

Colloid Surfactants for Emulsion Stabilization**

By Jin-Woong Kim, Daeyeon Lee, Ho Cheung Shum, and David A. Weitz*

In the classic solid particle-stabilized emulsions, typically referred to as Pickering emulsions, particles accumulate at the interface between two immiscible liquids and stabilize the emulsion drops against coalescence by forming a mechanically robust monolayer at the liquid-liquid interface.^[1,2] Particles adsorb to the interfaces to form a dense monolayer only under limited conditions that depend on particle size and shape, wettability, and interparticle interactions.^[2] Adsorption is typically obtained when the particles are wetted by both liquids; another strategy to bring particles to the interface is to introduce a chemical anisotropy to the stabilizing particles, making the particles themselves amphiphilic.^[3,4] Such particles are often referred to as "Janus" particles. These particles adsorb to interfaces more easily than isotropic particles due to their amphiphilicity and more strongly than molecular surfactants due to their larger size.^[3,5] Therefore, truly amphiphilic "Janus" particles combine the advantages of particle stabilization of emulsions and the amphiphilicity of molecular surfactants to afford better emulsion stabilization.^[6,7]

A number of different techniques have been developed to generate amphiphilic colloidal particles. These methods include formation of colloid clusters,^[8] stamping^[9] and sputtering of materials onto selected regions of colloids,^[10] and controlled assembly of materials in microfluidics.^[11] Nevertheless, the relationship between the geometry of these amphiphilic particles and the emulsion structure and stability has hardly been explored.^[12] In the case of molecular surfactants, the geometry is typically characterized by the packing parameter,^[13,14] P_{packing} , which is defined as $v/a_0 l_c$, where v is the volume of hydrophobic tail, a_0 is the optimum surface area of the headgroups, and l_c is the fully extended chain length of the tail. Depending on their Ppacking, surfactant molecules assemble into different aggregate structures including micelles, vesicles, planar bilayers, and inverted micelles. This parameter is also used for predicting whether oil-in-water (O/W) structures or water-in-oil (W/O) structures are preferred for a given surfactant.^[14] Similar concepts of packing should, in principle, also be applicable to colloidal particles. If so, it might be possible to control the emulsion drop size and shape with the same strategy as used for molecular surfactants, providing considerable flexibility control to the emulsion. However, the applicability of the concept of the packing parameter to colloidal particles has never been considered. To test the applicability of P_{packing} for predicting their aggregate structures as well as their ability to stabilize emulsions, it is important to develop a technique for fabricating particles with both amphiphilicity and tunable geometry.

In this communication, we introduce a robust and straightforward approach to synthesize uniform amphiphilic dimer particles, consisting of a hydrophilic bulb and a hydrophobic bulb. We call these particles "colloid surfactants", analogous to molecular surfactants. The synthesis method is based on the seeded polymerization technique.^[15–17] as schematically illustrated in Figure 1a and b. Our approach is advantageous because we can precisely tune the relative bulb size ratio of our dimer particles and effectively their P_{packing} . By varying the amount of monomer used during the elastic stress-driven phase separation of monomer-swollen polymer particles, we can manipulate the relative bulb size ratio of the resulting dimer particles, as shown in Figure 1b.^[15,16] Moreover, by further modifying the surface chemistry of one of the bulbs, amphiphilicity can be imparted. In this study, we make amphiphilic dimer particles and demonstrate that they assemble at liquid-liquid interfaces and effectively stabilize the emulsions.

In a typical synthesis, $\sim 0.8 \,\mu m$ linear polystyrene (PS) seed particles are swollen with styrene, divinylbenzene (1 vol %, 55% isomer), 3-(trimethoxysilyl) propyl acrylate (TMSPA) (10 vol %), and initiator (V-65B, 2,2'-azodi (2,4'-dimethylvaleronitrile), 0.5 wt %). The volume ratio of the monomer solution to the seed particles is 4 to 1. Polymerization is carried out at 70°C for 8h, which results in the formation of crosslinked PS (CPS) spherical particles with trimethoxysilane groups on the surface. The crosslinking density of the CPS particles is $\sim 60 \text{ mol m}^{-3}$ as estimated by the relative amount of crosslinker to monomer added.^[15,16] In the second step, the CPS particles are swollen with styrene, divinylbenzene (1 vol %), and V-65B. Dimerization proceeds while the dispersion of swollen particles is being heated; an elastic stress generated by heating partially squeezes the newly formed polymer phase out of the CPS seed particles to form the second bulb (see Supporting Movie S1). The exact mechanism of the formation of snowman-like dimer particles rather than spherical particles, however, remains unclear. The size of the second bulb relative to the first can be controlled by

 ^[*] Prof. D. A. Weitz, Dr. J.-W. Kim, Dr. D. Lee, H. C. Shum School of Engineering and Applied Sciences and Department of Physics, Harvard University Cambridge, Massachusetts, 02138 (USA) E-mail: weitz@seas.harvard.edu
 Dr. J.-W. Kim Amore-Pacific Co. R&D Center 3141-1, Bora-dong, Giheung-gu, Yongin-si Gyeonggi-do, 446-729 (Korea)

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Figure 1. Synthesis of amphiphilic dimer particles with tunable geometry. a) Scheme for synthesis of amphiphilic dimer particles by using the seeded monomer swelling and polymerization technique. b) Definition of packing parameter of amphiphilic dimer particles. c) Characterization of amphiphilicity of PS dimer particles by using a bright field microscope image (left) and a fluorescence microscope image (right) at the same location. Hydrophilic bulbs are labeled with fluorescein isothiocyanate (FITC).

simply changing the amount of monomer in the pre-dimerized CPS seed particles. During the phase separation, the acrylate groups of TMSPA are covalently linked to the network of the CPS particles so that they do not migrate into the second bulb.^[16] The trimethoxysilane groups, chemically linked to the first bulb, are coupled to N-[3-(trimethoxysilyl)propyl] ethyleneamine, thus creating amine groups on the surface of the CPS, and renders that bulb hydrophilic. This is confirmed by adding fluorescein isothiocyanate (FITC), which is attached only to the hydrophilic bulbs, as shown in Figure 1c.

Our approach is unique in that the elastic stress, created by the thermal treatment of the monomer-swollen polymer network, causes macroscopic deformation of the swollen CPS spherical particles and leads to the formation of nonspherical dimer particles. In addition, the formation of nonspherical dimer particles is enhanced by the incompatibility-driven phase separation between the two polymer networks.^[16] If the seeded polymerization is carried out with linear PS seed particles, dimerization does not occur due to the absence of the elastic stress induced by the cross-linking; instead uniform spheres are produced, as shown in both the scanning electron micrograph (SEM) image and the corresponding size distribution in Figure 2a. However, by inducing an elastic stress in the swollen CPS seed particles, we can obtain amphiphilic dimer particles; the proper range of crosslinking density^[16] typically ranges from 30 to 80 mol m^{-3} . The resulting dimers are approximately 2 μ m long in the long axis and are highly uniform in size and shape, as shown by the SEM images and particle size distributions for two samples with different shapes in Figure 2b and c. Control over the geometry of the particles, and the size ratio of the two bulbs, can also be achieved by changing the volume ratio of the monomer solution to the CPS seed; in our study, P_{packing} is precisely tunable from 0.6 to ~1.

Surfactant molecules are known to form molecular aggregate structures of various shapes above a critical concentration. By analogy, our amphiphilic dimer particles interact with each other and form clusters in water, as shown in Figure 3a. We do not observe well-defined clusters as a function of the number of the dimer particles (n); thus, the precise aggregation number is not well defined. Nevertheless, the clusters we do observe confirm that the hydrophobic PS bulbs of the dimer particles interact with each other, possibly driven by the hydrophobic



Figure 2. Characterization of amphiphilic PS dimer particles with different P_{packing} . a) A scanning electron microscope (SEM) image of amine group-containing spherical PS particles and their size distribution. These particles were synthesized using the seeded polymerization with linear PS particles. PS dimer particles with P_{packing} of b) ~ 0.6 (CPS/monomers = 1/1, v/v) and c) ~ 0.8 (CPS/monomers = 1/2, v/v). The size distributions of the dimer particles were characterized for both hydrophilic bulb and hydrophobic bulb and shown next to SEM images. Black curves in each histogram represent Gaussian fits to the size distribution. Scale bars in each SEM micrograph represent 5 μ m. The size distribution of each particle was obtained by measuring the size of at least 30 particles from a SEM image.

interaction, to form aggregate structures in water. This observation suggests that when they reside at the interface between the oil and the water phases, hydrophobic PS bulbs would segregate into the oil phase.^[18] The propensity for the particles to orient with specific directionality is essential to form dense assemblies of particles at the interface, and to achieve stronger adsorption to interfaces.^[3,5,7]

To experimentally confirm this hypothesis, we emulsify a hydrocarbon oil, hexadecane, with the dimer particles in water. We choose hexadecane due to its high wettability on bulk

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hydrophobic PS surfaces.^[19] The amphiphilic dimer particles strongly adsorb at the hexadecane-water interface at high density, as shown in Figure 3b; by contrast, the spherical particles with the same volume and with the same surface-amine groups as the dimer particles do not effectively stabilize the interface (Fig. 3c). These results demonstrate that our amphiphilic dimer particles have "surfactancy" at oil-water interfaces.

The size of our colloid surfactants, unlike their molecular counterparts, allows us to directly visualize their adsorption at liquidliquid interfaces and study how their presence at the interfaces affects the morphology of emulsion droplets. Remarkably, some of the emulsion drops stabilized by the amphiphilic dimer particles are nonspherical as shown in Figure 4. Ellipsoidal as well as cylindrical drops are present together with spherical drops in the same suspension. The formation of these nonspherical emulsion drops may be due to the fusion of two or more partially covered droplets until the interface is fully filled with the amphiphilic dimer particles. The drops cannot relax to a spherical shape due to the jamming of the particles at the interface. Since the jammed interface prevents further coalescence, the drops maintain their shapes.^[20] Nonspherical emulsion drops could also result from the uneven dissipation of energy during the emulsion formation process. Some nonspherical drops formed by uneven shearing might be stabilized before they can relax back to a spherical shape. Interestingly, studies using spherical Janus particles as stabilizers have only produced spherical emulsion droplets.^[21] This unique behavior of our amphiphilic dimer particles highlights the difference from molecular surfactants which do not jam at the interface due to a much shorter relaxation time and a dynamic exchange between the adsorbed molecules and freely diffusing species in the continuous phase.^[22] In addition, due to their amphiphilic nature, the dimer particles are

able to adsorb to interfaces more easily and strongly than the isotropic particles. Such tendency leads to jamming of the dimer particles and thus to the stabilization of nonspherical drops, which is not typically observed in emulsions stabilized by isotropic particles.

In summary, we introduce a flexible synthesis approach for fabricating amphiphilic dimer particles, providing control over their geometry and surface chemistry, while maintaining their uniformity in shape and size. We have demonstrated that our amphiphilic dimer particles can assemble at liquid-liquid

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Figure 3. Stabilization of oil drops by using the amphiphilic dimer particles as surfactants. a) Colloidal clusters formed by interactions between amphiphilic dimer particles in water with different aggregation number (n). P_{packing} for this sample is ~0.9. b) Stabilization of hexadecane drops with amphiphilic PS dimer particles. Amphiphilic PS dimer particles with $P_{\text{packing}} \sim 0.6$ are used. c) Stabilization of hexadecane drops with amine group-treated spherical PS particles. Only sparse coverage of particles on the oil drop surface is observed.





Figure 4. Stabilization of emulsion drops by adsorption of amphiphilic dimer particles at the water and oil interface. The shapes of resulting hexadecane drops included spheres (a), ellipsoids (b), and cylinders (c). In this experiment, we emulsified ${\sim}0.05\,$ ml hexadecane in a 3 ml aqueous dispersion of \sim 2 vol % amphiphilic PS dimer particles by vigorously vortexing the mixture for 2 s at room temperature. We used the dimer particles with $P_{\text{packing}} \sim 0.6$.

interfaces and stabilize emulsion drops. Moreover, in some cases, they pack closely at the interface to stabilize nonspherical drops. The ability to jam at the interface in observable time-scales leading to a mechanically stable emulsion with polydispersity in droplet shape and size highlights a fundamental difference between colloid surfactants and molecular surfactants. We expect that the properties of surfactant colloid-stabilized emulsions, such as their shape, size, characteristic curvature and stability, can be controlled by varying P_{packing} of the particles; however, the correlation still has yet to be established.

Experimental

Synethsis of Colloids Surfactant: Spherical silane-functionalized cross-linked polystyrene (CPS) seed particles were synthesized by using the seeded polymerization method. A 2.5 mL dispersion of monodisperse linear PS templating particles (~0.8 µm, 20 vol %) was prepared in a 1% w/v PVA (87–89% hydrolyzed, 8.5×10^{4} –1.24 × 10⁵ gmol⁻¹, Aldrich) aqueous solution. A 20 vol % monomer emulsion was also prepared in a 1% w/v PVA aqueous solution by homogenizing at 8000 rpm, and mixed with the seed particle dispersion. The monomer solution consisted of styrene, divinylbenzene (DVB, 55% isomer, 1 vol %, Aldrich), 3-(trimethoxysilyl) propyl acrylate (10 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. 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. Then, polymerization was performed by tumbling again at 100 rpm for 8h at 70 °C in a reaction bath. These silane-functionalized CPS particles have semi-interpenetrating polymer network (~20 vol % linear PS). Their crosslinking density, measured for the gel fraction, was $\sim 60 \text{ mol m}^{-3}$.

To synthesize amphiphilic dimer particles, the seeded polymerization was carried out again with the silane-functionalized CPS particles. CPS seed particles in a 2.5 mL dispersion in 1% w/v PVA (20 vol %) were swollen again with a monomer emulsion. The monomer solution consisted of styrene monomer, DVB (1 vol %), and V-65B (0.5 wt %). Swelling and tumbling were performed as in the CPS particle synthesis. To control $P_{packing}$, the volume ratio of the monomer solution to the CPS particles was varied between 2:1 and 4:1. After the polymerization, unreacted monomers and additives were removed by repeated washing with methanol. Then, chemical treatment was carried out to incorporate hydrophilic groups to one of the bulbs of the dimer particles containing reactive sites. For this, we mixed 0.2g dimer particles, dispersed in 5 mL ethanol solution, with 0.5 ml silane coupling agent (N-[3-(trimethoxysilyl)propyl]

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ethyleneamine, Aldrich) and 1 ml ammonium hydroxide (\sim 30%, Aldrich). Then, the silane groups located on the surface of the particles were reacted with the coupling agent for 24 h at room temperature. After completely removing excess coupling agent and ammonium hydroxide from the aqueous phase by repeated centrifugation and replacement of the solvent with water, the recovered amphiphilic dimer particles were dispersed in a mixture of methanol and water (95/ 5, v/v).

Emulsion Stabilization Using Dimer Particles: Using these amphiphilic dimer particles, we stabilized hydrocarbon oils. To adsorb the particles onto the hexadecane drops, we added a small amount of hexadecane in the particles dispersion in water and vortexed for $\sim 2 \, \text{s}$ at room temperature. Then, we removed the supernatant particles by repeated decantation.

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. The synthesized particles were observed with a field emission scanning electron microscope (FE-SEM, Leo 982) at an acceleration voltage of 1 kV. 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.

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