

Foam Superstabilization by Polymer Microrods

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Few foam systems stabilized by solid particles have been reported, and usually the particles have been used in combination with surfactants. We report how foams can be stabilized solely with a new class of anisotropic particles, hydrophobic polymer microrods of diameter less than 1 μm and length of a few tens of micrometers. The obtained foams were extraordinary stable, retaining a constant volume over many days and even surviving drying of most of the free liquid. The bubbles in these foams were sterically stabilized by dense thick “hairy” layers. The rigid intertwined protective shells around the bubbles did not allow the formation of thin films between them. The lifetime of these foams was orders of magnitude longer than the ones stabilized with typical foaming surfactants such as sodium dodecyl sulfate. The addition of sodium dodecyl sulfate led to hydrophilization of the microrods and suppressed the superstabilization effect. Thus, common foaming agents effectively act as defoamers for the ultrastable foams stabilized by microrods.

Introduction

Foams of different types are used in many products, in industrial processes, and for synthesis of new materials.^{1–4} Long-term stability is desirable for many foam-based systems, but achieving it is rather difficult. The foams are both thermodynamically and kinetically unstable systems that readily destruct as a result of liquid drainage, drying, film breakup and gas diffusion. Typical foaming agents used in industrial formulations are ionic surfactants such as sodium dodecyl sulfate (SDS) and surface-active polymers. Foam stabilization may also be promoted or inhibited by the presence of solid particles.^{1,2,5} In most of the foams studied previously, the solid particles are used in combination with surfactants. The stability of such foams has been found to depend on the particle size, shape, concentration, and hydrophobicity, as well as on the type of surfactant used.^{1,2,5} Data and theoretical conclusions in the literature point out that hydrophobic spherical particles may initiate foam destruction by rupturing the foam films (“lamellae”) via a bridging–dewetting mechanism.^{1,2,5–8} On the contrary, if the particles are hydrophilic, they could collect in the plateau borders slowing down the liquid drainage and kinetically increasing the foam stability. Very few studies of foams stabilized solely by solid particles are reported,⁵ which include foams formed by a latex suspension close to its coagulation point⁵ or short living foams stabilized by sludge particles.⁹ A large

number of nano- and microparticles of various sizes and shapes synthesized recently following the thrust in nanoscience remain largely unexplored. Foam stabilization solely by particles may be valuable for applications in which surfactants are to be avoided, for synthesis of advanced materials, or for formation of ultrastable foams, which is the case described in this Letter.

We report how extremely stable aqueous foams can be formed from suspensions of polymer rodlike particles. The process for synthesis of the new “microrods” used for stabilizing these foams was developed recently in our group.¹⁰ We describe the structure of foams and single foam films of extraordinary long-term stability. The results on foamability and stability of the microrod-containing systems are compared to those of foams stabilized with SDS and its mixture with microrods. We discuss the factors making these rod-stabilized foams of almost infinite lifetime and resistant to drying.

Experimental Section

Polymer Microrod Preparation. The polymer rodlike particles used for foam stabilization were synthesized from epoxy-type photoresist SU-8 (MicroChem, MA) using the liquid–liquid dispersion technique described in detail elsewhere.¹⁰ Typically, 0.2 mL of 50 wt % solution of SU-8 in γ -butyrolactone (GBL) (Aldrich, WI) was injected into 50 mL of a 1/1 v/v mixture of glycerol and ethylene glycol (Fisher Scientific, PA) subjected to a viscous shearing by an impeller. The polymer solution was emulsified, and the emulsion droplets deformed and solidified into cylinders with high aspect ratio. The polymer particles were strengthened by cross-linking with UV light. Then the dispersion was diluted twice with deionized (DI) water (from a Millipore RiOs 16 RO unit) and filtered through a 0.45 μm Durapore membrane (Millipore, MA) to separate the particles. The SU-8 rods collected on the membrane were repeatedly washed with DI water to remove any organic solvent traces and then suspended into deionized water to give a dispersion of 2.18 wt % solid content. Microscopy measurements determined that the samples consisted of polydisperse cylindrical rods of 23.5 μm average length and 0.60 μm average diameter (Figure 1a and Supporting Information).

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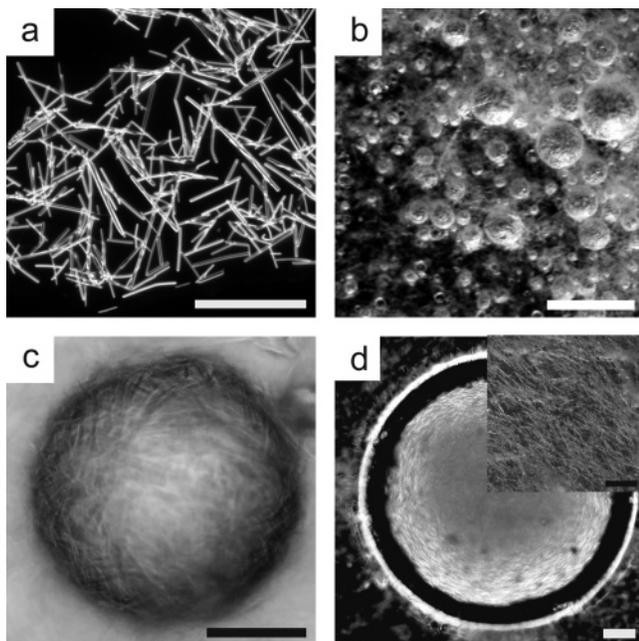


Figure 1. (a) Optical micrograph of the SU-8 microrods used as superstabilizers; (b) foam stabilized by rods; (c) micrograph of a single hairy air bubble covered by a layer of adsorbed rods; (d) single thin aqueous film formed from a suspension of SU-8 rods. The inset in image d is a highly magnified area near the film center. The scale bar is 50 μm for images a and c and the inset of image d and 200 μm for images b and d.

Foam Preparation and Characterization. Foams stabilized by SU-8 rods only were prepared directly from the above microrod suspension or after its further dilution with DI water. For a reference surfactant system, we used an 8.7 mM solution of SDS in water. The SDS concentration is close to its critical micellar concentration (cmc) where it shows maximum foamability.² All foams were formed by the same protocol from 2 mL of liquid measured by a pipet into a 10 mL glass cylinder. They were prepared at room temperature by hand-shaking for a period of 30 s by the same operator. The foamability was estimated by measuring the foam volume, V_f , immediately after preparation, while the foam stability was assessed by monitoring V_f over time. The cylinders were kept closed except for the case when the stability of the rod foam upon drying was evaluated.

The structure of small foam bubbles and thin liquid films was observed by an Olympus BX-61 microscope equipped with long working distance objectives. The bubbles were mounted in a thick film on microscope slides. Single foam films were formed inside 1.4 mm holes in a polycarbonate slide of 0.1 mm thickness by introducing a drop of the SU-8 rod suspension into the hole and sucking out the excess liquid. The observations were performed in transmitted phase contrast or dark field illumination.

Results and Discussion

Phenomenology. The microrod suspensions readily produced foams upon shaking. Batches of foams with four different concentrations of SU-8 rods were prepared and monitored. Initially, the air bubbles formed were spread throughout the entire volume of the samples, making them milky. In a few minutes, most of the air bubbles accumulated in the top phase, leaving a less turbid lower phase of SU-8 rods dispersed in water. The foam volume, V_f , recorded as a function of time for all samples stabilized by rods only is given in Figure 2a. V_f decreased noticeably only within the first few minutes (see the inset) and then remained approximately the same for more than 3 weeks. The long-term values of V_f as a function of the rod concentration are presented in Figure 3. They show a possible initial threshold concentration where stabilization

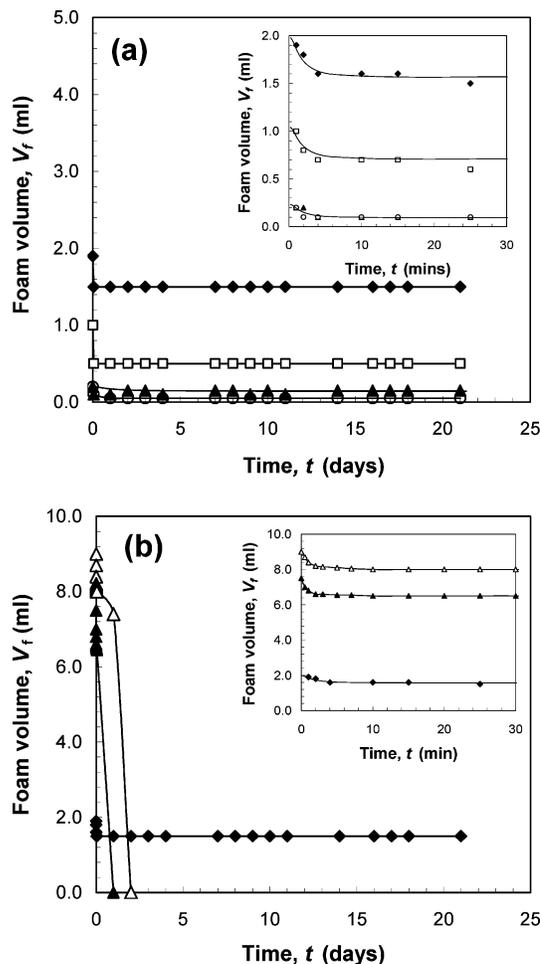


Figure 2. (a) Time dependence of the volume of foams, V_f , formed with SU-8 rods. The lines of experimental points (lack of any foam breakdown) correspond to different solid concentrations: (\blacklozenge) 2.18 wt %, (\square) 1.09 wt %, (\blacktriangle) 0.44 wt %, (\circ) 0.22 wt %. The inset shows the volume changes for the first 30 min. (b) Time dependence of the volume of foams, V_f , formed in the presence of (\triangle) 8.7 mM SDS, (\blacktriangle) 2.18 wt % SU-8 rods mixed with 8.7 mM SDS, and (\blacklozenge) 2.18 wt % SU-8 rods only. The inset shows the volume changes for the first 30 min. The curves are guides to the eye.

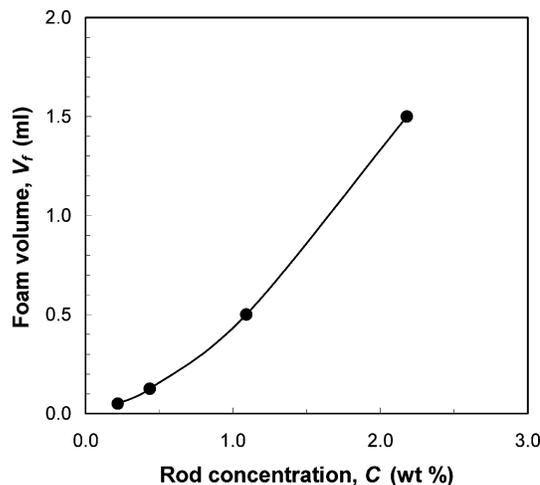


Figure 3. Volume of the foam formed as a function of SU-8 microrod concentration in the water phase. The data correspond to plateau values for V_f in Figure 2a. The line is a guide to the eye.

begins and a rapid increase of the foam volume with the particle content.

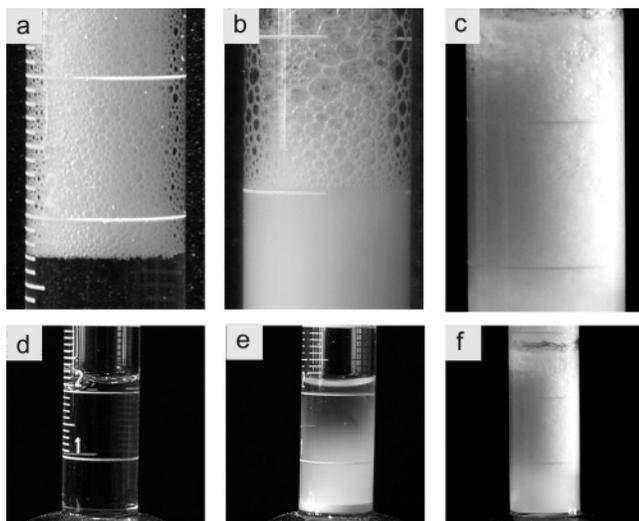


Figure 4. Comparison of the appearance and structure of foams stabilized by (a,d) 8.7 mM SDS, (b,e) a mixture of 8.7 mM SDS and 2.18 wt % SU-8 rods, and (c,f) 2.18 wt % SU-8 rods. The top images (a–c) were obtained 10–15 min after the foam was formed. The bottom images (d–e) are of the top system after 2 days of storage. Note that SDS not only makes much less stable foams than the microrods but effectively acts as a defoaming agent for the microrod foams.

A more stringent test for foam stability is the resistance to drying, which typically destroys any surfactant-stabilized foam. The resistance of microrod foam (2.18 wt % SU-8) to water evaporation was examined by monitoring its state in a cylinder open to the air. For more than a week, the volume of the foam remained at a constant value of 1.3 mL (similar to the V_f of the same foam kept in a closed cylinder), even though the liquid below it slowly evaporated through the foam layer. The evaporation possibly occurs by capillary suction from the subphase. After a week, we tried to destroy the remaining foam by fast drying and expansion in a vacuum. When the pressure was reduced, the foam started increasing in volume and reached twice its initial volume where it remained constant for hours. The major part of the (already dried) foam collapsed only when the vacuum was released, and air rushed into the vessel. Thus all tests prove an extraordinary effect of “superstabilization” by the microrods.

It is instructive to compare the properties and the structure of microrod-stabilized foams to the ones made from common surfactants such as SDS. The stabilities of foams prepared with pure SDS, pure 2.18 wt % SU-8 microrods, and a mixture of SDS and 2.18 wt % microrods are compared in Figure 2b. Despite the large difference in the foamability (the initial V_f is about 5 times larger for surfactant-stabilized foams), the shape of the short-term stability plot (the inset) is similar for all foams and indicates similar draining changes in the initial period. However, the long-term plots show that the microrod-stabilized foam has strikingly superior stability compared to the SDS-containing samples, both of which are completely destroyed in less than 48 h. This effect is also demonstrated by the images of the fresh and 2-day-old foams in Figure 4.

The sample containing mixed SDS and microrods was expected to show an intermediate stability; however, it behaved as pure SDS foam except for the slightly smaller initial volume and lifetime. This can be readily explained by the adsorption of SDS monomers on the hydrophobic SU-8 rod surface. These hydrophilized rods lose their affinity for adsorption at the solution/air interface and in addition repel from it electrostatically. Instead of protect-

ing the bubbles, they remain well dispersed in the liquid phase and slowly sediment to the bottom (Figure 4e). Estimates show that if the surface of all rods present in a 2.18 wt % dispersion is covered by densely packed SDS monomers, the initial surfactant concentration is reduced by only about 5%. These data lead to an unusual conclusion. SDS, which is used typically as a strong foaming agent, in this case acts as a *defoamer* suppressing the stabilizing effect of the microrods. This was also proved by adding gently a few drops of 10 wt % SDS to a stable few-days-old foam from 1.09 wt % SU-8 rods. Soon after the surfactant was introduced, the microrod particles began to transfer from the foam into the liquid and to sediment at the bottom. More than 70% of the foam phase was destroyed in the first 30 min.

Factors Contributing to the Superstabilization Effect. We assume that the initial compression of the foam volume was a result of liquid drainage and bubble compaction, rather than loss of any entrapped air. Closer examination of the microrod foam under a microscope showed that it was made of small roughly spherical randomly distributed bubbles (Figure 1b). Each air bubble was covered by a dense shell of adsorbed entangled polymer rods extending into the water phase (Figure 1c).

The key to making stable foams is ensuring that the thin films formed between the bubbles do not thin and break easily.^{12–14} We examined single foam films in order to observe the structure of the SU-8 rods adsorbed between the two air/water interfaces. The whole surface of such films was densely covered by intertwined rods (see Figure 1d and Supporting Information, Figure 4). The rods entangle, overlap, and sometimes form small oriented domains. The film thickness corresponds to at least two opposing layers of rods, or ca. 1–2 μm . This is an overwhelmingly thick film compared to the equilibrium thickness of surfactant foam films stabilized by electrostatic repulsion (≈ 100 nm)^{12,13} or the thickness of common “black” films with steric repulsion between surfactant monolayers adsorbed on the opposing surfaces (≈ 12 nm).^{12,13} Thus, the first factor of stability of the superstabilized foam is the steric repulsion between the adsorbed layers of solid rods, which keeps the films very thick, preventing breakage and suppressing gas diffusion. Even though there are some empty spaces between the rods, the capillary pressure in the system would not be enough to locally thin and break the films there.

The second unique factor of superstabilization is the mechanical rigidity of the continuous net of overlapping and entangled microrods at the film surface (cf. inset in Figure 1d). The microrods did not rearrange as previously observed with spherical particles entrapped in thin foam films.¹⁵ The stability of the formed microrod net is impressive. Similarly to the foam systems, single films with concentration above ≈ 1 wt % were infinitely stable and were not destabilized by drying, which leads to rapid breaking down of films made with SDS only. The films and membranes from intertwined rods could be dried and kept intact for more than a week.

One of the major factors for the formation of thick and rigid films between the bubbles is the strong adsorption of the polymer rods on the air/water interface. The degree

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of rod hydrophobicity was characterized by measurements of the contact angle on single rods by a recently developed gel trapping technique.¹¹ The contact angle between SU-8 rods and water was estimated to be between 80° and 90° corresponding to intermediate hydrophobicity (see Supporting Information). The adsorbed microrods were partially immersed in the water phase but did not aggregate spontaneously when dispersed in the bulk. It has been reported that partially hydrophobic particles are optimal stabilizers of various foam and emulsion films.^{1,2,15–17} We also observed by scanning electron microscopy (SEM) entanglement of the rods adsorbed at the interface (Supporting Information). The strong adhesion between the adjacent and overlapping rods in the films (responsible for the rigidity of the adsorbed layer) is probably augmented by their hydrophobicity and high friction. The rod entanglement appears to be the major difference between the superstabilized foams reported here and previously studied foams containing spherical particles.^{1,2,15,18} The effect is lost when the particles are hydrophilized and desorbed from the interface due to SDS adsorption, whence the superb stability is lost when common surfactant is added.

The bulk structure of the superstabilized foams was also very different from that of common foams stabilized by surfactants. The microrod foams were made of approximately spherical air bubbles (Figure 1b) not only for the very first stage of the foam formation but for the whole period of observation. Such structure is typical for unstable wet transient foams which contain large amounts of water and live only seconds.¹⁹ These bubbles did not deform to reach the second (kugelschaum) and third (polyederschaum) stages of foam evolution² in which air bubbles in common foams deform, the liquid from the films between them drains, and a “dry” foam with thin films and plateau borders separating large polyhedral air cells forms (cf. Figure 4a,c). Yet, the rod-stabilized foams show remarkably long lifetimes exceeding dramatically even the lifetime of the dry metastable foams. The reason for the lack of deformation is probably the rigidity of the dense “hairy” shells around the bubbles. We have recently shown that rods form similarly rigid shells around emulsion droplets.²⁰

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The effects presented here also differ significantly from literature data for other particle-stabilized foams. It has been reported that strongly hydrophobic particles decrease foam stability by breaking the lamellae by a “bridging–dewetting” mechanism.^{1,5} Foam stabilization with slightly hydrophobic and with hydrophilic particles is usually a result of collecting of the particles in the plateau borders, which slows down the liquid drainage and therefore the thinning and rupture of the lamellae.^{1,2} In the case of polymer microrod foams, the stabilization mechanism includes the formation of a thick rigid net of entangled rods around the bubbles. The bubbles do not coalesce because of the strong steric hindrance from their shells. Diffusion of air between the bubbles is not likely to occur because the liquid films between them are very thick and small¹⁸ and because the bubbles covered by a rigid shell cannot readily shrink or expand. The strong rod adsorption and entanglement, formation of rigid hairy shells, and sustaining of thick films makes possible the superstabilization effect.

Concluding Remarks. We have shown that superstabilization of aqueous foams can be achieved by using polymer microrods in the absence of any surfactant. Due to their rigid structure and resistance to mechanical perturbations, the polymer rodlike foams can be used in applications where the common foam stabilizers are not effective. Foams based on polymer microrods and their mixtures or composites with other nano- and microparticles may also serve for synthesis of new materials. In a more general plan, we believe that this work shows how progress in the area of controlled synthesis of new nanoparticles and nanostructures can dramatically enhance the control over the properties of “classical” colloidal systems such as foams and emulsions.

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Supporting Information Available: SEM and optical micrographs and size distribution of the microrod samples; SEM images of polymer cylinders adsorbed at replicas of air–water interfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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