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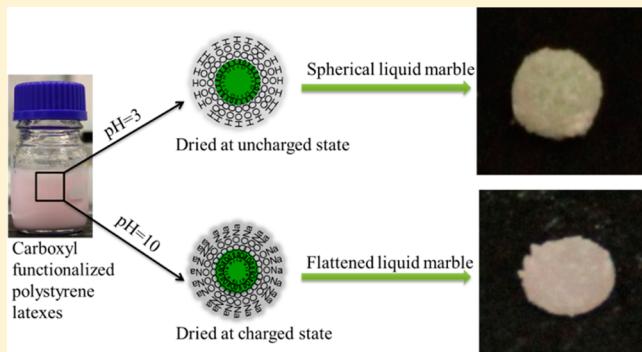
Liquid Marbles Stabilized by Charged Polymer Latexes: How Does the Drying of the Latex Particles Affect the Properties of Liquid Marbles?

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ABSTRACT: The coating of solid particles on the surface of liquid in air makes liquid marbles a promising approach in the transportation of a small amount of liquid. The stabilization of liquid marbles by polymeric latex particles imparts extra triggers such as pH and temperature, leading to the remote manipulation of droplets for many potential applications. Because the functionalized polymeric latexes can exist either as colloidally stable latex or as flocculated latex in a dispersion, the drying of latex dispersions under different conditions may play a significant role in the stabilization of subsequent liquid marbles. This article presents the investigation of liquid marbles stabilized by poly(styrene-co-methacrylic acid) (PS-*co*-MAA) particles drying under varied conditions. Protonation of the particles before freeze drying makes the particles excellent liquid marble stabilizers, but it is hard to stabilize liquid marbles for particles dried in their deprotonated states. The static properties of liquid marbles with increasing concentrations of protonating reagent revealed that the liquid marbles are gradually undermined by protonating the stabilizers. Furthermore, the liquid marbles stabilized by different particles showed distinct behaviors in separation and merging manipulated by tweezers. This study shows that the initial state of the particles should be carefully taken into account in formulating liquid marbles.



INTRODUCTION

Liquid marbles, also termed nonstick water, were first prepared by Aussillous and Quéré in 2001 by simply rolling small water droplets on hydrophobic lycopodium grains or other types of hydrophobic particle beds.^{1,2} Unlike conventional approaches of chemical modification of the surface of the substrates, the coating of the particles at the air–liquid interface proved to be an effective way to reduce the adhesion forces of water droplets with the substrates, which thus is a promising way to overcome the difficulties in transportation of a small amount of liquid in microfluidics devices. Since this pioneering work, there has been growing research effort in both theoretical and application studies during the past decade.^{3–6} The properties of liquid marbles, such as the ability to deform their shapes,⁷ the effective surface tension,^{8–10} and the evaporation rate^{11,12} have been subject to intensive investigations. Various potential applications, such as microreactors,^{13–15} gas sensing,¹⁶ and pollution detection¹⁷ have also been explored. However, the major obstacle of the practical use of liquid marbles is the fast evaporation rate of the encapsulated inner liquid, mostly water. One approach to solving this problem described by Gao and McCarthy was to use ionic liquids, which are nonvolatile and versatile solvents, encapsulated by fluoropolymer-based particles.^{18,19} Hence, in order to make use of liquid marbles in

potential applications, the evaporation rate of the encapsulated liquid must be controlled.

Liquid marbles are usually prepared from relatively hydrophobic particles that adsorb at the gas–liquid interface, but there are investigations that report the liquid marbles stabilized by hydrophilic carbon black.²⁰ Much of the literature has initially been focused on using inorganic particles, such as hydrophobic silica particles,^{21,22} carbon black,²⁰ and graphite powder.²³ Recently, organic polymer latexes as liquid marble stabilizers have become more widespread. It was claimed that these polymer particles can be tailor made with specific surface chemistry (and hence wettability) using various functional monomers, and thus they are particularly attractive for preparing liquid marbles and can also be used as templates for the production of microcapsules.²⁴ In addition, a variety of stimulus-responsive characters can be easily introduced into polymer particles so that one might wonder if the particle stabilizers can under some conditions impart to the resulting liquid water marbles their responsiveness to external stimuli, showing promising applications as smart materials. Armes and Fujii have recently employed a series of sterically stabilized

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polystyrene (PS) latex particles made by dispersion polymerization using a macroinitiator as the marble stabilizer for making stimulus-responsive liquid marbles.^{25,26} For example, PS latexes synthesized from poly[2-(diethylamino)ethyl methacrylate] macromonomer (PS-*co*-PEDA) were used for the preparation of liquid marbles that were stable when placed on the surface of water at neutral or alkaline pH but disintegrated upon addition of acid. This is because the protonation of the tertiary amine-based stabilizer chains changes the latex surface from hydrophobic to hydrophilic, resulting in destabilizing the liquid marbles.²⁵ The chemically grafted PEDa was considered to play an essential role in the stabilization of liquid marbles because it was argued that no liquid marbles could be formed using either simple charged PS latexes or sterically stabilized PS latexes made using hydrophilic poly(ethylene glycol) (PEG) chains. Moreover, for liquid marbles prepared using a polyacid-stabilized PS latex particle as a stabilizer, they remain intact when placed in an acidic aqueous solution. However, the addition of base to the aqueous solution causes the immediately disintegration of the liquid marble because the stabilizer chains on the latex surface become highly hydrophilic at alkaline pH. Such liquid marbles thereby exhibit complementary behavior to those stabilized by PS-*co*-PEDA latex particles.²⁶

In both pH-responsive liquid marble cases discussed above, we can see that importance of using PS latex particles coated with an outer layer of a stimulus-responsive polymer to confer stimulus-responsive behavior to the resulting liquid marbles. Because the coated polymer chains become neutral (and hence hydrophobic) or hydrophilic depending on whether they are in an ionized or unionized state in the dispersions, the functionalized PS particles can exist either as a colloidally stable latex with highly charged outer layer chains or as a flocculated latex with neutral/hydrophobic outer layer chains in the dispersions under different pH values. In this way, one may wonder if drying the latex particles at different pH values will lead to latex powders with different forms and properties, which then may affect their ability to stabilize the liquid marbles. However, the question regarding how drying of the functionalized polymer latexes influences liquid marble formation and their consequent stimuli-responsive property has not been studied.

In this article, we examine in detail the formation and properties of liquid marbles stabilized by polymer latex particles that are dried under different initial conditions. The particles we used are poly(styrene-*co*-methacrylic acid) (PS-*co*-MAA) particles that can be easily synthesized via simple surfactant-free emulsion polymerization. Copolymerization with MAA provides the carboxyl groups ($-\text{COOH}$) that allow us to vary the surface charge, that is, the wettability of the particles, by changing the solution pH. Previously, we reported that PS-*co*-MAA latexes with predominantly un-ionized carboxyl group at the low pH value are expected to be more hydrophobic and stabilize water droplets in oil. In contrast, at the high pH value, deprotonation of the carboxyl groups on the surfaces results in the surface charge or hydrophilicity of these particles increasing significantly, and they can stabilize oil droplets in water.²⁷ Herein we show that drying the PS-*co*-MAA dispersions to powders from either the un-ionized (at pH 3) or ionized state (at pH 10) will significantly affect the stability and property of the resulting liquid marbles, which has not been discussed for liquid marbles stabilized by both PS-*co*-PEDA and polyacid-stabilized latex particles. In addition, we also investigate the shape evolution of a liquid marble with increasing water volume

and the mechanical integrity of liquid marbles stabilized by charged PS latex particles dried under different ionizations from the dispersions.

MATERIALS AND METHODS

Materials. Styrene (99% stabilized by 4-*tert*-butylcatechol, Sigma-Aldrich) was purified through a basic alumina column, and potassium persulfate (KPS) was purified by recrystallization from deionized water. Divinylbenzene (DVB, 80%, Sigma-Aldrich), methacrylic acid (MAA, Sigma-Aldrich), methacryloyloxyethyl thiocarbamoyl rhodamine B (MRB, Polysciences, Inc.), hydrochloric acid (analytical grade, Lab-scan Ltd.), and sodium hydroxide (analytical grade, Lab-scan Ltd.) were used without purification. Deionized water (DI water, resistivity $>18.2 \text{ M}\Omega\text{-cm}$) was used throughout all of the experiments.

Synthesis and Characterization of Poly(styrene-*co*-methacrylic acid) (PS-*co*-MAA) Particles. The particles are synthesized via a typical surfactant-free emulsion polymerization. Briefly, 5 g of styrene, 0.1 g of DVB, 0.25 g of MAA, and 5 mg of MRB were dissolved in 140 mL of DI water in a 250 mL three-necked reactor fitted with a nitrogen bubbling inlet and outlet and a reflux condenser and were stirred with a magnetic stir bar. The temperature of the reaction medium was controlled by an oil bath that was heated with a magnetic hot plate (Cimarec, Thermal Scientific). The reaction medium was stirred at about 400 rpm with nitrogen bubbling for 40 min at ambient temperature. Then 0.15 g of KPS dissolved in 10 mL of DI water was injected into the reaction medium to initiate the free-radical polymerization as soon as the temperature was increased to 70 °C. The reaction medium was kept at 70 °C for 24 h. The as-obtained latex particles were subjected to repeated centrifugation at 10 000g (3–18 K, Sigma Laborzentrifugen GmbH) for 30 min to remove the unreacted monomers and any free polymer chains. Then final particle sediments were redispersed in DI water to obtain the particle suspension. The size of the latex particles was measured using a Coulter Counter LS 230, which is shown in Figure 1a. The average diameter of the particles was around 350 nm. For SEM observation, a diluted PS-*co*-MAA suspension was dried at room temperature for 24 h and then coated with Au before imaging PS-*co*-MAA on an FEI Quanta 400 FEG microscope operating at 10 kV (inset of Figure 1a).

For the freeze drying of the PS-*co*-MAA particles, the pH of the suspension was adjusted to the desired value with 1 M HCl(aq) or 1 M NaOH(aq), and then the suspension was quenched with liquid nitrogen. The water of particle suspension was then sublimated under vacuum pumped by an oil pump (Alcatel Adixen 2015SD, Ideal Vacuum Products, LLC). The dried particles were ground into fine powders using a mortar and pestle before the preparation of liquid marbles.

Liquid Marble Formation and Characterization. Liquid marbles were prepared by simply rolling a specific amount of water on the particle bed to get the water droplet fully coated. The volume of the water was controlled by an autopipette (Eppendorf, Germany). It is typically 10–15 μL . The photographs of the liquid marbles were taken with a Canon 60D DSLR camera with an 18–135 mm zoom lens (Canon, Japan) equipped with wireless control (Yongnuo, China). For the width over height ratio determination of the liquid marble, the captured photographic images were measured using ImageJ to get the value

RESULTS AND DISCUSSION

The PS-*co*-MAA latex particles used to stabilize liquid marbles were prepared by surfactant-free emulsions polymerization as described in the Materials and Methods. The COOH-coated PS-*co*-MAA particles have an average hydrodynamic diameter of around 350 nm as determined by a Coulter counter (Figure 1a). Note that such charged PS-*co*-MAA latex particles not only are responsive to pH values but also are sensitive to the presence of salts as a result of the presence of the carboxyl functional groups on the latex surface. The latexes were freeze dried at pH 3 and pH 10 to obtain fine particle powders. It can

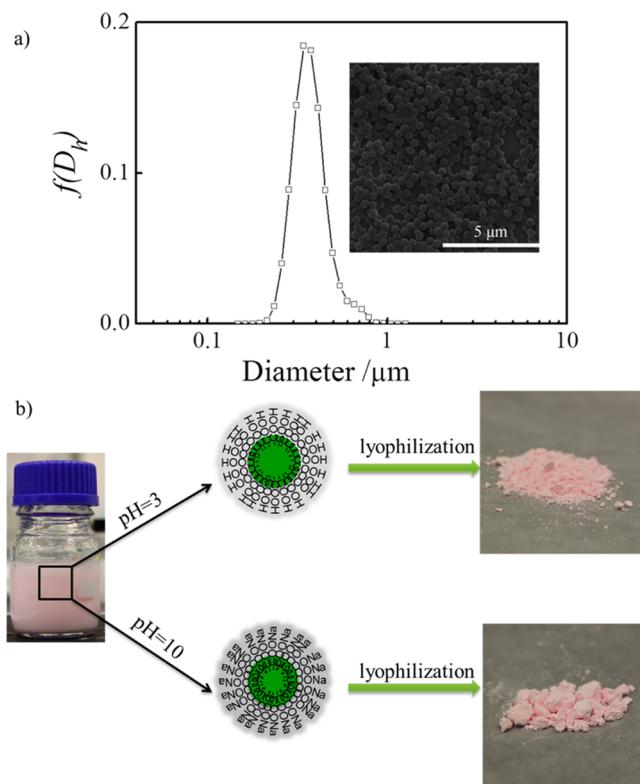


Figure 1. (a) Size distribution of the synthesized PS-*co*-MAA latex particles as measured by a Coulter Counter LS 230. The inset shows a typical SEM image of the PS-*co*-MAA particles. (b) Scheme to illustrate the influence of drying the PS-*co*-MAA dispersion under different initial conditions on the final state of the powder.

be seen that the powder looks fluffy when the latex is dried at pH 3 (Figure 1b). This is because the PS-*co*-MAA particles in the aqueous dispersions before drying were flocculated into larger domains at such low pH value because of the absence of repulsion between uncharged carboxyl groups on the particle

surface. It was observed that a water droplet of pH 3 formed a sphere with a contact angle of 132° on a thin layer of PS-*co*-MAA particles, indicating that the resulting dried powder is relatively hydrophobic. In contrast, the powder is more concrete when dried at pH 10 because the latex particles exist as a colloidally stable latex in the aqueous dispersions before drying and individual particles tends to crystallize during lyophilization. When a water droplet at pH 3.0 was used, a contact angle of 108° was obtained, revealing that the resulting dried power is more hydrophilic compared to drying at low pH. Individual liquid marbles were prepared by rolling a droplet of water over the dried particle beds. The powders can spontaneously coat water droplets to form nonwetting liquid marbles, but the property and final shape of the marble were found to be strongly dependent on how the latex particles are dried.

To illustrate further the effect of latex particle drying on the final shape of the marbles, a series of liquid marbles with varied pH values of the inner water decorated with PS-*co*-MAA latex particles dried at pH 3 or 10 were prepared. As can be seen in Figure 2a–c, spherical liquid marbles can be formed regardless of the encapsulated inner water adjusted to various solution pH values if the latex particles are dried at pH 3. Moreover, all three liquid marbles can be stable for over 90 min without the leakage of water. They eventually become buckled and collapsed due to water evaporation. To further investigate the stability of the as-prepared liquid marbles, the shrinkage rate of the liquid marbles is recorded. As shown in Figure 2d, the time needed to lose half of the weight of liquid marbles shows little difference, indicating that the liquid marbles that are formed have similar stabilities regardless of the inner water pH values. This result is in stark contrast to liquid marbles stabilized by pH-responsive PS-*co*-PEDA latex particles in which varying the inner water pH has greatly affected the stability of the resulting marbles.²⁵ However, for particles dried at pH 10, no liquid marbles can be formed when the pH of the inner water is higher (pH 10). When the pH is decreased to 5, liquid marbles can be formed,

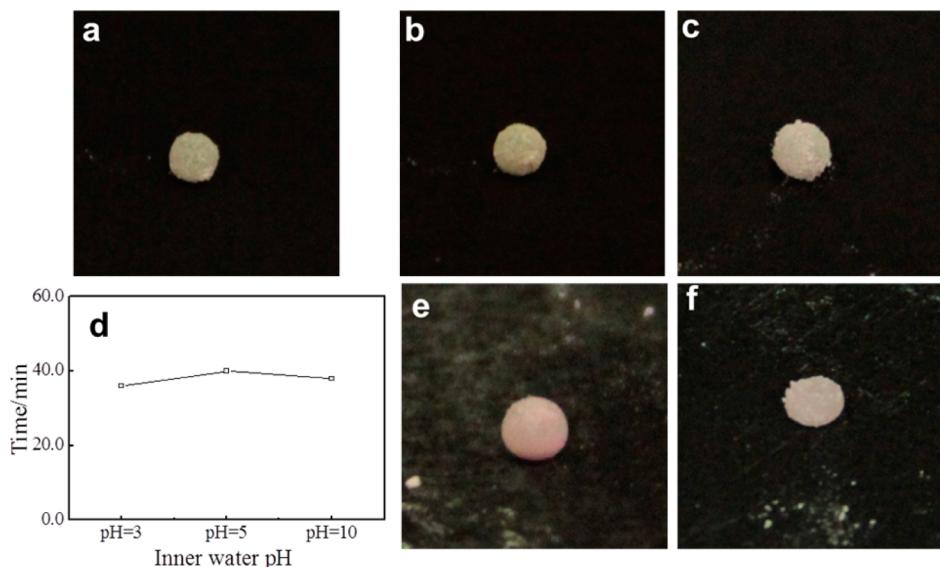


Figure 2. Photographic images of the effect of the inner liquid on the final marble shapes stabilized by PS-*co*-MAA latex particles dried at pH 3 or 10. (a–c) Liquid marbles decorated by latex particles dried at pH 3, with pH values of the inner water at 3, 5, and 10, respectively. (d) Time needed to lose half of the weight of the formed liquid marbles with different inner water pH values. (e, f) Liquid marbles decorated with latex particles dried at pH 10 with the pH values of the inner water at 3 and 5, respectively. The volume of all droplets is $10 \mu\text{L}$.

but the shape of the marble become disc-like quickly because of gravitational forces (Figure 2f). This indicates that the decrease in interfacial energy is not enough to support the weight of the water droplet. For further decreases in the pH of inner water to 3, a spherical droplet can be formed and rolls freely on the surface of a glass slide (Figure 2e). Clearly, the shape and stability of the resulting liquid marbles correlate closely with how the particle stabilizers are dried. This phenomenon was reported by Dupin et al., when they prepared stimulus-responsive liquid marbles using PS-*co*-PEDA particles.²⁵ They discovered that in order to prepare stable liquid marbles, the sterically stabilized latex particles must be dried at a high pH value, in which the protonated particles exist as a flocculated latex in solution before drying. However, no further study was conducted to explain the observation. We argue that for our synthesized PS-*co*-MAA latex particles dried at low pH (3), the particles in the aqueous dispersion are strongly flocculated because of the presence of un-ionized carboxylic groups on the surface. The resulting powder consisting of such particle aggregates is rendered to be hydrophobic so that they are preferentially coated water droplet with multilayer latex, leading to nonwetting and very stable liquid marbles that are even insensitive to the pH of the encapsulated water. However, at pH 10 the dried particles are highly charged in the aqueous dispersion because of ionized COO^- groups on the surface. The resulting powder containing colloidally stable, ionized particles may be rather hydrophilic, and they are not good particle stabilizers, especially when the pH of the inner water is high, in which the highly ionized particles are likely moved into the water phase so that no stable liquid marbles are formed.

The static properties of the liquid marbles stabilized by PS-*co*-MAA latex particles were also investigated by gradually increasing the volume of the inner water at pH 3. The gravity of the liquid marble will press it into more disclike shapes. Figure 3 shows the ratio of diameter over the height of liquid marbles

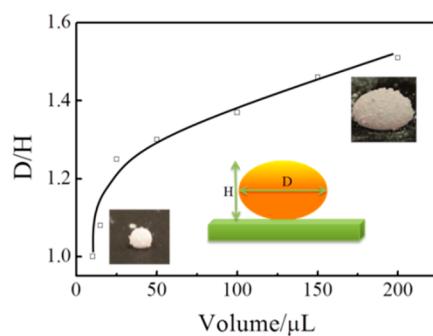


Figure 3. Shape evolution of liquid marbles stabilized by PS-*co*-MAA particles dried at pH 3 with increasing inner water volumes. The pH of the inner water is 3. (Lower left inset) Liquid marbles with 10 μL of inner water. (Middle inset) Definition of liquid marble diameter D and height H . (Upper right inset) Liquid marbles with 200 μL of inner water.

with increasing inner water volume. When the inner volume is 10 μL , the shape of the resulting liquid marble is very spherical and thus the ratio is 1. With increasing inner water volumes, gravity gradually overcomes surface forces, and the ratio has been increased from 1.0 to over 1.5. Because the synthesized PS-*co*-MAA particles are functionalized by carboxyl groups and the addition of alkali can render the particles more hydrophilic by deprotonation of the surface carboxyl groups, we have

further investigated the influences of the concentration of alkali in the inner water on the shape of liquid marbles stabilized by latex particles dried at pH 3. As shown in Figure 4, the ratio of

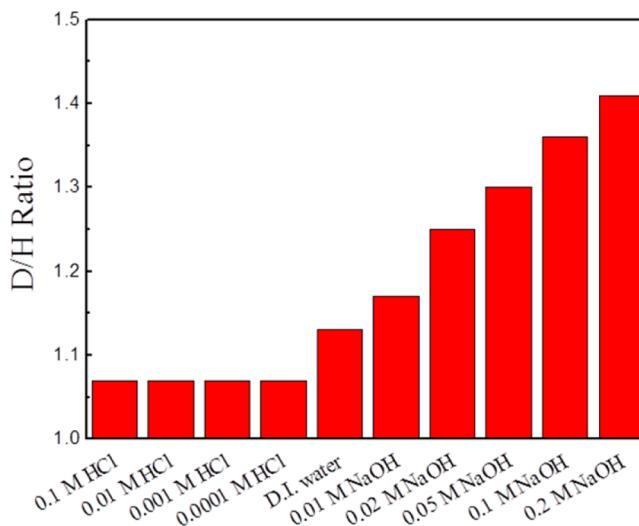


Figure 4. Effect of increasing alkali concentration in the inner water on the shape evolutions of liquid marbles stabilized by PS-*co*-MAA particles dried at pH 3. The volume of the inner water is 25 μL .

the horizontal diameter D over the height of the liquid marble H was gradually increased as more and more NaOH (deprotonation reagent) was added to the inner water droplets. The gradual collapse of the liquid marble reflects the fact that the surface forces cannot hold the weight of the water droplets to keep it in a spherical form. With increasing concentration of NaOH, the particles adsorbed at the air–water interface are deprotonated more readily and are dissolved in the water droplets. Full incorporation of the particles into the aqueous phase undermines the shape of the liquid marbles.

To gain more knowledge of the properties of the as-prepared liquid marbles, the behavior of the liquid marbles under mechanical forces is investigated with the pH of inner water at 3. Figure 5 shows that when the liquid marbles are stabilized by particles dried at pH 3, the liquid marbles are very elastic and can be split into two liquid marbles without the leakage of water (Figure 5a,b), which thus have similar mechanical properties to those stabilized by specially designed Janus particles.²⁸ In addition, the two small liquid marbles can be merged into one marble by carefully gathering the droplets (Figure 5c,d). This coalescence process can thus be applied to realize on-demand chemical reactions in droplets by encapsulating different chemical reactants in different liquid marbles. It is worth noting that the splitting and merging of the liquid marbles have been mentioned in the literature separately.^{29,30} However, our results show that conventionally synthesized charged particles perform quite similar to those specially designed Janus or sterically stabilized latex particles if the dry condition is carefully controlled.

For liquid marble stabilized by latex particles dried at pH 10, the behavior is totally different. When the tweezers cross through the marble, it remains intact after the removal of the tweezers (Figure 5e,f). The marble is easily deformed by the tweezers (Figure 5g). By slightly tapping the marble with the tweezers, the marble can be reshaped into a rodlike structure. It will not be restored to the spherical shape spontaneously, and the particles buckled at the interface can support the shape for

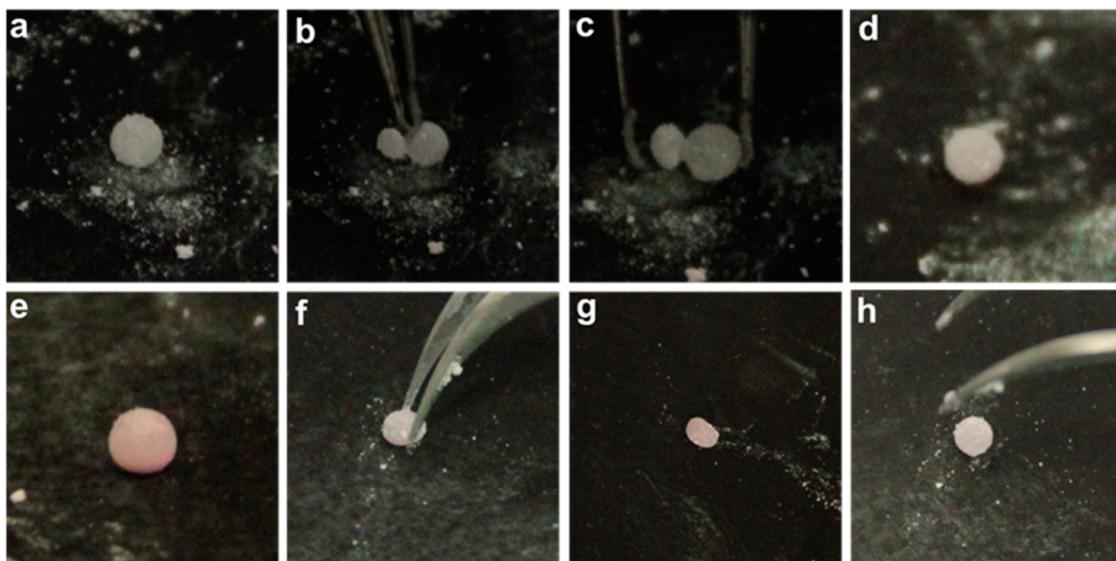


Figure 5. Manipulation of liquid marbles stabilized by PS-*co*-MAA particles with the pH of inner water at 3 by tweezers. (a–d) Liquid marble stabilized by latex particles dried at pH 3. The liquid marble can be split and then merged again. (e–h) Liquid marbles stabilized by particles dried at pH 10. The tweezers can cut through the liquid marble without damage to it, and the shape of it can be elongated by mechanical forces and restored again with the tweezers.

the time observed. The spherical shape can be restored with the help of the tweezers (Figure 5h). These different behaviors of the liquid marbles may imply that the particle behaviors at the air–water interface are different. The former may have formed a tight particle film and the latter may have formed a buckled particle film depending on the property of the particle powder dried at different pH values.

CONCLUSIONS

To conclude, charge-stabilized PS-*co*-MAA particles dried at an un-ionized (protonated) status can stabilize liquid marbles whatever the inner water droplets are. The inner water evaporation rates are similar for different water conditions. The prepared liquid marbles are very robust in that they can be split and merged back and forth. However, for particles dried under ionized (deprotonated) conditions, liquid marbles cannot be formed, which is similar to previously reported results. This indicates that the initial state of the particles is much more important than the inner condition of water in determining liquid marble formation. Because functionalized polymer latex particles are widely employed for the preparation of liquid marbles and many questions remain regarding liquid marble formation, this work opens a new and simple way to control the properties of the liquid marble formation, in particular, the preparation of stimuli-responsive liquid marbles for different applications.

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Notes

The authors declare no competing financial interest.

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