

Synthesis of Nonspherical Colloidal Particles with Anisotropic Properties

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Abstract: We describe a promising and flexible technique for fabricating uniform nonspherical particles with anisotropic phase and surface properties. Our approach is based on the seeded polymerization technique in which monomer-swollen particles are polymerized. The polymerization causes a phase separation to occur, giving rise to two-phase nonspherical particles. We show that the elastic contraction of the swollen polymer particles induced by elevated polymerization temperatures plays an important role in the phase separation. Moreover, chemical anisotropy of nonspherical particles can be obtained by using immiscible polymer pairs and by employing surface treatments. Furthermore, we are able to produce amphiphilic dumbbell particles consisting of two different bulbs: hydrophilic poly (ethylene imine)-coated polystyrene and hydrophobic polystyrene. Controlled geometries of these amphiphilic nonspherical particles will allow a wide range of potential applications, such as engineered colloid surfactants.

Introduction

In the field of colloid science, there is growing interest in the synthesis of anisotropic particles.^{1–8} Particles may be anisotropic in shape and/or surface chemistry. The physical properties of nonspherical particles differ from those of spheres. This makes them highly desirable for controlling light scattering and fluid properties^{1,2} and for engineering biomaterials³ and colloid structures.⁴ Sophisticated techniques, including clusterization,⁵ stamping,⁶ microfluidics,⁷ and controlled nucleation and

precipitation,⁸ are being developed to create nonspherical particles. Particles with chemical rather than shape anisotropy also have potential importance and can play a role in recognizing specific molecules,⁹ self-assembling colloids,¹⁰ forming Pickering emulsions,¹¹ and stabilizing bubbles.¹²

One can impart chemical anisotropy to particles by using various synthetic routes.^{4a,9,13} One particularly useful example of chemical anisotropy is “amphiphilicity” induced by hydrophilic organic or biological (macro)molecules. However, chemistry on the surface or inside of the particles is commonly spotty, heterogeneous, and uncontrollable. Whether they are anisotropic in shape or chemistry, ideal anisotropic “building blocks” should be uniform and should have excellent “monodispersity” in size and shape. Such precision may allow us to tune the assembled structures of colloidal building blocks. For example, by controlling the shapes of particles embedded on interfaces, one may be able to engineer the curvature of interfaces. This is why it is important to develop methods for fine-tuning both the geometry and chemical compositions of anisotropic particles. Moreover,

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to make these particles practical, they should be produced in bulk rather than a particle-by-particle basis.

In this article, we describe a flexible approach for fabricating uniform anisotropic nonspherical particles in a bulk process. This approach allows us precise control over particle shape and size, as well as control of their phase and surface chemistries. This work is inspired by recent advances¹⁴ in the synthesis of nonspherical polymer particles by the seeded polymerization method; on heating monomer-swollen cross-linked particles, the elastic stress driven by the entropy change of the swollen networks¹⁵ causes phase separation and eventually results in macroscopic deformation of the particles. This exquisite behavior provides a convenient means to manipulate the geometry and surface properties of nonspherical particles. In this study, we fabricate dumbbell-type particles and characterize their anisotropic properties in shape and chemistry. Furthermore, we produce amphiphilic dumbbell particles and assemble them at interfaces to experimentally confirm the applicability as colloid surfactants.

Experimental Section

Synthesis of Spherical Cross-Linked Seed Particles. Spherical cross-linked polystyrene (CPS) seed particles were synthesized by using the seeded polymerization method.^{14,16} A 2.5 mL dispersion of monodisperse linear PS templating particles ($\sim 1.7 \mu\text{m}$, 20 vol %) was prepared in a 1% w/v PVA (87–89% hydrolyzed, 8.5×10^4 – $1.24 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$, Aldrich) aqueous solution. A 20 vol % monomer emulsion was also prepared in a 1% w/v PVA aqueous solution by homogenizing at $8 \times 10^3 \text{ rpm}$, and mixed with the seed particles dispersion. The monomer solution consisted of styrene, divinylbenzene (DVB, 55% isomer, 1 vol %, Aldrich), and initiator (0.5 wt %, V-65B, 2,2'-azodi (2,4'-dimethylvaleronitrile), Wako). The volume ratio of the monomer solution to the templating particles was 4:1. When incorporating reactive sites to the CPS particles, we selectively copolymerized 5 vol % functional monomers, such as, glycidyl methacrylate (GMA), vinylsilane, and 9-vinylanthracene. The mixture was tumbled at speed of 40 rpm for more than 10 h at room temperature to allow the seed particles to swell. Then, polymerization was performed by tumbling again at 100 rpm for 8 h at 70 °C in an oil-filled bath. These CPS particles were 2.7 μm in diameter and have semi-interpenetrating polymer network (IPN, $\sim 20 \text{ vol } \%$ linear PS). Their cross-linking density, measured for the gel fraction, was $\sim 61 \text{ mol}\cdot\text{m}^{-3}$.

Synthesis of Anisotropic Dumbbell Particles. To prepare dumbbell particles, the seeded polymerization was carried out again with the CPS particles. A 2.5 mL dispersion of CPS seed particles in a 1% w/v PVA (20 vol %) were swollen again with a 20 vol % monomer emulsion. The monomer solution consisted of monomer, DVB (1 vol %), and V-65B (0.5 wt %). The monomers used in this process were styrene, methyl methacrylate (MMA), or butyl methacrylate (BMA). We could also use other types of monomers as well, if they dissolve PS. Swelling and tumbling were performed as in the cross-linked seed particle synthesis. After the polymerization, unreacted monomers and additives were removed by repeated washing with methanol.

Chemical Treatment of Dumbbell Particles. Chemical treatment was carried out to incorporate hydrophilic groups to one of the bulbs of the dumbbell particles containing reactive sites. In this case, we used the dumbbell particles containing GMA. We mixed 0.2 g dumbbell

particles, dispersed in 2 mL Pluronic F68 (80% PEO, $\sim 8000 \text{ g}\cdot\text{mol}^{-1}$, BASF) aqueous solution (0.05% w/v), with 10 mL poly (ethylene imine) (PEI, $2.5 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$) solution (10% w/v). Then, the epoxy rings located on the surface of the particles were reacted with PEI for 3 h at 60 °C. After completely removing excess PEI from the aqueous phase by repeated centrifugation and replacement of the solvent with water, the recovered dumbbell particles were dispersed again in the Pluronic F68 aqueous solution and labeled with fluorescein sodium salt to observe the location of PEI chains.

Microscopic Observations. Bright-field and fluorescence images were obtained with a 40 \times objective at room temperature using a Leica inverted fluorescence microscope equipped with a digital camera (Hamamatsu, C4742–95) and Simple PCI acquisition software (Compix). All monomer swelling processes and the shapes of resulting particles were monitored with the microscope. When imaging the phase separation process, we sealed the monomer-swollen dumbbells in flat glass capillaries (100 μm inner diameter), mounted them on a temperature-controlled stage of the bright-field microscope and imaged the phase separation process with the digital camera every 3 s for 15 min at 70 °C. The synthesized particles were observed with a field emission scanning electron microscope (FE-SEM, Leo 982) at an acceleration voltage of 1kV. 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.

Results and Discussion

Formation of Nonspherical Particles in the Seeded Polymerization. Optical microscopy measurements showed that the swollen particles were spherical. The particles did not become nonspherical until polymerization. The elevated polymerization temperature causes a phase separation to occur such that most of the monomers form a new bulb that is attached to the seed particle. Therefore, the final dumbbell particles consist of two bulbs: one bulb contains most of the original seed particle and the other bulb mostly contains the newly polymerized material, as illustrated in Figure 1. The geometry of these dumbbell particles is simply tunable by controlling the swelling ratio of added monomers (see Figure S1).

Characterization of Phase Separation Process. To obtain a better understanding of the phase separation process, we use optical microscopy to monitor the evolution of the phase separation at the polymerization temperature, 70 °C. We observe that even without initiator, on increasing the temperature, the styrene-swollen CPS particles phase-separate and form small monomer bulbs that are attached to the CPS particles. This shows that the phase separation is driven by the elastic stress of the contracting seed particle.^{14a} When there is no initiator present, there is no growth of the bulbs after 100 s. By contrast, in the presence of initiator, the bulbs continue growing well after 100 s until nearly all of the monomers are converted to polymers. These results are summarized in Figure 2 and in movies S1 and S2 in the Supporting Information. These results indicate that the initial phase separation is predominantly driven by the elastic stress; then, as the polymerization proceeds, the phase separation is enhanced due to the difference of free volumes between the seed polymers and newly generated polymers,¹⁷ which eventually results in rigid dumbbell particles.

Control of Anisotropic Properties of Nonspherical Particles. When the dumbbell particles are prepared with the CPS particles and MMA, the phase separation at polymerization

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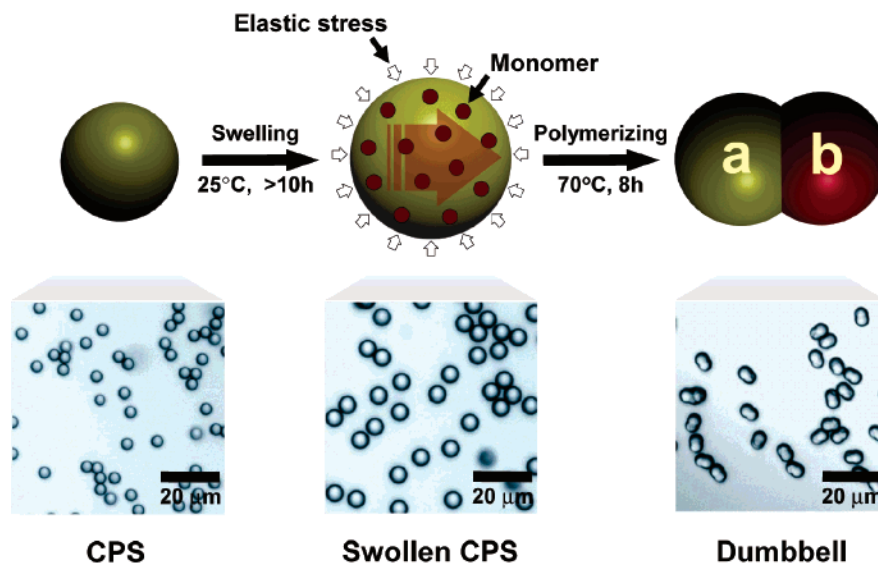


Figure 1. A scheme for synthesis of anisotropic nonspherical dumbbell particles by using the seeded polymerization technique. Bright-field microscope (BFM) images exemplify the synthesis of PS/PBMA dumbbell particles.

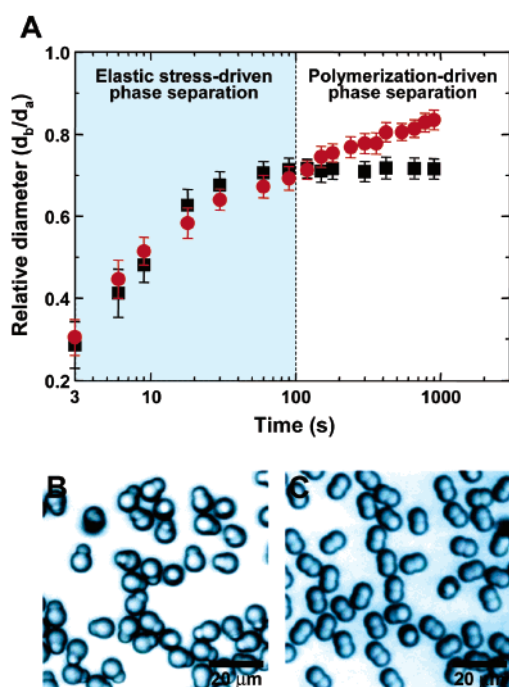


Figure 2. (A) Effect of heating on the diameter, d_b , of the new bulb, bulb **b**, relative to the diameter, d_a , of the seed bulb, bulb **a**. Experiments were performed both without initiator (■) and with initiator, 0.5 wt % V-65B (●). Bright Field Microscopy (BFM) images of the phase-separated PS particles (CPS/Styrene = 1/3, v/v) prepared by heating at 70 °C for 3 h without initiator (B) and with 0.5 wt % V-65B (C). Substantial phase separation occurs without initiator, but it is more complete when initiator is included.

occurs more readily due to the immiscibility between PS and PMMA.¹⁸ A similar trend is observed in the pair of PS and PBMA.¹⁹ Both systems produce dumbbells-shaped particles (Figure 3A and B). We cannot observe any defects on the surface of the synthesized dumbbell particles. In the case of

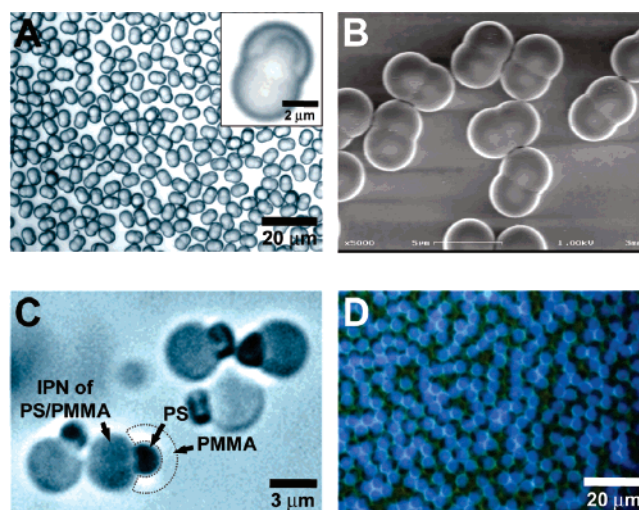


Figure 3. (A) A BFM image of PS/PMMA dumbbell particles (CPS/MMA = 1/2, v/v). (B) An SEM micrograph of PS/PMMA dumbbell particles. (C) A BFM image of PS ($n = 1.5894$)/PMMA ($n = 1.4893$) dumbbell particles dispersed in a silicone oil (Dow Corning #550, $n = 1.4945$). n is the refractive index. (D) A fluorescence microscope image of biphasic PS/PBMA dumbbell particles (CPS/BMA = 1/2, v/v). The CPS particles were labeled with 9-vinylanthracene. This shows that all the PS stayed in the original bulb upon polymerization and that the new bulb consisted of PBMA.

PS/PMMA, we are able to see the particle structure by dispersing the particles in a fluid that is refractive index matched to the PMMA. Optical microscopy images show that the particles consist of three phases: linear PS (from the templating particles, ~7 vol %), IPN of PS and PMMA, and PMMA (Figure 3C). In the case of PS and PBMA, we show that the dumbbells consist of two distinct phases; this is done by dyeing the CPS particles with 9-vinylanthracene before swelling with BMA. The optical microscopy image shows that the fluorescent PS did not migrate to the newly formed PBMA phase (Figure 3D). These results show that, in addition to the elastic effect, polymer–polymer immiscibility can play an important role in creating compartmentalized nonspherical particles.

Amphiphilic Nonspherical Particles. We exploit the compartmentalization of our particles to fabricate amphiphilic non-

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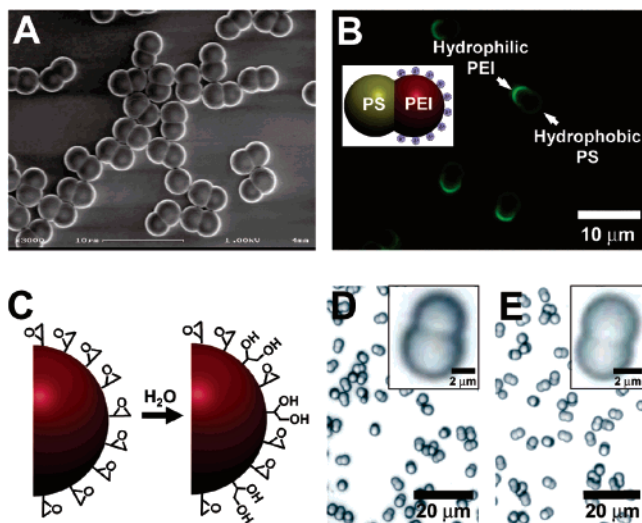


Figure 4. (A) A SEM micrograph of amphiphilic PS dumbbell particles obtained by the reaction of the epoxy groups with PEI. (B) A fluorescence microscope image of fluorescein-labeled amphiphilic PS dumbbell particles. (C) A schematic presentation for the hydrolysis reaction of GMA. (D) A BFM image of asymmetrically phase-separated PS particles (CPS/Styrene = 1/3, v/v). (E) A BFM image of symmetrically phase-separated PS dumbbell particles (CPS/Styrene = 1/4, v/v).

spherical particles. This is done by copolymerizing 5 vol % GMA into the CPS particles. The epoxy rings of GMA units on the CPS particles offer reactive sites for hydrophilic chemicals that have active hydrogen. After a second swelling with a styrene monomer solution and subsequent polymerization, dumbbell particles are formed. Selective reaction of PEI with the epoxy rings imparts amphiphilicity to the dumbbell particles. Symmetric amphiphilic particles are shown in a SEM micrograph in Figure 4A. A fluorescence image achieved by labeling fluorescein to PEI demonstrates that the dumbbell particles indeed consist of two different bulbs; hydrophilic PEI-coated PS and hydrophobic PS (Figure 4B). This means that the epoxy rings stay in the CPS network during the phase separation and do not migrate to the newly polymerized bulb. This synthetic process for producing amphiphilic dumbbell particles can be widely applicable to other reactive species (see Figure S2).

Incorporating additional species into the CPS particles not only allows chemical anisotropy; it can also modify the subsequent phase separation, providing an additional control over particle geometry. The presence of GMA in the CPS particles lowers the surface tension of the styrene-swollen particles by partial hydrolysis by water molecules at high temperatures, as illustrated schematically in Figure 4C.²⁰ The lowered surface tension diminishes the stress due to the Laplace pressure and causes less phase separation during polymerization. This gives rise to snowman-shaped particles rather than the dumbbell-shaped particles produced under similar conditions without GMA (Figure 4D). To create the symmetric amphiphilic particles of Figure 4E, we compensated for this by increasing the amount of swelling monomers. By increasing the swelling ratio of monomers to the CPS particles from 3 to 4, we can increase the elastic stress by $\sim 2.5\times$,¹⁵ thereby enhancing the phase separation. This example illustrates that particle geometry can be controlled by both the surface tension of the seed particles and monomer swelling ratio.

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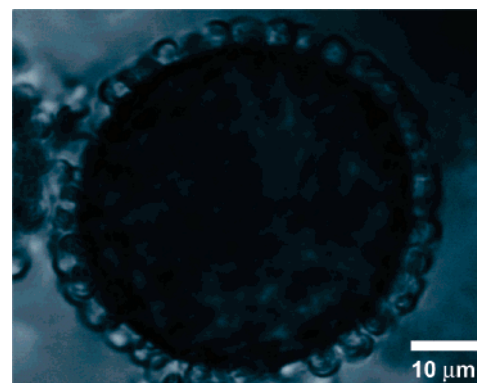


Figure 5. A BFM image for the assembly of amphiphilic PS dumbbell particles at water/1-octanol interface. The amphiphilic PS dumbbell particles are composed of a PEI-treated hydrophilic PS bulb and a hydrophobic PS bulb.

Assembly of Amphiphilic Nonspherical Particles at Interfaces. Amphiphilic nonspherical particles can find applications in stabilizing interfaces. The amphiphilicity of these particles makes them strongly adsorb at interfaces, as illustrated by the solid shell of adsorbed particles on the surface of a water drop in 1-octanol shown in Figure 5. Thus, these amphiphilic particles are potentially useful as colloid surfactants. For example, they may be able to impart improved stability to foams and emulsions owing to their strong adsorption at interfaces^{10a} and may significantly alter the mechanical properties of these systems. Further control of such systems is possible by tuning the geometry of the amphiphilic particles from symmetric dumbbells to asymmetric cone-like shapes. The precise shape of the cone-like particles may determine the preferred curvature of the interface that the particle occupies.²¹ Such interfacial control through particle geometry could, for example, determine a preferred drop size in an emulsion.^{21b}

Conclusion

In this paper, we demonstrate a flexible approach for fabricating the anisotropic nonspherical particles with well-controllable shape and surface chemistry. We show that the elastic effect of polymer network in the monomer-swollen particles induces their macroscopic shape deformation, and that chemical anisotropy of nonspherical particles is achievable by using immiscible polymer pairs and by employing surface treatments. Controlled shape anisotropy, together with the chemical anisotropy, creates new possibilities for assembling complex material structures, and perhaps even tuning the curvature of interfaces. This technology may allow a wide range of potential applications, such as colloid surfactants.

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Supporting Information Available: More examples of anisotropic nonspherical particles and the movies for the phase separations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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