy experiments, the monomer-swollen dimers were sealed in flat glass capillaries (100 μm inner diameter) and mounted on a temperature-controlled stage of an optical microscope (Leica) equipped with a digital camera (Hamamatsu, C4742-95) that was operated by Simple PCI software (Compix). Phase separation was monitored at 70 ± 0.1 °C.

Sedimentation experiments were performed on spherical particles, triple rods, and triangle particles that were synthesized with the same individual particle volume, ca. $38 \mu\text{m}^3$. Dispersions were prepared in 0.05 % w/v Fluronic F-68 aqueous solution at 23.8 vol %. The particle dispersions were completely sealed in round capillaries (inner diameter ca. 2.1 mm). The particles sedimented until there were no changes in the packed volume (about 35 days). To enhance packing, we gently sonicated the particle-packed capillaries several times during sedimentation.

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