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Direct Observation of pH-Induced Coalescence of Latex-Stabilized Bubbles Using High-Speed Video Imaging

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The coalescence of pairs of 2 mm air bubbles grown in a dilute electrolyte solution containing a lightly cross-linked 380 nm diameter PEGMA-stabilized poly(2-vinylpyridine) (P2VP) latex was monitored using a high-speed video camera. The air bubbles were highly stable at pH 10 when coated with this latex, although coalescence could be induced by increasing the bubble volume when in contact. Conversely, coalescence was rapid when the bubbles were equilibrated at pH 2, since the latex undergoes a latex-to-microgel transition and the swollen microgel particles are no longer adsorbed at the air–water interface. Rapid coalescence was also observed for latex-coated bubbles equilibrated at pH 10 and then abruptly adjusted to pH 2. Time-dependent postrupture oscillations in the projected surface area of coalescing P2VP-coated bubble pairs were studied using a high-speed video camera in order to reinvestigate the rapid acid-induced catastrophic foam collapse previously reported [Dupin, D.; et al. *J. Mater. Chem.* **2008**, *18*, 545]. At pH 10, the P2VP latex particles adsorbed at the surface of coalescing bubbles reduce the oscillation frequency significantly. This is attributed to a close-packed latex monolayer, which increases the bubble stiffness and hence restricts surface deformation. The swollen P2VP microgel particles that are formed in acid also affected the coalescence dynamics. It was concluded that there was a high concentration of swollen microgel at the air–water interface, which created a localized, viscous surface gel layer that inhibited at least the first period of the surface area oscillation. Close comparison between latex-coated bubbles at pH 10 and those coated with 66 μm spherical glass beads indicated that the former system exhibits more elastic behavior. This was attributed to the compressibility of the latex monolayer on the bubble surface during coalescence. A comparable elastic response was observed for similar sized titania particles, suggesting that particle size is a significant factor in defining the interfacial elasticity of particle-coated bubbles.

Introduction

The stabilization of bubbles and foams by adsorbed particles has been known for over a century.¹ This phenomenon is very important in both food science^{2,3} and mineral flotation.^{4,5} In the former field, bubble stability dictates everything from physical appearance to sensory factors such as “mouth feel”. In the latter field, bubble stability dictates whether the bubble–particle aggregate reaches the froth phase and hence whether the mineralized froth is efficiently collected in the concentrate. In most, if not all, applications, the precise control of foam stability is integral to either process or product performance.

The generally accepted mechanism of particle adhesion to bubbles consists of three elementary stages.⁶ The first step is the approach of a solid particle to the air bubble forming a thin liquid film which has a typical thickness of a few micrometers. The second stage is interfilm drainage due to both gravity and capillary forces. The thinning of the film can be affected by the addition of surface-active molecules or particles, which can

modify the interfacial surface tension and hence stabilize the bubbles. The final stage is the thinning of the interfilm to some critical thickness at which rupture occurs, leading to coalescence. This last step may be affected by the presence of particles in the film layer, which may arise from complete particle dewetting.^{7,8}

The adsorption of relatively large particles depends on the collision probability of a particle hitting a bubble.^{9–12} The collision rate is mostly influenced by fluid dynamics and long-range forces, whereas short-range forces are predominant for particle attachment to the bubble.¹⁰ For smaller particles of colloidal dimensions, Reay and Ratcliff used the Stokes–Einstein equation to calculate the viscous forces acting on a spherical particle approaching a spherical bubble in a quiescent liquid in creeping flow.¹³ Others have extended this early work to include hydrodynamic forces and Brownian diffusion but still failed to account for the influence of particle surface charge.¹⁴ Recently, George et al. proposed a new model that accounts for this important parameter by including terms for the attractive van

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der Waals, electrical double layer, and hydrophobic forces for particle collection by diffusion.¹⁵

Once particles are adsorbed at an air–liquid interface, a rigid film can be created that prevents film destabilization. The foam stability mainly depends on the number and properties of the adsorbed particles, rather than the film properties.^{7,16} Particles that adhere to air–water interfaces modify the curvature of the gas–liquid interface, which in turn reduces the pressure difference between the plateau border and the three films associated with it.¹⁷ This retards film drainage and hence increases the foam stability. The presence of attached particles at the air–liquid interface may also stabilize the froth by blocking liquid drainage within the film. The stability of such films or foams strongly depends on the particle size, shape, concentration, hydrophobicity, and the orientation of particles at the interface as well as the type of surfactant, if any, that is present.

Highly hydrophobic colloidal particles (i.e., with contact angles of 70°–90°) have relatively high interfacial detachment energies.¹⁸ This leads to much better resistance toward desorption during foam drainage, allowing very stable bubbles and foams to be prepared that can remain intact over time scales of months. This enhanced stability is attributed primarily to a strong steric barrier to bubble coalescence.^{19–22} Less hydrophobic particles can also kinetically stabilize bubbles by retarding drainage,^{19,23} either by physically “entrapping fluid”,²⁴ altering bubble curvatures and threshold capillary pressures,^{25–27} or by stratifying in films.^{28,29} Indeed, even weakly hydrophobic latex particles can form stable foams by undergoing a 2D phase transition to form a crystalline surface layer with long-range periodicity.³⁰ Surface charge also plays a very important role with weakly hydrophobic particles, since this can dramatically affect the interfacial interactions. It is well-known that the air–water interface is hydrophobic and also has anionic character.³¹ Hence, reduction of the anionic particle surface charge by judicious adjustment of the dispersion pH can significantly increase the propensity of inorganic oxide particles to adsorb at the air–water interface, thus enhancing foam stability.^{32–34}

Recent advances in so-called “Pickering” or particle-stabilized emulsions³⁵ has led to increasing interest in designing surface-active colloidal particles for the generation of highly stable foams.¹⁹ Armes and co-workers designed a series of surface-active latexes for use as particulate stabilizers of foams in the absence of

any added surfactant.^{36–41} For example, micrometer-sized polystyrene latexes with no ionic surface groups but a poly(*N*-vinylpyrrolidone) steric stabilizer layer were shown to stabilize foams, but similar submicrometer-sized latexes proved to be much less effective.^{36,37} Charge-stabilized polystyrene latexes prepared using a *cationic* radical initiator could also stabilize foams, but only at solution pH values below their isoelectric point, where they acquired strong cationic surface charge.³⁸ Conversely, similar latexes prepared using *anionic* initiators such as persulfate did not lead to stable foams under any circumstances. Submicrometer-sized poly(ethylene glycol) monomethacrylate (PEGMA) stabilized polystyrene latexes with cationic surface character can also stabilize foams, but the best results were obtained at relatively low pH. In this case, the latex was sufficiently small and near-monodisperse to enable its contact angle to be determined by ellipsometry.⁴⁰ Finally, Dupin et al. used the same combination of a PEGMA steric stabilizer and a cationic azo initiator to prepare submicrometer-sized surface-active poly(2-vinylpyridine) (P2VP) latexes.⁴¹ These particles also proved to be very effective foam stabilizers. For example, when formed at pH 10, the resulting foams were stable for up to 6 months. Moreover, wet foams proved to be pH-responsive: addition of acid led to protonation of the cross-linked P2VP chains, and the highly swollen cationic microgel particles were spontaneously desorbed from the air–water interface, leading to rapid bubble coalescence.

Recently, Ata has reported a powerful direct method for investigating bubble coalescence using a high-speed video camera.⁴² Using glass beads with a mean diameter of 66 μm adsorbed onto ~2 mm diameter bubbles, average coalescence times were recorded at up to 3700 frames/s while varying the particle surface coverage of the bubbles over the range 0–94%. Analysis of the coalescing bubble projected area revealed damped simple harmonic motion for particle-coated bubbles compared to particle-free bubbles. These experiments were also performed for a particle-coated bubble coalescing with a naked bubble. Subsequently, Ata focused on the phenomenon of particle detachment during coalescence of a bubble pair in this system.⁴³ The presence of adsorbed glass beads reduces the frequency of the oscillatory motion generated on coalescence by providing a semirigid shell around the bubble wall, which increased the inertia of the surface. Particle size was shown to be an important parameter in this investigation, with larger beads detaching from the interface more readily than smaller ones due to their higher mass and hence momentum on the surface during the bubble oscillation. Particle hydrophobicity also played an important role, with adsorbed surfactant used to increase contact angle and thus reduce bead detachment upon coalescence.

In this study, coalescence events between two bubbles in the presence of near-monodisperse, lightly cross-linked, sterically stabilized P2VP latex particles dispersed in aqueous solution have been observed directly using the same high-speed video camera. Unlike in the previous bubble coalescence studies, these submicrometer-sized latex particles were invisible to the naked eye.

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Table 1. Summary of Bubble Interaction Experiments Investigated

pH	in absence of particles	in presence of particles	particle state
10	2 naked bubbles	2 coated bubbles	380 nm latex
2	2 naked bubbles	2 naked bubbles	swollen microgel
10 → 2 jump	2 naked bubbles at pH 10, then jump to pH 2	2 coated bubbles at pH 10, then jump to pH 2	latex-to-microgel transition

Nevertheless, such particles have already been demonstrated to have strong interfacial activity,⁴¹ and their presence at the air–water interface can be inferred from the oscillatory motion of the coalescing bubbles. In particular, the effect of lowering the solution pH on the kinetics of bubble coalescence induced by the latex-to-microgel transition was investigated and compared with that observed for the nonswollen latex at pH 10.

Experimental Section

Materials. The synthesis and aqueous solution behavior of the PEGMA-stabilized P2VP latex used in this study have been reported previously.⁴⁴ This latex was prepared by a one-shot batch synthesis involving 2-vinylpyridine, a cationic α,α' -azodisobutyramide dihydrochloride initiator, a divinylbenzene (80% 1,4 isomer) cross-linker, a cationic surfactant (Aliquat 336), and a poly(ethylene glycol) monomethacrylate (PEGMA) steric stabilizer. The surface tension of the supernatant after purification by repeated centrifugation–redispersion cycles was 72.4 mN/m, indicating that there is no surfactant or excess stabilizer present after purification. Above pH 4.5, the particles are in their non-swollen latex form, with an intensity-average hydrodynamic diameter of 380 ± 10 nm as judged by dynamic light scattering. The zeta potential becomes increasingly positive below the latex isoelectric point of pH 6.5. The latex has a critical swelling pH of 4.0–4.5, where the particles become protonated and swell rapidly.⁴⁵ Below pH 4.0, the swollen microgel has an intensity-average diameter of 1290 ± 100 nm and a maximum zeta potential of $+22 \pm 2$ mV. The size changes that occur during pH cycling are reversible. For these experiments, 14 μ L of a 10 wt % aqueous latex dispersion was diluted to 50 mL, giving a final concentration of 2.8×10^{-5} wt %. At this dilution the latex has no discernible turbidity to the naked eye and is therefore ideal for high-resolution video capture.

Millipore water was used throughout for rinsing glassware and preparing solutions. 10^{-3} M aqueous KCl solution (Sigma-Aldrich) was used as the background electrolyte for all experiments. A 0.5 M KOH (Merck Pty Ltd.) solution was used to adjust the solution to pH 10. 11.78 M HCl (AnalaR) was used to adjust the solution to pH 2–3. The solution acidity was simply adjusted to a pH known to be well below the critical swelling pH of the latex, rather than to a particular pH value.

Apparatus and Data Analysis. The experimental apparatus has been described previously.⁴² Two master microsyringe pumps (Sarasota, FL) were used to produce air bubbles at the tip of two adjacent capillaries, tipped with stainless steel needles of 1.07 mm and 0.69 mm outer and inner diameter, respectively. The needles were inserted into a beaker containing 50 mL of electrolyte solution and a magnetic stirrer bar. During the experiment the stirrer was set at 350 rpm, which was slow enough to avoid displacement of the bubbles from the needles.

To clean the glassware, needles, and stirrer bar before the experiment, a hydrogen peroxide and ammonia solution was used. The equipment was cleaned and then thoroughly rinsed with Millipore water several times in order to remove any residual

contaminants. This cleaning regime followed the methodology developed in previous studies.⁴²

Coalescence data were obtained using a Phantom V5.0 Mono high-speed camera (Vision Research) at a rate of up to 3773 frames/s. The video footage was assessed frame by frame in order to monitor the appearance and measure the area of the bubbles throughout the coalescence process. The footage was collected on a computer with Phantom 6.30 (Nikon) software at 512×512 resolution. Every fifth frame was analyzed using the Optimus 6.5 software (Media Cybernetics Inc., Silver Spring, MD) to draw around the edges of the bubbles and hence calculate the projected area, which was then plotted against time.

The zero time point was taken to be the point one frame prior to coalescence and defines the original size of the two bubbles. In order to normalize the various coalescence runs, the calculated projected bubble area throughout the experiment was divided by the original bubble area at zero time. Any subsequent area oscillation during coalescence is presented as a fractional change in area relative to this value. The error was calculated from the difference between each run and the averaged runs. The highest error was found to be 5%, indicating that the runs were reproducible.

Experimental Protocol. The direct bubble interaction experiment was performed at two different pH values: 10 and 2. In addition, a third approach used was to grow the bubbles at pH 10 and then rapidly adjust the pH to 2 as shown in Table 1. In each case the experiment was run both in the presence of the P2VP particles and in their absence. This was in order to establish whether the particles provided any stabilization against coalescence and also to determine whether the solution pH alone had any effect on the stability of the two air bubbles.

The bubble coalescence experiments were initially carried out in two modes. In the first mode (grown together), two bubbles were grown to a known size at adjacent capillaries and then brought close together. They were then forced to impinge on each other by adding further air so as to promote coalescence. In the second mode (moved together), two similar-sized bubbles were initially moved close enough together so that a thin film of uncontrolled thickness could be formed between them. The bubbles were then left in this position until the liquid in the film drained out and the film ruptured. It was found that these two modes produced distinctly different oscillation behavior. The resultant bubble formed in the “grown together” mode oscillated at a somewhat higher amplitude and over a longer period of time than the bubbles formed in the “moved together” mode. One reason for this difference in behavior might be that when the bubbles were grown toward each other, the pressure in the film between the bubbles increases as a result of bubble deformation. This higher pressure will cause the film to drain more rapidly and may also result in premature film failure if the approach velocity of the bubbles is large enough not to allow the film to drain to its natural rupture thickness. When the film ruptures, the strain energy stored in the deformed bubbles acts as a driving force for the coalesced bubbles to exhibit high-frequency oscillations. We note that the bubbles formed in the “grown together” mode are about 20% larger than those created in the “moved together” mode. The larger size of the bubbles may also have contributed to the increased oscillation strength observed. It should be noted that the “grown together” mode highlights the difference between the particle-coated bubbles and the uncoated bubbles better than the “moved together” mode, and therefore all the data reported here were gathered by growing bubbles toward each other to initiate their coalescence.

Bubble Coalescence in the Presence of Particles. Two 2 mm diameter air bubbles were grown at a rate of 0.3 mL/h in an aqueous dispersion of P2VP latex in electrolyte solution held at pH 10. This solution was stirred for 2 min to ensure that the latex particles were evenly dispersed. Subsequently, the air bubbles were brought close together (but not to the point of touching) and grown into each other by adding air at the same flow rate to force

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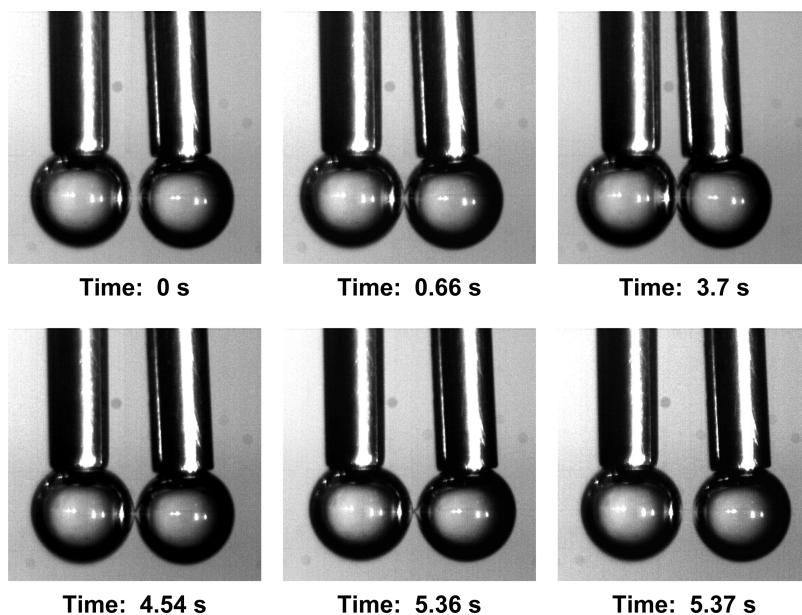


Figure 1. Photos taken from 100 fps video footage of latex-coated bubbles pushed into each other (0–3.7 s) at pH 10 and then moved apart (4.54–5.37 s). Note that the outer diameter of the needles is 1.07 mm; this serves as an appropriate scale bar.

bubble coalescence while being filmed using the high-speed video camera. The same rate of air flow was used in all bubble experiments described in the present work.

Two more bubbles of similar size were then formed in this pH 10 suspension. The air bubbles were brought close together (but not to the point of touching). With the stirrer turned on, concentrated HCl was added to reduce the solution pH to ~2. The system was stirred for a further 5 s before being turned off. The bubbles were then grown together to coalesce while being filmed. This is hereafter referred to as a “pH jump” experiment.

After at least 2 min with stirring two more bubbles were then grown in this aqueous dispersion at pH 2, brought close together (but not to the point of touching) and then grown into each other to promote coalescence while being filmed. The solution was then brought back to pH 10 by the addition of 0.5 M KOH, and this series of experiments was repeated. This cycle was performed two more times until the aqueous dispersion was considered spent.

Bubble Coalescence in the Absence of Particles. The above series of experiments was repeated to the same specification in the absence of any microgel/latex particles in order to assess the impact on bubble coalescence, if any, of the solution pH and total electrolyte concentration. These control experiments were also used to compare hindered and unhindered coalescence.

Viscosity Measurement. The viscosity of the 2.8×10^{-5} wt % P2VP microgel/latex dispersion was measured at pH 2 and 10 using a TA Instruments AR G2 rheometer. A cup (15 mm inner radius) and bob (radius 14 mm) geometry was used with a bob cone angle of 2° .

Surface Tension Measurement. The surface tension of a pendant drop of 2.8×10^{-5} wt % P2VP microgel/latex dispersion at pH 2 and 10 was monitored over 15 min using an OCA20 instrument (DataPhysics Instruments, Germany).

Results and Discussion

Bubble Coalescence in the Presence of P2VP Latex at pH 10.

The latex-coated bubbles proved to be very stable at pH 10 with coalescence being observed only rarely. The coalescence probability, which is defined as the percentage of the number of coalescing bubble pairs divided by the total number of pairs contacted, was $\sim 10\%$. However, in the majority of experiments, the expanding bubbles merely pushed against each other until they became dislodged from the needles, without any coalescence

occurring. Alternatively, the bubbles could be moved apart without coalescence after being initially in contact. Figure 1 shows some of the individual frames obtained for this process (see also Supporting Information video 1). Upon touching (0.66–3.7 s), the contact zone becomes flattened. A bridge is formed upon moving the bubbles apart (4.54–5.37 s), most probably due to long-range capillary forces.⁴⁶ The fact that coalescence is rare under these conditions and that the two bubbles can be pushed together and then retracted simply emphasizes the excellent stability of these latex-coated bubbles. These findings are also consistent with the observed long-term stability of foams stabilized solely by these particles at pH 10.⁴¹

A significant force is required to initiate coalescence by overcoming the steric resistance to film rupture conferred by the latex monolayer surrounding the bubbles. Where bubbles are grown in the presence of the P2VP latex, once the bubble surface is completely coated by the particles, further bubble expansion is resisted. As the air pressure is increased to induce expansion, the fresh interface created on the growing bubbles is immediately coated by further latex adsorbing from solution; this re-establishes monolayer coverage by the latex and reduces the likelihood of bubble coalescence. Occasionally, two or more bubbles coalesced to form a single larger bubble (Figure 2 and Supporting Information video 2). Bubble coalescence begins with rupture of the thin liquid film that separates the two bubbles. Initially, a neck of air is formed between the coalescing bubbles while the outer edges of the bubbles remain unaffected. This causes a surface wave to propagate across the bubble surface, whereby the bubble first expands in the horizontal plane and then contracts and expands to a lesser extent in the vertical plane.

The occasional coalescence is attributed to defects in the latex monolayer, which allow direct contact between the surfaces of the two air bubbles. Dupin et al. previously used SEM to observe perfect hexagonally close-packed crystalline domains of at least 500 P2VP particles in dried foams with defects observed at greater length scales.⁴¹ For the particles adsorbed at the air–aqueous solution interface there are likely to be a greater number of packing defects per interfacial unit area, suggesting that there

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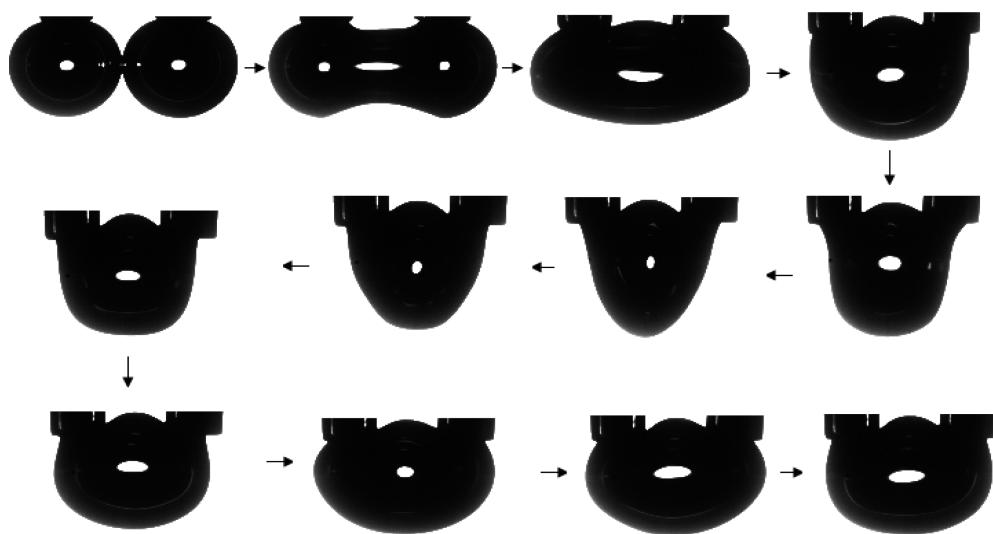


Figure 2. Selected images taken from video footage of the coalescence of latex-coated bubbles at pH 10. The first frame corresponds to zero time. The time difference between each subsequent frame is 1.3 ms. The outer diameter of the needles is 1.07 mm; this serves as a convenient scale bar.

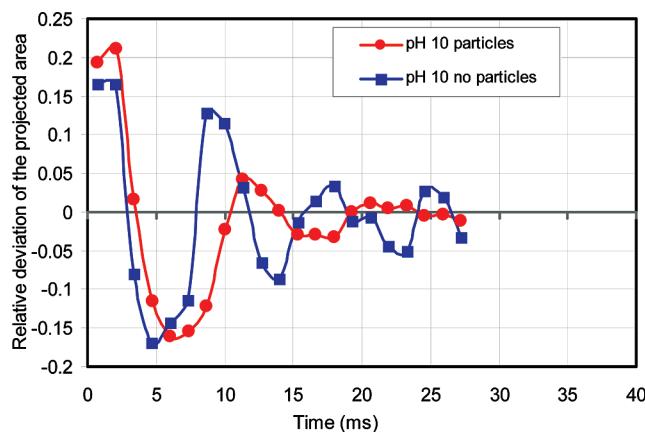


Figure 3. Comparison of the coalescence of P2VP latex-coated bubbles and naked bubbles in terms of the evolution in the normalized fractional change in area over time at pH 10.

will be packing defects on the 2 mm diameter bubbles used here. However, the submicrometer dimensions of the particles prevents direct visualization of their packing at the air–aqueous solution interface; thus, it is difficult to confirm this hypothesis.

When the two original bubbles coalesce, the resulting single bubble experiences both a volume oscillation and a surface area oscillation. The former is caused by the pressure difference between the two smaller bubbles and the final coalesced bubble while the latter is due to the surface energy difference. The oscillation is eventually damped by various processes such as acoustic, thermal, and viscous damping, and the bubble returns to its equilibrium state. Figure 3 shows a typical normalized fractional change in the area of two coalescing bubbles over time at pH 10 in both the presence and absence of P2VP latex particles. The coalesced bubble oscillates between its expanded and contracted state at a characteristic rate. The initial high amplitude quickly decays over time due to strong damping.

The coalescence of two bubbles grown in the presence of aqueous P2VP latex at pH 10 was indeed different relative to coalescence in the absence of any latex (see Figure 3). By comparing these two curves, it is clear that the oscillatory behavior of bubbles grown together in pure electrolyte decays with a shorter

period (higher frequency) than that of the bubbles grown in the presence of the latex. Moreover, the curve of the latex-coated bubble projected area is damped within 20 ms as the new coalesced bubble acquires sphericity, whereas the naked coalesced bubble continues to oscillate irregularly with significant amplitude over a longer period of time (> 25 ms). This suggests that the adsorbed latex monolayer increases the rigidity of the bubble surface and therefore enhances damping. The oscillation frequency is also reduced, probably due to the increased inertia of the surface.

It is important to note that the background electrolyte used for all experiments was KCl. Cain and Lee investigated the coalescence of captive bubbles in aqueous KCl and found greater film stability with increasing salt concentration.⁴⁷ However, it was found that, at a critical KCl concentration of 0.3 M, the electrolyte no longer stabilized the film. This is known as the transition concentration: it is the concentration of solute which must be present in order to arrest film drainage and prevent the same level of coalescence that occurs in pure liquids. Similarly, Lessard and Zieminski reported a KCl transition concentration of 0.23 M.⁴⁸ However, the maximum electrolyte concentration used in the present study is about an order of magnitude lower than these critical values, and therefore it is not expected to have a significant effect on the bubble stability. Indeed, similar coalescence dynamics were observed in the absence of P2VP particles at both pH 10 and pH 2 throughout the investigation.

Bubble Coalescence in the Presence of P2VP Microgel Particles at pH 2. At pH 2, the particles undergo a latex-to-microgel transition via protonation of the pyridine residues and swell up to 37 times their original latex volume.⁴⁴ Figure 4 shows the coalescence of a bubble pair at pH 2 in the presence of swollen P2VP microgel particles, which is similar to the coalescence process at pH 10 (Figure 2). However, in contrast to the latex-stabilized bubbles formed at pH 10, bubbles formed in the presence of swollen cationic microgel particles at pH 2 coalesced on contact with a probability of 100% (see Supporting Information video 3).

Figure 5 shows the coalescence dynamics of a bubble pair in the presence of swollen P2VP microgel particles both in pH 2 solution

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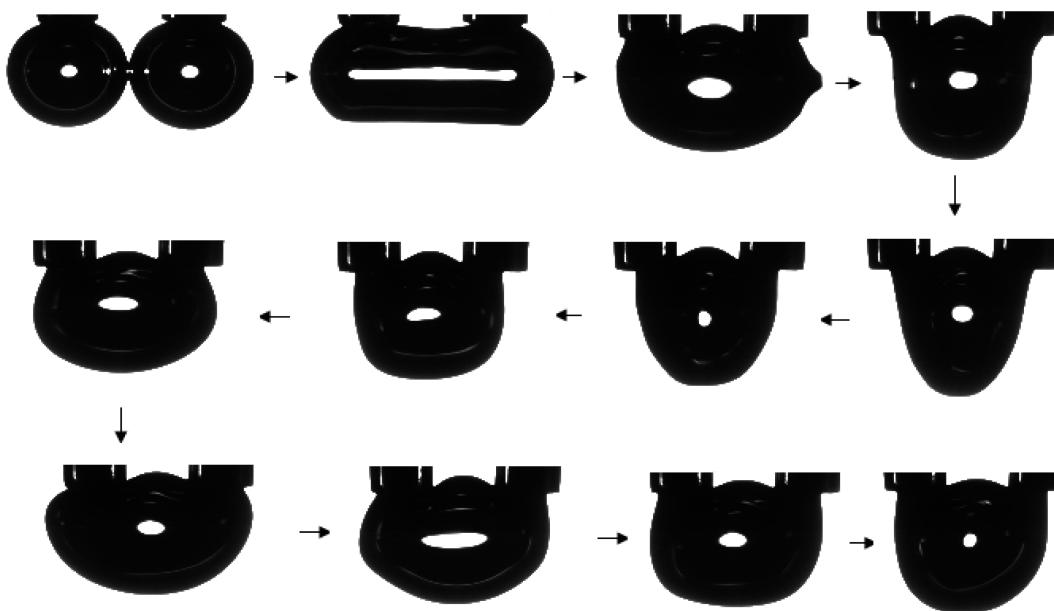


Figure 4. Photos taken from digital footage (every fifth frame) of bubble coalescence in the presence of an aqueous dispersion of P2VP microgel particles at pH 2. The first frame corresponds to zero time. The time difference between each subsequent frame is 1.3 ms. The outer diameter of the needles is 1.07 mm.

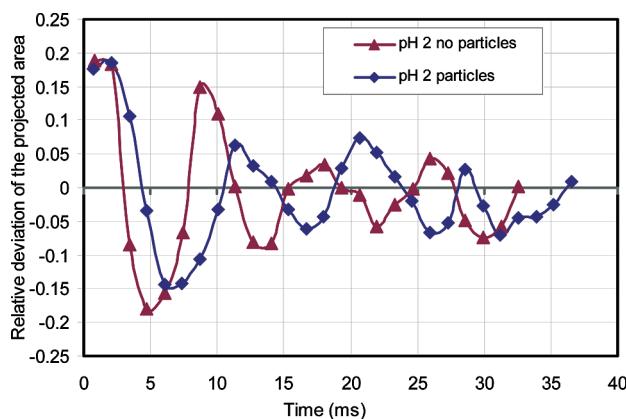


Figure 5. Comparison of the coalescence dynamics of a bubble pair at pH 2 in the presence and absence of swollen P2VP microgel particles in terms of the normalized fractional change in area over time.

and also in electrolyte alone. It is noteworthy that the coalescence dynamics in the absence of any particles in the aqueous solution shown in Figure 5 are almost equivalent to those at pH 10 shown in Figure 3. The bubbles grown in the presence of P2VP microgel particles at pH 2 rather surprisingly exhibit reduced oscillation amplitudes and an increased period of oscillation compared to the bubbles grown in electrolyte alone.

In principle, the swollen P2VP microgel particles in the aqueous phase can affect the bubble oscillation behavior by increasing the solution viscosity above that of the background electrolyte. Indeed, a free-standing cationic gel was formed at ~ 3 wt % when these lightly cross-linked P2VP particles become swollen at low pH. However, the solution viscosity of the 2.8×10^{-5} wt % P2VP dispersion used for the bubble coalescence experiments was the same at pH 2 as that observed at pH 10 and is equal to that of the 10^{-3} M background electrolyte within experimental error. Thus, the P2VP latex concentration is so low it has a negligible effect on the solution viscosity, so the observed difference between the pH 2

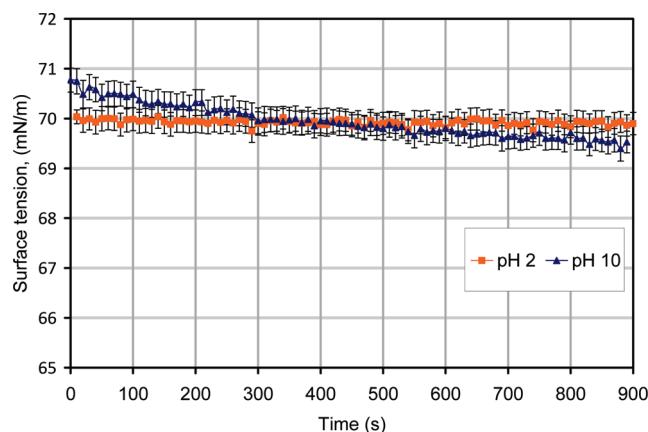


Figure 6. Dynamic surface tension for a pendant drop of 2.8×10^{-5} wt % P2VP microgel/latex dispersion at pH 2 and 10. It is clear that the swollen microgel particles at pH 2 do not influence the surface tension, while the solid latex particles at pH 10 result in a small decrease in surface tension when they adsorb.

experiments conducted in the presence and absence of P2VP particles is unlikely to be due to changes in solution viscosity.

A second possibility is that the cationic P2VP microgel particles formed at pH 2 might simply be electrostatically attracted to the anionic gas–liquid interface, retarding the bubble motion. However, dynamic surface tension measurements did not detect any reduction in surface tension of the air-swollen microgel solution interface below the 70 mN/m recorded for the background electrolyte at pH 2 (see Figure 6). Thus, there is no simple explanation for the damping of the coalescence oscillation observed at pH 2 since there is no measurable change in the bulk solution viscosity, nor any evidence for adsorption of the swollen microgel particles at the air–aqueous solution interface. Hence, it was decided to investigate pairs of bubbles initially coated with nonswollen latex particles at pH 10, followed by exposure to acid.

Bubble Coalescence in the Presence of Particles: pH Jump Experiments. A pair of bubbles was initially grown in the

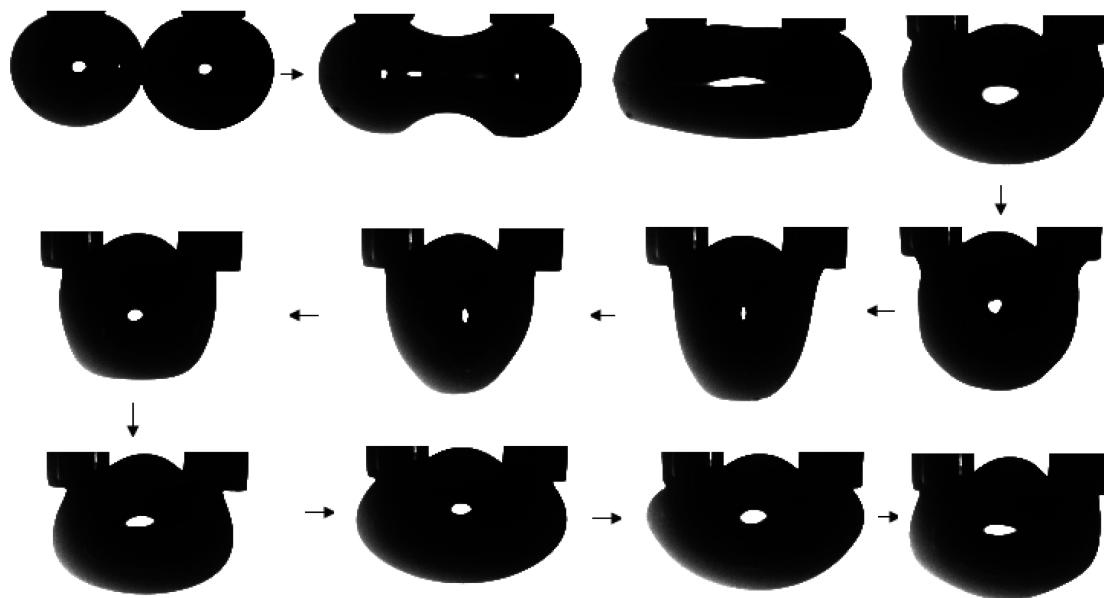


Figure 7. Selected frames taken from digital video footage (every fifth frame) of bubble coalescence in an aqueous P2VP dispersion initially at pH 10 (latex state) and rapidly adjusted to pH 2 (microgel state). The first frame corresponds to zero time. The time difference between each subsequent frame is 1.3 ms. The outer diameter of the needles is 1.07 mm.

presence of the P2VP latex particles at pH 10 and were therefore coated by close-packed latex monolayers.⁴¹ The solution pH was then adjusted to pH 2, and the two bubbles were grown together, resulting in rapid coalescence with a probability of 100% as shown in Figure 7. The P2VP particles are known to undergo a rapid latex-to-microgel transition upon lowering the solution pH below their critical swelling pH of 4.0–4.5.⁴⁵ The characteristic swelling times for these particles was determined to be of the order of tens of milliseconds using stopped-flow kinetics. Their volumetric increase upon protonation and swelling with solvent has been measured to be a factor of around 37.⁴⁴ The increased size and high cationic charge density of the swollen P2VP microgel particles at pH 2 should lead to rapid microgel desorption from the bubble interface prior to the bubbles being grown together. The video images shown in Figure 7 suggest that the bubble surfaces are indeed now free of adsorbed P2VP particles. This direct time-resolved bubble experiment is analogous to the observation of catastrophic foam breaking reported by Dupin et al. under similar conditions.⁴¹

The coalescence behavior in Figure 7 is similar to that observed for the P2VP latex at pH 10 alone and the swollen P2VP microgel at pH 2, but with some notable differences. The major difference in the expansion and contraction cycle is that the coalesced bubble appears to oscillate over a longer time period than the latex-coated bubble at pH 10 (see Supporting Information video 4). It is noteworthy that, even though the elapsed time between the consecutive frames shown in Figures 2, 4, and 7 is the same, caution should be exercised when making a frame-by-frame comparison. This is because film rupture can be very fast during bubble coalescence⁴⁹ and may well occur on time scales shorter than the difference between two consecutive frames (270 μ s) captured in the present study. Therefore, it is unlikely that the image series shown in these figures actually correspond to the same stages of coalescence. The overall bubble coalescence events for the three systems are best compared in their respective supporting videos, which contain significant additional dynamic information.

The differences in bubble coalescence dynamics observed in both the presence and absence of the P2VP latex/microgel particles in the pH jump regime shown in Figure 7 provides a more detailed understanding of bubble coalescence behavior. A comparison of the relative deviation in the projected area over time for bubbles grown in both the presence and absence of P2VP particles in the pH jump regime is shown in Figure 8. The curve obtained for the latex-coated bubble at pH 10 flattens out after \sim 20 ms (Figure 3), whereas the pH jump curve continues to oscillate over a longer period of time with a significant amplitude. The latter behavior is similar to that of bubbles grown in an electrolyte solution containing no P2VP particles or bubbles equilibrated at pH 2 in the presence of P2VP microgel particles (Figure 5). However, the characteristic period for the pH jump coalescence dynamics in the presence of P2VP particles is significantly longer than that obtained in the absence of particles; this finding merits further discussion.

The oscillatory behavior of the coalescing bubble is affected significantly by viscous stress. However, viscosity measurements conducted at pH 2 confirmed that the swollen microgels do not have any effect on the bulk viscosity of the solution. An alternative explanation could involve the kinetics of P2VP particle desorption from the bubble surface at lower pH. As stated earlier, the P2VP latex is pH-responsive and becomes substantially protonated at around pH 4, leading to a latex-to-microgel transition for isolated particles within time scales of \sim 10 ms.⁴⁵ However, when swelling is induced at the bubble surface, the process is likely to be hindered by neighboring latex particles within the monolayer coating the bubble. This may lead to significant overlap between the period required for latex swelling and that required for bubble coalescence. The minimum experimentally accessible time interval from acid addition to bubble coalescence in the pH jump regime is estimated to be 15 s, with the solution stirred for the first 5 s, and the bubbles subsequently grown together. The time scale for bubble coalescence, from initial film rupture until the bubble oscillations are finally damped, is around 45–50 ms. Thus, it appears at first sight that there is plenty of time for the P2VP latex particles to both swell and detach from the bubble surface. However, if these processes

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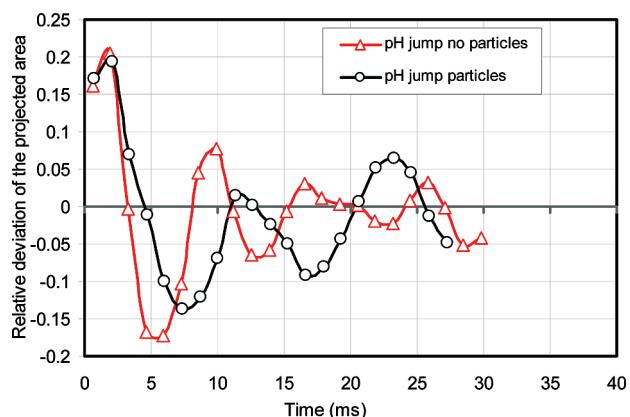


Figure 8. Comparison of bubble coalescence dynamics in the presence and absence of P2VP latex/microgel in terms of the normalized fractional change in projected area over time in the pH jump regime.

are significantly retarded, the P2VP latex may still be swelling as the film ruptures. Alternatively, the desorbed P2VP microgel may still be in close proximity to the bubble. Clearly, if any P2VP particles are still adsorbed at the bubble surface or if there is a high local P2VP microgel concentration in the immediate vicinity of the bubbles, their oscillatory behavior upon coalescence is likely to be affected.

However, this hypothesis does not explain the oscillation behavior of the coalesced bubble equilibrated for at least 2 min at pH 2 in the presence of P2VP microgel shown in Figure 5. This coalesced bubble oscillates at lower frequency and amplitude than that produced in the absence of any P2VP particles at the same pH. These bubble coalescence experiments were certainly conducted after sufficient time was allowed for the P2VP particles to attain their microgel state, and hence no swollen microgels are expected to be adsorbed at the bubble surface.

In Figure 9, the bubble oscillation behavior observed in the presence of the P2VP latex at pH 10 and the P2VP microgel at pH 2 are compared to that in the pH jump regime. The coalesced bubbles in the acidic solutions oscillate over a relatively long time scale, while the latex-coated coalesced bubble stabilizes quickly after only ~ 2 periods. Interestingly, the bubbles have almost the same initial period and amplitude for each of the three systems, although the first period is slightly longer in the pH jump experiment. The reason for this similarity is not immediately clear. During coalescence of a bubble pair, the surface energy release causes the interface to move at high velocity.⁴⁹ The surface wave starts from the contact point of the bubbles where film rupture first occurs and moves rapidly toward the extremities of the bubble, causing oscillatory axial motion. One possibility is that the surface waves formed at the gas–aqueous solution interface may disturb the organization of any adsorbed particles. This could create packing defects or even leave the surface partially bare, requiring dissipation of the increased surface energy. Any adsorbed particles should eventually regain their original local structure once the oscillating bubble loses its momentum, and there is sufficient time for particle rearrangement to occur on the bubble surface.

The fact that the coalesced bubble formed in acidic solution oscillates over a longer total time interval than the latex-coated bubbles at pH 10 (see Figure 9) suggests that the P2VP microgel particles either increase the bubble rigidity or confer stabilization only for the first period of oscillation. This hypothesis is supported by the slightly longer first period in the pH jump experiment,

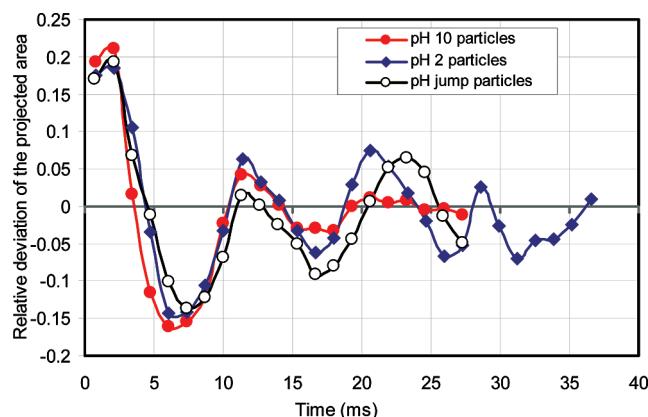


Figure 9. Evolution of bubble oscillation behavior with time observed in the presence of the P2VP particles at pH 10, pH 2, and in the pH jump experiment expressed in terms of the normalized fractional change in area over time.

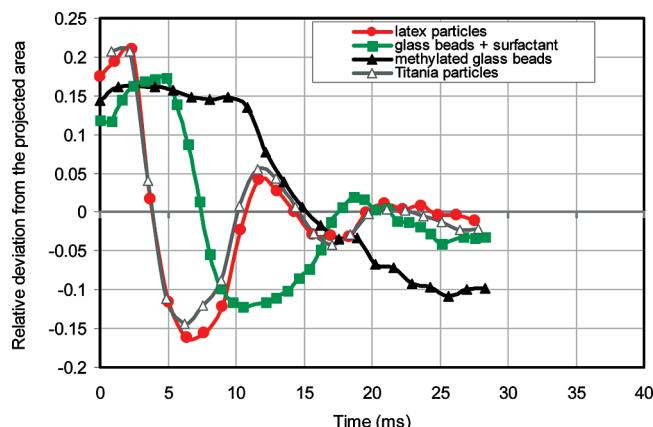


Figure 10. Evolution of oscillatory behavior of coalescing bubbles coated with 380 nm P2VP latex at pH 10, 200 nm hydrophobized titania, and 66 μm glass beads as a function of time.

which may indicate the short-lived presence of swelling microgel particles at the air–water interface. It is concluded that, in the presence of acid, swollen microgel particles are weakly attached to the bubble surfaces initially but are desorbed from the surface after the coalesced bubble starts to contract and expand rapidly during the subsequent oscillations.

Oscillations of Bubbles Coated with Different Particle Types and Sizes.

The oscillatory behavior of the forced coalescence of bubbles coated with either P2VP latex particles at pH 10, similarly sized titania (anatase) particles with an average diameter of 200 nm, and large glass beads of arithmetic mean diameter of 66 μm coated with cationic CTAB or chemically hydrophobized glass beads having the same mean diameter are compared in Figure 10. The titania particles were hydrophobically modified by low-temperature plasma treatment in the presence of a vapor-phase silane coupling agent.⁵⁰ The titania concentration was 0.02 wt %, and the bubbles were equilibrated in this dispersion for 5 min before contact with the adjacent bubble. In the presence of CTAB, the surfactant concentration and the contact angle of the glass beads were 1×10^{-4} mM and 30°, respectively. The two bubbles grown at adjacent capillaries were both visibly coated with a monolayer of glass beads. Coalescence was achieved by growing these bubbles toward each other.⁴² The hydrophobized

(50) Pugh, R. J. *Langmuir* 2007, 23, 7972.

glass beads were treated with trimethylchlorosilane in *n*-hexane to yield methylated beads with a contact angle of 90°. The capillaries in this system were positioned in a vertical arrangement.⁴³ The bead-coated bubbles were forced into contact by lowering the uppermost bubble using a microtranslator so as to increase the likelihood of coalescence. The contact angles of the P2VP latex at pH 10 and the titania particles are likely to lie somewhere between these two contact angles.⁴⁰

Inspecting Figure 10, it is clear that the P2VP latex-coated and titania-coated bubbles have a relatively short period and high amplitude and oscillate over a longer period of time. In contrast, the glass bead-coated bubbles exhibit more strongly damped oscillatory motion with reduced amplitudes, suggesting that the surface of these bubbles is more rigid (and able to support a greater shear stress) than a latex-coated interface.⁵¹ Comparing the bubbles covered with glass beads of differing hydrophobicity, the particles with the higher contact angle stabilize more rigid bubbles, as expected. Indeed, the coalesced bubble does not even complete a full oscillatory cycle before it attains its final shape. There are also qualitative differences in the formation of the neck during bubble contact in these three systems. For latex-coated bubbles, neck growth occurs rapidly, starting from a point contact followed by a relatively fast increase over time. In contrast, neck formation for the more hydrophobic glass beads is slower, since the particles are more strongly adsorbed to the interface.

The results clearly suggest that the coalescing latex-coated and titania-coated bubbles exhibit much more elastic behavior than the relatively rigid, nondeformable bubbles coated with glass beads. One difficulty is that, unlike the larger glass beads, the latex and titania particles are too small to be directly observable. It is therefore theoretically possible that the coalescing bubbles may not be fully coated with these particles or that the coating contains minor packing defects, rather than being a perfect hexagonally close-packed monolayer. Any packing defects are expected to reduce the damping of the coalescence oscillation. However, from our previous work on latex-stabilized foams gross packing defects seem unlikely; SEM studies have confirmed that the P2VP latex particles form highly ordered monolayers at the air–liquid interface.⁴¹ Moreover, if locally organized patches of latex and titania particles are the preferred arrangement on individual air bubbles, the surface area that is lost during bubble coalescence should draw any such patches closer together, thus enhancing the surface organization. In addition, although the glass beads are in direct contact with each other, only imperfect packing occurs at the bubble interface,⁵² yet the adsorbed beads confer strong damping on the oscillatory behavior of the coalescing bubbles.

A more likely explanation for the observed elasticity of the latex-coated bubble interface lies in the short-range interparticle forces. The P2VP latex particles are sterically stabilized by ~3.6 nm of nonionic poly(ethylene glycol) monomethacrylate.⁴⁰ Indeed, the consequent steric repulsion is largely responsible for the excellent colloidal stability of dispersions of these particles. This dominant repulsion will also maintain the particles at a finite separation on the bubble interface in the absence of any applied force. In addition, this steric repulsion and finite interparticle separation are likely to absorb the energy of the forced coalescence and yield the observed elastic interfacial compression. Indeed, interfacial elasticity at the air–water interface has been reported by Ravera and co-workers for silica particles in the presence and absence of CTAB.⁵³ Recently, it has also been

observed for surfactant-free sterically stabilized silica particles of comparable dimensions to the P2VP latex under investigation here.⁵⁴ These hydrophobized silica particles had a measured contact angle of 73.5°.²³ Such interfacial elasticity is concluded to be responsible for the previously reported high stability of foams stabilized by these P2VP particles,⁴¹ since the latex-coated bubble interface can recover from certain applied stresses. We are currently conducting a detailed investigation of the titania-coated interface and will address the mechanism that underpins the behavior of this system in a subsequent publication.

Conversely, the interparticle forces between the 66 μm glass beads used in the experiments shown in Figure 10 are dominated by capillary attractions. Neither the methylated glass beads nor the surfactant charge-compensated glass beads should exhibit significant interparticle repulsion and in fact may well experience a hydrophobic interparticle attraction. The average interparticle distance is therefore expected to be shorter than that within the latex monolayer since the glass beads are in direct contact with each other. Hence, the glass bead coatings are not expected to be able to adsorb much energy upon coalescence and should simply resist surface deformations.

Comparing the two glass bead systems, the interparticle distance is more likely to be much shorter for the hydrophobized glass. The total surface area of the resulting bubble formed by the coalescence of the two bubbles is ~20% smaller than the sum of the surface areas of the individual bubbles before coalescence. It is therefore expected that, in the case when two completely coated bubbles coalesce, some of the particles are expelled from the interface due to insufficient surface area. However, upon bubble coalescence the visible hydrophobized particles appear to remain attached with hardly any particle expulsion from the interface despite a significant reduction in the total surface area. Moreover, coalescence would reduce the interparticle distance to within the range of the hydrophobic attraction and even force some particles to form a bilayer (or perhaps multilayers) on the surface,⁴³ resulting in the rigid and nondeformable surface observed in Figure 10. Unlike the hydrophobized glass beads, the surfactant-treated glass bead-coated coalesced bubble exhibited both more elastic behavior and also compression/expansion cycles. During the compression cycle the visible individual beads appeared to roll over each other and form irregular multilayered regions. It was also observed that some particles detached from the interface probably due to instability in the movement of the three-phase contact line on the particle surface during the oscillation process.⁵¹ It is noteworthy that no indication of gross folding or buckling of the particle layer was observed during the coalescence of bubbles coated with either type of glass beads.

Forced coalescence of the latex-coated bubbles at pH 10 most likely does, however, lead to folding or buckling of the compressed latex monolayer rather than latex particle detachment, since these P2VP particles are likely to be strongly attached to the air–water interface.¹⁸ Detachment has been observed for 122 nm PEGMA-stabilized polystyrene latexes on the surface of a Langmuir trough at pH 2.⁴⁰ However, this polystyrene latex had a contact angle of 43° and stabilizes much weaker foams than those obtained with the larger P2VP latex under investigation here. Folding of the particle monolayer has been directly observed for 270 nm silica particles with a contact angle of 37° at the air–water interface using Brewster angle microscopy.⁵⁵ Both these literature examples suggest a relatively high contact angle for the P2VP

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latex at pH 10, but unfortunately this parameter could not be determined due to the relatively small difference between the refractive indices of P2VP and water.⁴⁰ It is perhaps worth emphasizing that, since there are excess P2VP particles available in solution during the coalescence of the latex-coated bubbles, further latex adsorption is possible if any fresh interface is created during the expansion cycle of the area oscillation. Such *in situ* adsorption would restabilize the expanding interface.

The elasticity of hard particle layers at fluid interfaces has been the subject of a number of prior studies.^{56–58} Overall, the elasticity observed in the postrupture oscillation in the current work is expected to be determined by the compressibility of the particles, which is in turn influenced by interparticle forces, the interfacial particle packing, and the capacity for rearrangement of the particles on the surface during compression/expansion cycles. Our results strongly suggest that particle size is a dominant factor in defining the interfacial elasticity of particle-coated bubbles.

Conclusions

The high-speed video images and projected area oscillation patterns obtained for the bubble coalescence dynamics are information-rich. The P2VP latex particles very effectively stabilize the bubbles at pH 10 by adsorbing in a close-packed monolayer, making the bubbles relatively rigid and hence unlikely to undergo coalescence without a significant applied force. Conversely, the catastrophic foam collapse reported previously upon exposure to acid is consistent with the rapid bubble coalescence observed at pH 2. Control experiments performed in the absence of any P2VP particles confirm that the swollen microgel particles do actually affect bubble coalescence by increasing the period and also damping the area oscillations. Thus, there must be highly cationic microgel particles in the vicinity of the air–water interface. While not reducing interfacial tension, the relatively high

local particle concentration appears to increase the local interfacial viscosity, at least for the first period of the coalescence oscillation.

Comparing the bubble coalescence results in the presence of the P2VP microgel latex to the coalescence of bubbles coated with large glass beads indicates that the P2VP latex monolayer formed at pH 10 yields an elastic compressible barrier to coalescence. This provides an effective barrier to film rupture that prevents bubble coalescence in the majority of cases. In those cases when coalescence does occur, it may be due to one or more defects within the latex monolayer that allows contact between the two bubbles and thus coalescence. Comparable elastic coalescence dynamics were observed for bubbles coated with hydrophobically modified titania particles of similar dimensions, which suggests that this is a more general phenomenon.

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Supporting Information Available: Four representative videos of two approaching bubbles recorded in 2.8×10^{-5} wt % microgel/latex dispersions: (1) two very stable bubbles coated with P2VP latex approaching and moving apart without coalescence at pH 10; (2) an example of the rare coalescence of two bubbles coated with P2VP latex at pH 10; (3) an example of the rapid coalescence of two bubbles in a dispersion of a swollen P2VP microgel at pH 2; (4) an example of the rapid coalescence of two bubbles during a pH jump from pH 10 to pH 2 (the videos contain every 6th frame of original recording at 3700 fps). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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