

Long-Range Structural Order, Moiré Patterns, and Iridescence in Latex-Stabilized Foams

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Abstract: We describe the facile production of highly stable foams stabilized solely by micrometer-sized, sterically stabilized polystyrene (PS) latex particles. Such foams can survive for more than one year in the wet state and remain intact after drying. In contrast, foams stabilized with either sodium dodecyl sulfate or poly(*N*-vinylpyrrolidone) were destroyed after removal of the aqueous phase. Scanning electron microscopy studies reveal hexagonally close-packed arrays of PS particles within the dried foam, which suggests high colloid stability for the PS particles prior to their adsorption at the air–water interface. Localized moiré patterns are observed by optical microscopy due to the formation of well-defined latex bilayers with exquisite long-range order. Moreover, the dried foams are highly iridescent in bright transmitted light, which may offer potential applications in security inks and coatings.

Introduction

Foams of various types are widely used in many products and formulations, in various industrial processes, and also for the synthesis of advanced materials of controlled porosity.^{1–5} Long-term foam stability is desirable in many cases, but achieving this is rather difficult in fluid systems. Foams are typically stabilized with either conventional surfactants, surface-active polymers, or globular proteins; there are relatively few reports of foams stabilized solely by solid particles.^{6–12}

Although solid particles were first used by Ramsden⁶ and Pickering¹³ to stabilize emulsions and foams approximately one hundred years ago, there is considerable renewed interest in this area. For example, Binks and co-workers reported that silica sols, carbon black, and polystyrene latexes can be used as particulate emulsifiers to prepare both oil-in-water and water-

in-oil emulsions.^{8,14} There are a number of studies of foams that are stabilized by a combination of solid particles with surfactants and/or surface-active polymers^{1,2,8} but relatively few reports of foams stabilized solely by solid particles.^{6–12} Foam stabilized solely by solid particles should be of particular interest for applications where the use of surfactants should be avoided or minimized, such as cosmetic formulations and food manufacturing and perhaps for the synthesis of new materials.

Herein we report that micrometer-sized, near-monodisperse, sterically stabilized polystyrene (PS) latex particles can be used to prepare highly stable foams in the absence of any surfactants or surface-active polymers. Moreover, foam formation results in exquisite long-range ordering of the latex particles in well-defined bilayers, which in turn produces interesting optical properties.

Results and Discussion

Near-monodisperse PS latex particles were successfully prepared by conventional nonaqueous dispersion polymerization in 2-propanol using poly(*N*-vinylpyrrolidone) (PNVP) as a steric stabilizer.^{15,16} Prior to purification, this milky-white dispersion contained excess PNVP, and no foam was observed after vigorous agitation. After two centrifugation/redispersion cycles to remove the nonadsorbed stabilizer, a weak, short-lived foam was observed that collapsed within 10 s. After the third centrifugation/redispersion cycle, highly stable foams were obtained that remained stable for more than one year.

Typically, the foam volume produced by hand-shaking is around 60–70% of the volume of the original aqueous latex.

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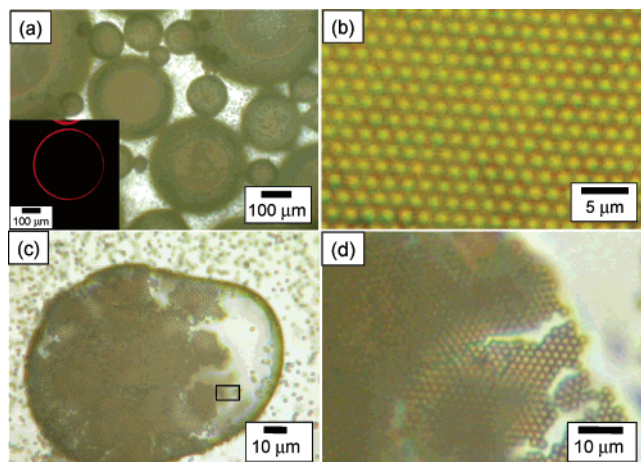


Figure 1. Optical micrographs of the latex foam prepared using $1.57\ \mu\text{m}$ sterically stabilized polystyrene latex particles. (b) Magnified image that shows hexagonally ordered latex particles at the surface of one of the air bubbles shown in (a). (c) Optical micrograph of a crushed air bubble. (d) Magnified image of the area shown in (c).

After two further centrifugation/redispersion cycles, the supernatant surface tension was $72.1\ \text{mN m}^{-1}$, which is very close to that of pure water. This confirms that the concentration of nonadsorbed PNVP stabilizer in the aqueous phase is essentially zero.

Figure 1 in the Supporting Information depicts digital photographs of foam stabilized solely with the purified PNVP-stabilized PS particles (a) before and (b) after removal of the aqueous phase. Before drying, the foam was readily discernible above the latex phase. After evaporation of the aqueous phase overnight at ambient temperature, solid foams were obtained on a Petri dish. The foam volume and shape were almost unchanged before and after drying. Even after drying, the foam retained its three-dimensional structure, see Figure 1b in the Supporting Information. Very little coalescence occurred and both visual inspection and optical microscopy studies indicated that the bubble size distribution was almost unchanged after drying. In contrast, foams prepared with sodium dodecyl sulfate, which is widely used for industrial formulations, or PNVP homopolymer, which is the surface-active polymeric stabilizer at the surface of the PS latex particles, disappeared almost completely after evaporation of the aqueous phase. The surface tensions determined for the aqueous latex dispersion at 1.0 and 8.8 wt % solids were 69.7 and $69.1\ \text{mN m}^{-1}$, respectively. These values are slightly lower than those determined for the respective latex supernatants obtained after centrifugation. The driving force for the adsorption of the PS latex particles is the elimination of the high-energy air–water interface.⁸ Given that charge-stabilized PS latexes of comparable size are poor foam stabilizers,⁷ this adsorption may be enhanced by the well-known surface activity of PNVP homopolymer,¹⁷ which is located on the surface of the sterically stabilized PS latex particles.

Bubble diameters varied from around $10\ \mu\text{m}$ up to approximately $3\ \text{mm}$ ($3000\ \mu\text{m}$), as shown in Figure 1a. Confocal laser scanning microscopy (CLSM) studies on an individual bubble (see inset shown in Figure 1a) revealed a red halo, which demonstrates that fluorescently labeled PNVP-stabilized PS

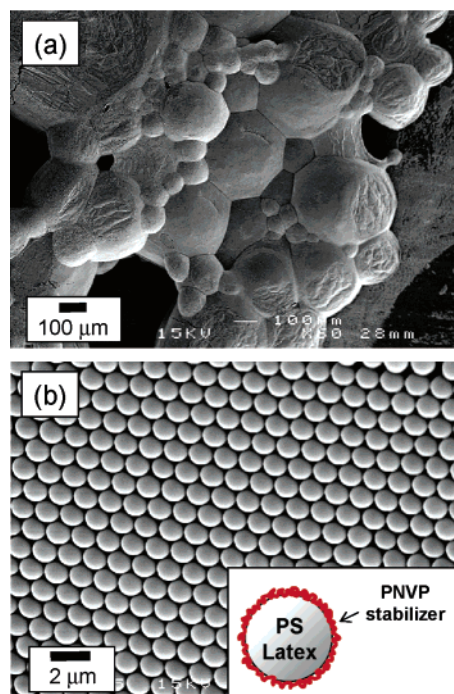


Figure 2. Scanning electron micrographs of: (a) polystyrene latex-stabilized foams obtained after the removal of excess, nonadsorbed latex and (b) a high magnification image of the sample shown in (a). (Inset) Schematic representation of an isolated PNVP-stabilized PS latex particle. In the dried foam, the outer layer of PNVP stabilizer collapses onto the latex surface to form an overlayer of negligible thickness.

particles were adsorbed at the air–water interface, which is a necessary and sufficient condition for stabilization of the air bubbles. Optical microscopy studies confirmed that hexagonally close-packed (hcp) arrays of micrometer-sized, near-monodisperse PS latex particles were formed on the surface of the bubbles (see Figure 1b). Similar two-dimensional latex arrays have been reported at the planar air–water interface.^{18–21}

Figure 2a shows an SEM image of the dried foam obtained after removal of excess, nonadsorbed PS particles by careful washing. Surprisingly, the majority of this foam remained stable even under the ultrahigh vacuum conditions required for electron microscopy. Figure 2b shows a highly magnified image of the foam surface shown in Figure 2a: almost perfect hcp arrays of PS latex particles were observed, which is in good agreement with the optical microscopy studies. The inset in Figure 2b is a schematic representation of an isolated PNVP-stabilized PS latex particle. The PNVP stabilizer is mainly located on the surface of PS particles, as confirmed by X-ray photoelectron spectroscopy studies. This is consistent with the work by Deslandes et al., who reported that PS latex particles synthesized by dispersion polymerization in the presence of PNVP stabilizer using the same protocol were coated with PNVP.²² A fast Fourier transform (FFT) analysis of the SEM image of the hcp array of PS latex particles confirmed that these PS particles are exquisitely ordered. (Figure 2 in Supporting Information). On average, there are around several thousand latex particles per

(17) Our measurements on 0.5 wt % PNVP aqueous solution and pure water indicated surface tensions of 68.6 and $72.2\ \text{mN m}^{-1}$, respectively, at $20\ ^\circ\text{C}$.

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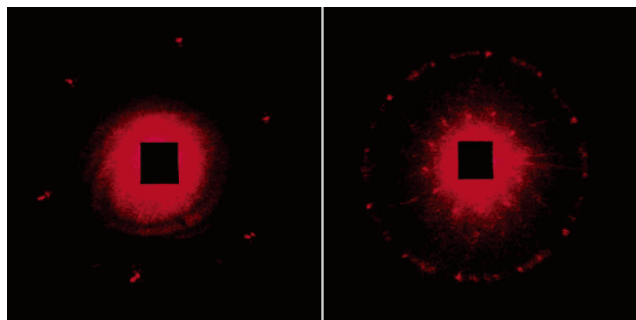


Figure 3. Typical laser diffraction patterns obtained from a small piece of dried foam prepared using $1.57\ \mu\text{m}$ polystyrene latex particles.

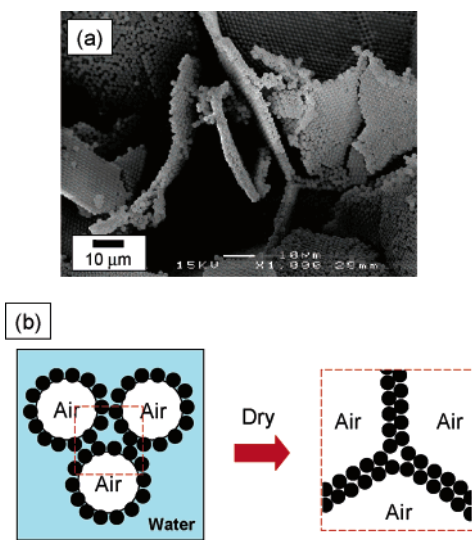


Figure 4. Scanning electron micrograph shown in (a) was obtained after rupturing a dried foam using a razor blade: it provides direct evidence for the latex bilayer structure of these foams. As the aqueous phase evaporates and the foam dries, such latex bilayers are formed from the latex monolayers that encapsulate each air bubble, as shown schematically in (b).

single two-dimensional (2D) crystal domain, encompassing length scales of more than $90\ \mu\text{m}$. Close inspection confirmed that the ordered domains of these hcp latex particles exhibited the typical features of 2D crystals, including both grain boundaries and point defects.

Figure 3 shows the two types of diffraction patterns that were observed, depending on the precise sample area that was interrogated. One pattern has 6-fold symmetry and corresponds to diffraction from hexagonally close-packed particles. The second pattern suggests twinning, with the inner ring of twelve diffraction spots corresponding to the superlattice setup between the bilayers. It is this second structure that gives rise to the moiré patterns observed by optical microscopy.

To investigate whether these PS latex arrays comprised latex monolayers or multilayers, light pressure was applied to the wet bubbles on the slide glass during optical microscopy studies. Figure 1c,d suggests that the bubbles are stabilized by single PS monolayers. Similarly, one of the dried foams was deliberately ruptured to allow SEM studies of the foam structure. Mainly latex bilayers were observed (see Figure 4a). This indicates that each air bubble was originally stabilized by a monolayer of adsorbed PS particles, with highly ordered particulate bilayers being formed after loss of the aqueous phase during drainage, see Figure 4b. This result is in good agreement with the optical microscopy studies shown in Figure 1c,d. It is

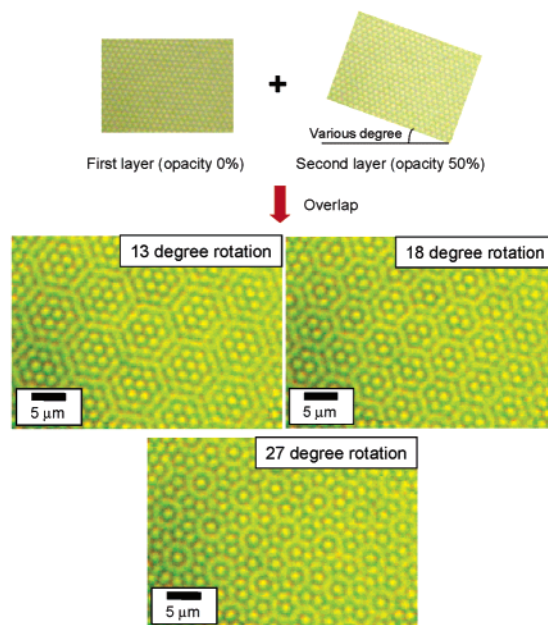
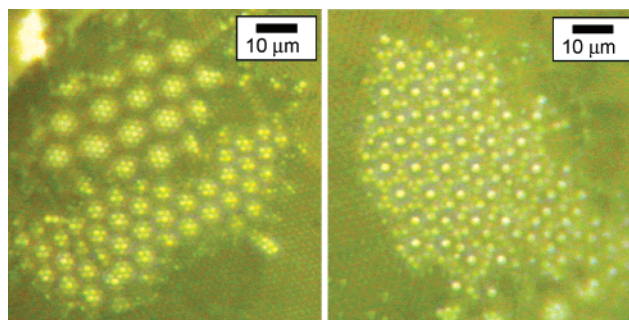


Figure 5. Moiré patterns produced by polystyrene latex bilayers as observed by optical microscopy. Simulation of these images using a PC was achieved by superimposing a semi-transparent (50% transmission) optical micrograph image of a hexagonally ordered latex array onto the identical nontransparent image after rotation of the semi-transparent image through angles of 13, 18, and 27° relative to the nontransparent image.

noteworthy that particle monolayers are also generally formed in solid-stabilized emulsions.^{23–26}

Moiré patterns were observed by optical microscopy when light pressure was applied to a small piece of *dried* foam placed under a microscope slide glass, see Figure 5.²⁷ Complex patterns were obtained, with 3-fold symmetry over two length scales. The smaller length scale is constant and correlates with the hcp structure of the latex spheres. The longer length scale varies from location to location within the foam and is due to optical interference between the latex bilayers, which comprise grains of oriented 2D crystals. Essentially identical moiré patterns can be simulated using a PC by superimposing a digitized optical micrograph of an hcp PS latex monolayer *onto the same image that has been rotated through angles of 13, 18, and 27°* . The formation of such moiré patterns indicates a very high degree

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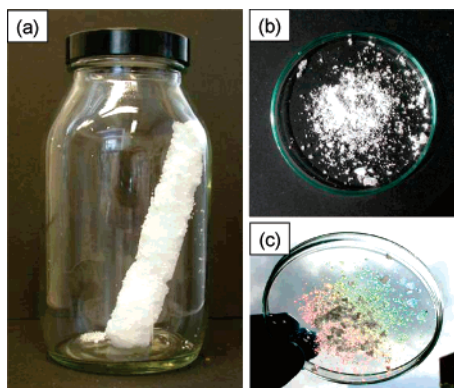


Figure 6. Digital photographs of polystyrene latex-stabilized foams (a) after removal from the foam column and foam fragments viewed (b) under normal light and (c) in transmitted sunlight.

of order within the particulate bilayer foams. Similar moiré patterns were reported when two latex sheets comprising arrays of micrometer-sized polymer particles were overlapped at different angles.^{28–30} However, such latex sheets are much more difficult to fabricate on a large scale than the dried latex foams described in this work.

Wilson has also shown that micrometer-sized PS latex can be used to stabilize bubbles and foams.^{7,8} However, we emphasize that Wilson was only able to obtain stable foams when the colloidal stability of the anionic latex was compromised by the addition of either electrolyte or cationic surfactant or by lowering the solution pH.⁷ In contrast, latex colloid stability is an important aspect of the present work, because it leads to exquisite long-range 2D ordering of the latex particles at the surface of the air bubbles, which is retained in the dried foam. As far as we are aware, the present study is also the first report of foam production using *sterically stabilized* latexes. In contrast, Wilson worked exclusively with *charge-stabilized* latexes, which can be flocculated relatively easily.

A foam column was used to generate PS latex-stabilized foams. The resulting dried foams could be removed from the column as brittle monoliths, see Figure 6a. Such foams were readily broken into small fragments using a spatula, see Figure 6b. When strong sunlight illuminated these foam fragments, the randomly oriented latex bilayer arrays caused light diffraction, producing iridescence, see Figure 6c. Such optical effects are well-known for near-monodisperse *submicrometer-sized* latexes,^{31–35} where the mean particle diameter is comparable to the wavelength of visible light. However, there are relatively few reports describing iridescence effects for latex superstructures based on *micrometer-sized* latexes.^{19,36} It is clear that such iridescence must be due to higher-order reflections from the colloidal crystals, because the length scale of the primary latex particles would only be expected to lead to diffraction at near-infrared wavelengths.

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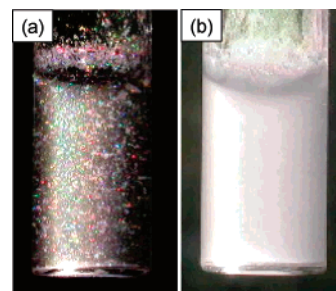


Figure 7. Digital photographs of polystyrene latex-stabilized foam fragments redispersed in water viewed under transmitted sunlight (a) after annealing at 105 °C for 10 min (due to the randomly oriented foam fragments) and (b) without annealing (which allows spontaneous redispersion of the individual latex particles).

The foam fragments were annealed at 105 °C for 10 min in an oven to allow the surfaces of the latex particles to fuse with each other and hence stabilize the foam structure.²⁴ After annealing, the foam fragments could be dispersed in water to produce strongly iridescent aqueous solutions when viewed in strong sunlight, see Figure 7a. Again, each of the randomly oriented colloidal crystal domains acts as a grating to diffract light of a given wavelength, depending on the angle of incidence and orientation of the lattice. In contrast, if the dried foam was not annealed, the dried foam fragments dispersed spontaneously in the aqueous solution and only a turbid milky-white dispersion was produced, see Figure 7b.

We emphasize that the formation of highly stable solid foams is not limited to PNVP-stabilized PS particles. Our preliminary experiments (to be reported elsewhere) indicate that various other types of sterically stabilized latexes also form very stable foams, e.g. poly(acrylic acid)-stabilized PS particles, poly[2-(dimethylamino)ethyl methacrylate]-stabilized PS particles, and PNVP-stabilized poly(methyl methacrylate) particles. Thus, this phenomenon appears to be quite general, because it does not depend on the chemical nature of either the latex core or the latex stabilizer. We are currently exploring a wider range of conditions for bubble formation such as particle size, latex concentration, and the chemical structure of the particle surface and particle core. We believe that such latex-stabilized foams offer considerable potential for new security inks, cosmetics, and coatings, and possibly for the synthesis of advanced materials.

Conclusions

Micrometer-sized, sterically stabilized PS latex particles can be used to prepare highly stable aqueous foams. Such latex foams could be easily generated by either simple hand-shaking or using a foam column, without inducing colloidal destabilization of the latex or using a cosolvent. There was little or no change in foam volume on drying, and SEM studies confirm that the foams comprise latex bilayers, as expected. The exquisite long-range order of these latex bilayers leads to interesting optical properties such as moiré patterns and diffraction effects.

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Supporting Information Available: Full experimental details describing the synthesis and purification of the PS latex particles and the production of highly stable foams by either hand-shaking or using a foam column. Three digital photographs of the foam layer formed above the aqueous PS latex, the isolated wet foam, and the dried foam obtained after evaporation of the aqueous

phase. Fast Fourier transform (FFT) analysis of the SEM image shown in Figure 2b of the hexagonally close-packed PS latex particles. This material is available free of charge via the Internet at <http://pubs.acs.org> **Note Added in Proof.** After submission of this manuscript, another paper appeared in *Langmuir* on so-called “armored” (or latex-stabilized) bubbles, see Subramaniam, A. B.; Mejean, C.; Abkarian, M.; Stone, H. A. *Langmuir*, **2006**, ASAP. This *Langmuir* paper does not detract from the present work but is included here for the interested reader.

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