

## Stimulus-Responsive Liquid Marbles

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Over the past decade or so there has been increasing interest in the adsorption of colloidal particles at the air/water, oil/water and solid/water interfaces.<sup>1</sup> This emerging field has led to new concepts and materials such as “colloidosomes”,<sup>2,3</sup> “armored bubbles”,<sup>4</sup> “dry water”,<sup>5</sup> and “liquid marbles”,<sup>6</sup> with potential applications being suggested in microencapsulation and biotechnology. In particular, “liquid marbles” can be prepared by using highly hydrophobic particles based on either fluorinated lycopodium powder or partially alkylated silica.<sup>6–8</sup> In principle, polymer latexes should be particularly attractive for preparing “liquid marbles”, since they can be readily designed with specific surface chemistries.<sup>9</sup>

Recently we reported a series of sterically stabilized latex particles as stimulus-responsive microgels,<sup>10</sup> Pickering emulsifiers,<sup>11</sup> and foam stabilizers.<sup>12</sup> In each case the chemical structure of the steric stabilizer is the most important factor in determining the interfacial properties of the latex particles. In the present work we have designed novel sterically stabilized latexes for the production of *stimulus-responsive* “liquid marbles”. Although significant surface hydrophobicity is required to ensure effective “liquid marble” formation, these latexes can be readily synthesized by *aqueous emulsion polymerization*. The unprecedented stimulus-responsive character of these new “liquid marbles” is due to the nature of the steric stabilizer chains, which are based on well-defined poly(tertiary amine methacrylate) macromonomers.<sup>13</sup> This approach enables stable millimeter-sized “liquid marbles” to be prepared at a given solution pH which can be immediately destabilized on lowering the solution pH by addition of acid. Well-defined styrene-terminated PDEA<sub>50</sub>-St macromonomer (mean degree of polymerization = 50,  $M_w/M_n = 1.28$ ) was synthesized by oxyanion-initiated polymerization according to the literature.<sup>13</sup> PDEA-PS latex was prepared at 10% solids with minimal coagulum using this macromonomer stabilizer in a “one-shot” batch synthesis (see Supporting Information). The solution pH was adjusted to pH 6.9 to dissolve the PDEA<sub>50</sub>-St macromonomer prior to the *in situ* styrene polymerization. Since the  $pK_a$  of the conjugate acid form of PDEA is  $\sim 7.0$ ,<sup>14</sup> this means that the mean degree of protonation of the macromonomer chains is more than 50% and hence sufficiently hydrophilic to be water-soluble. SEM studies of this PDEA-PS latex confirmed the formation of spherical, albeit somewhat polydisperse, polystyrene particles ranging from 70 to 250 nm diameter (see Figure S1). DLS studies indicated a mean hydrodynamic diameter for this PDEA-PS latex of 150 nm (polydispersity = 0.165). A <sup>1</sup>H NMR spectrum of this latex dissolved in CD<sub>2</sub>Cl<sub>2</sub> indicated a PDEA content of 3.5 wt % (see Figure S2). Using the equation  $A_s = 3/\rho R$  (where  $A_s$  is the surface area per unit mass,  $\rho$  is the polystyrene latex density, and  $R$  is the latex radius), and assuming that all of the PDEA stabilizer is located on the outside of the latex particles, the adsorbed amount,  $\Gamma$ , of PDEA was calculated to be  $\sim 1.0$  mg

$m^{-2}$ . This is comparable to the values reported by Lascelles et al. for polystyrene latexes prepared by alcoholic dispersion polymerization using a closely related macromonomer stabilizer.<sup>13b</sup> On the other hand, if some of the PDEA chains are located within the polystyrene latex core, then this value of  $1.0$  mg  $m^{-2}$  may represent an upper limit for the actual adsorbed amount. XPS studies (see Figure S3) confirmed the presence of the PDEA macromonomer chains at the latex surface, as expected: the O1s signal at 530 eV observed in the PDEA-PS latex survey spectrum (which is absent in a reference spectrum recorded for a charge-stabilized PS latex) is assigned to the two oxygen atoms (C=O and C–O) on the methacrylic repeat units of the grafted stabilizer. Comparing the integrated intensity of this O1s signal relative to that obtained for the PDEA macromonomer alone allowed a surface coverage of 23% to be estimated for the PS latex particles by the PDEA stabilizer.



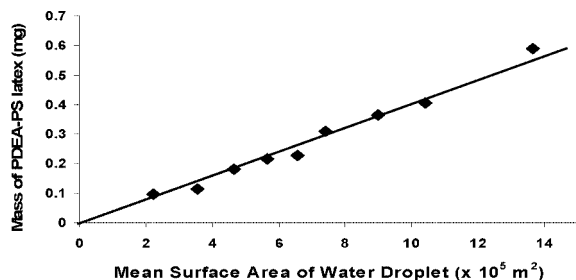
**Figure 1.** Schematic representation of a typical millimeter-sized “liquid marble” coated with latex multilayers. A digital image of such a “liquid marble” placed at the air/water interface is also shown.

Combined aqueous electrophoresis and DLS studies were conducted as a function of solution pH (see Figure S4). The PDEA-PS latex exhibits an IEP at approximately pH 8.8. Substantial flocculation occurs above approximately pH 7 since the PDEA stabilizer chains become progressively deprotonated (and hence hydrophobic) under these conditions. Conversely, protonation of the PDEA chains below pH 7 led to strongly cationic latex particles with very high degrees of dispersion. Thus this PDEA-PS latex can exist in two states in aqueous solution: (i) as a colloiddally stable latex with protonated, highly cationic PDEA chains below pH 7; (ii) as a flocculated latex with neutral PDEA chains in either neutral or alkaline solution. This is an important observation for the preparation of “liquid marbles”. It is well-known that the preparation of stable “liquid marbles” normally requires the use of highly hydrophobic particles, such as fluorosilane-treated lycopodium powder or alkylated silica particles.<sup>6,7,9</sup> However, in principle, it should be possible to vary the surface wettability of a sterically stabilized latex by selecting a suitable pH-responsive steric stabilizer such as PDEA. Thus neutral PDEA chains are hydrophobic at alkaline pH, whereas strongly hydrophilic character is expected at *low* pH since the protonated PDEA chains are in their polyelectrolytic form under these conditions.

Individual “liquid marbles” were prepared by rolling a 10  $\mu$ L droplet of deionized water over PDEA-PS latex powder previously

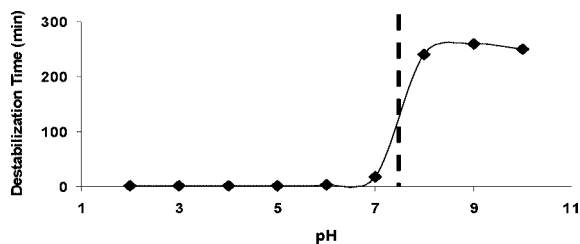
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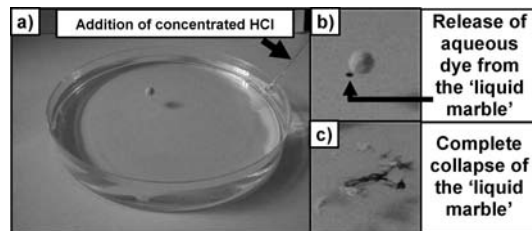
**Figure 2.** Adsorbed mass of latex vs mean surface area per millimeter-sized water droplet (10–150  $\mu\text{L}$ ) used to prepare “liquid marbles”.

dried at pH 10. The latex powder immediately coats the water droplet and renders it both hydrophobic and nonwetting (see Figure 1). These “liquid marbles” remained intact after transfer onto a glass slide or onto the surface of liquid water within a Petri dish. Partial buckling and collapse of the “liquid marbles” gradually occurred on time scales of several hours at 20  $^\circ\text{C}$  due to slow water evaporation. However, enhanced stability was obtained if the aqueous droplet phase contained added electrolyte, since this involatile solute reduced the rate of evaporation from the encapsulated droplets.



**Figure 3.** Effect of varying the solution pH on the stability of “liquid marbles” placed at the air/water interface.

These “liquid marbles” clearly have significant surface roughness, which suggests that they are coated with latex *multilayers*, rather than just a monolayer (see Figure 1). To evaluate the nature of this latex coating, we examined how the mean latex mass of such “liquid marbles” (determined gravimetrically after oven drying) varied with the surface area of the water droplets used for their preparation. An approximately linear relationship was obtained, as expected (see Figure 2). From the gradient of this line, we estimate that, on average, the “liquid marbles” coating comprises 40–50 latex particles, which corresponds to an estimated thickness of 4–10  $\mu\text{m}$ . A series of aqueous buffers was used to vary the solution pH of the underlying liquid water to examine its effect on the long-term stability of individual “liquid marbles” placed at the air/water interface (see Figure 3). The longer times observed above pH 7.5 simply indicate the onset of partial dehydration (i.e., buckling or collapse) of the “liquid marbles” due to slow water evaporation, whereas the much shorter times observed at lower pH indicate catastrophic destruction of the “liquid marbles”. Clearly, the minimum pH required for long-term “liquid marble” stability correlates closely with the critical solution pH observed for flocculation of the PDEA-PS latex (see Figure S4). Moreover, the weakly basic nature of the steric stabilizer chains confers pH-responsive behavior on the “liquid marbles”: they remain stable for hours when placed on liquid water at neutral or alkaline pH but immediately disintegrate on addition of acid (see Figure 4).



**Figure 4.** (a) Digital image of a “liquid marble” placed at the air/water interface; (b) initial release of a water-soluble Alizarin Blue Black B dye from “liquid marble” core on addition of acid; (c) subsequent rapid disintegration of the “liquid marble”.

In control experiments, no “liquid marbles” could be formed under any conditions using either charge stabilized PS latex or sterically stabilized PS latexes prepared using permanently hydrophilic stabilizers such as monomethoxy-capped poly(ethylene glycol) methacrylate. These observations confirm the essential role played by the chemically grafted PDEA chains in promoting “liquid marbles” formation.

In summary, sterically stabilized latexes can be employed for the preparation of “liquid marbles”. Although it is a prerequisite that such latexes must be highly hydrophobic, they can be actually prepared using *aqueous emulsion* polymerization.

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**Supporting Information Available:** PDEA-PS latex preparation and characterization details;  $^1\text{H}$  NMR and XPS spectra; combined DLS/ aqueous electrophoresis vs pH curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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