

## Supporting Information for

### Preparation of Stimulus-Responsive Liquid Marbles Using A Polyacid-Stabilised Polystyrene Latex

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#### Experimental Section

##### Synthesis of *N*-(dimethylamino)ethyl-2-bromoisobutyrylamide initiator

*N,N'*-Dimethylethylenediamine (6.00 g, 0.068 mol), triethylamine (27.5 g, 0.272 mol) and dichloromethane (120 ml) were placed in a 1 L three-necked round-bottomed flask and purged with nitrogen for 30 min. A white precipitate of triethylammonium bromide formed immediately on addition of 2-bromoisobutyryl bromide (15.65 g, 0.068 mol) to this solution. The reaction mixture was stirred for a further 5 h prior to removal of the precipitate by filtration. The solution was washed three times with 200 ml NaHCO<sub>3</sub> solution and dried with anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give a pale brown liquid (11.5 g, 72 % yield). <sup>1</sup>H NMR spectroscopy: δ 2.0 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>-C-Br), δ 2.4 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>N), δ 2.6 (t, 2H, (CH<sub>3</sub>)<sub>2</sub>-N-CH<sub>2</sub>CH<sub>2</sub>-), δ 3.4 (m, 2H, N-CH<sub>2</sub>CH<sub>2</sub>-NH).

##### Homopolymerisation of 2-hydroxypropyl methacrylate (HPMA)

*N*-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator (0.55 g, 2.31 mmol), bpy (0.72 g, 4.62 mmol) HPMA (10.0 g, 69.3 mmol, target degree of polymerisation = 30) were weighed into a 50 ml round-bottomed flask and degassed using a nitrogen purge. Isopropanol (11 ml) was degassed and transferred into the reaction solution under nitrogen. The Cu(I)Cl catalyst (0.23 g, 2.31 mmol) was added to the solution stirred with a magnetic stirrer at 250 rpm and a colour change from clear to brown was observed, indicating the onset of polymerisation. The solution was polymerised at 50 °C in an oil bath. After 24 h the solution was diluted with methanol and passed through a silica column to remove the spent Cu(II)

catalyst. The product was then dried on a vacuum line overnight to afford a white powder. The purified polymer was characterised by  $^1\text{H}$  NMR and GPC.

### **Quaternisation of poly(2-hydroxypropyl methacrylate) using 4-vinylbenzyl chloride**

Quaternisation of the PHPMA<sub>30</sub> homopolymer precursor was conducted as follows. PHPMA<sub>30</sub> (9.0 g, 1.97 mmol) was dissolved in methanol (27.0 ml). 4-Vinylbenzyl chloride (0.67 g, 3.94 mmol) was added to this solution and stirred at 250 rpm with a magnetic stirrer for three days. Excess 4-vinylbenzyl chloride was removed by repeated precipitation from a minimum amount of methanol into excess cyclohexane. The resulting macromonomer was dried under vacuum overnight to afford a white powder. The extent of quaternisation was initially monitored from Figure S2 (lower spectrum) by observing the disappearance of the six protons due to the dimethylamino end-group of the PHPMA precursor. The actual degree of quaternisation of the styrene-functionalised PHPMA macromonomer was calculated by comparing the broad signal at around 2 ppm due to the two methylene protons on the polymer backbone with the four aromatic signals between 7.5 and 7.8 ppm due to the terminal styrene unit. Full quaternisation was judged to have been obtained if this calculated ratio was equal to the degree of polymerisation, i.e. DP = 30.

### **Preparation of polyacid macromonomer (PSPMA)**

The general protocol for esterification of poly(2-hydroxypropyl methacrylate) (PHPMA) is described elsewhere.<sup>11</sup> PHPMA (5.0 g, 34.6 mmol OH residues) was dissolved in anhydrous pyridine (100.0 mL) in a 250 mL round-bottomed flask. Succinic anhydride (SA; 7.00 g, 70.0 mmol) was then added to the stirred solution at 250 rpm and esterification was allowed to proceed at 20 °C for 48 h. The reaction mixture was then precipitated into diethyl ether (500 mL). The solid was redissolved in THF (30 mL) and precipitated into diethyl ether (100 mL). This clean-up procedure was repeated three times. Finally, the off-white solid was dried for 48 h in a vacuum dessicator. The extent of esterification was calculated from Figure S2 (upper spectrum) by comparing the four new succinic methylene protons at 2.7 ppm with the

four aromatic protons between 7.5 and 7.8 ppm due to the terminal styrene unit. Full esterification was judged to have been obtained if this calculated ratio was equal to the degree of polymerisation, i.e.  $DP = 30$ .

### **Preparation of PSPMA-PS latex via aqueous emulsion polymerisation**

PSPMA macromonomer (1.50 g) was dissolved in de-ionised water (10.0 mL) adjusted to pH 9 using concentrated NaOH in a 100 ml single-necked round-bottomed flask. Styrene monomer (5.00 g) was then added to this solution and the solution pH was adjusted to pH 6.0 by addition of aqueous HCl. De-ionised water (also adjusted to pH 6.0) was added to produce a 38.50 g aqueous emulsion in the flask, which was sealed with a rubber septum. This reaction mixture was degassed at ambient temperature using five vacuum/nitrogen cycles, stirred at 250 rpm using a magnetic stirrer, heated at 60 °C with the aid of an oil bath and then the  $\alpha,\alpha'$ -azodiisobutyramidine dihydrochloride (AIBA) initiator solution (0.050 g AIBA dissolved in de-ionised water (5.0 mL, previously adjusted to the reaction pH using either HCl or NaOH) was added after 20 minutes. The polymerising solution turned milky-white within 15 minutes and stirring was continued at 250 rpm for 24 h at 60 °C. The resulting milky-white latex (denoted PSPMA-PS latex) was purified by repeated centrifugation-redispersion cycles [20,000 rpm for 4 h; each supernatant was carefully decanted, discarded and replaced with mildly alkaline de-ionised water (adjusted to pH 9 using aqueous NaOH)] to remove excess styrene monomer and any unreacted macromonomer.

### **Scanning electron microscopy**

SEM images were obtained using a FEI Inspect F field emission instrument operating at 20 kV. The PSPMA-PS latex was dried from aqueous dispersion at pH 8. The sample was sputter-coated with a thin overlayer of gold prior to inspection to prevent sample-charging effects.

### **X-ray photoelectron spectroscopy**

The surface compositions of the PSPMA-PS latex, the PSPMA macromonomer and the charge-stabilised PS reference latex were examined using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer equipped with a monochromatic Al x-ray source operating at 6.0 mA and 15 kV at a typical base pressure of  $10^{-8}$  torr. The step size was 1.0 eV for the survey spectra (pass energy = 160 eV) and 0.1 eV for the high resolution spectra (pass energy = 80 eV). Spectra were typically acquired from at least two separate sample areas. An aqueous dispersion of the PSPMA-PS latex at pH 8 (or an aqueous solution of PSPMA macromonomer at the same pH) was dried onto silicon wafer prior to analysis.

### **Dynamic light scattering**

Hydrodynamic diameters were measured at 25°C using a Malvern Zetasizer NanoZS Instrument equipped with a 4 mW He-Ne solid-state laser operating at 633 nm. Back-scattered light was detected at 173° and the mean particle diameter was calculated from the quadratic fitting of the correlation function over thirty runs of ten seconds duration. All measurements were performed in triplicate on 0.01 w/v % aqueous latex dispersions at the desired pH using 1 mM KCl as background electrolyte. Measurements on diluted aqueous latex dispersions (0.01 wt. % in 1 mM NaCl) were conducted as a function of pH by gradually adding 1 M HCl, starting from an initial pH of around 10. The time between each pH value was approximately ten minutes.

### **Aqueous electrophoresis**

Zeta potentials were calculated from electrophoretic mobilities using a Malvern Instruments Zetasizer NanoZS Instrument. Measurements were obtained as a function of pH on 0.01 w/v % aqueous dispersions in 1 mM KCl by gradually adding KOH, starting from an initial pH of around 3. Zeta potentials were averaged over at least twenty runs. The variance was typically within the size of the data points shown. Measurements on diluted aqueous latex dispersions (0.01 wt. % in 1 mM NaCl) were conducted as a function of pH by gradually adding 1 M HCl, starting from an initial pH of around 10. The time between each pH value was approximately ten minutes.

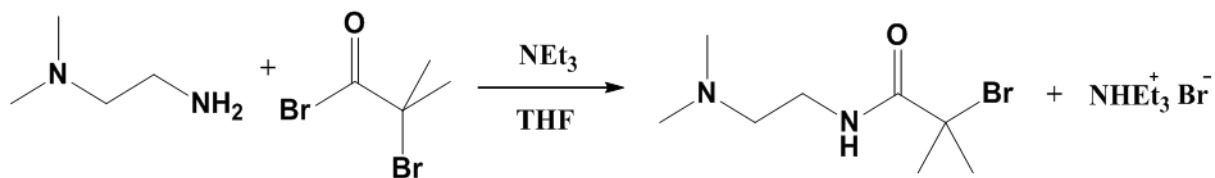
### **Preparation of ‘liquid marbles’**

De-ionised water adjusted to pH 2.5 by addition of concentrated HCl was dispensed as 10  $\mu$ L droplets using a 10-100  $\mu$ L Eppendorf micropipette and mixed with freeze-dried PSPMA-PS latex (adjusted to pH 2.5 using aqueous HCl prior to freeze-drying). Digital images of selected ‘liquid marbles’ were recorded using a Samsung ES71 digital camera.

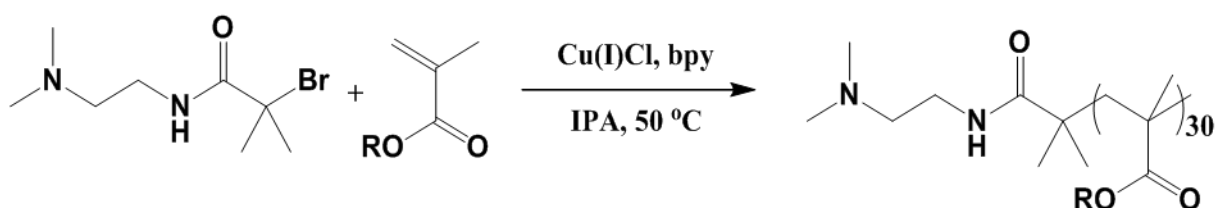
### **Effect of solution pH on the stability of ‘liquid marbles’**

The pH-responsive character of the ‘liquid marbles’ was assessed as follows. Individual 10  $\mu$ L ‘liquid marbles’ were placed on the surface of liquid water adjusted to various solution pH (ranging from 2 to 10). The number of ‘liquid marbles’ successfully deposited intact at this air-water interface was determined for fifty ‘liquid marbles’. The mean residence time for such ‘liquid marbles’ to remain stable with respect to either disintegration or buckling was also determined. Finally, stable ‘liquid marbles’ deposited onto acidified water (adjusted to pH 2.5 by addition of concentrated HCl) could be rapidly disintegrated *in situ* after addition of a few drops of 10 wt.% NaOH via pipette, which increased the solution pH to around 9.

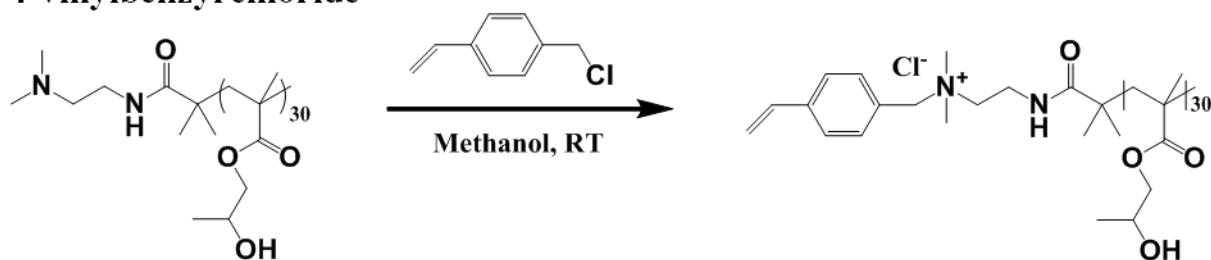
### 1. Synthesis of *N*-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator



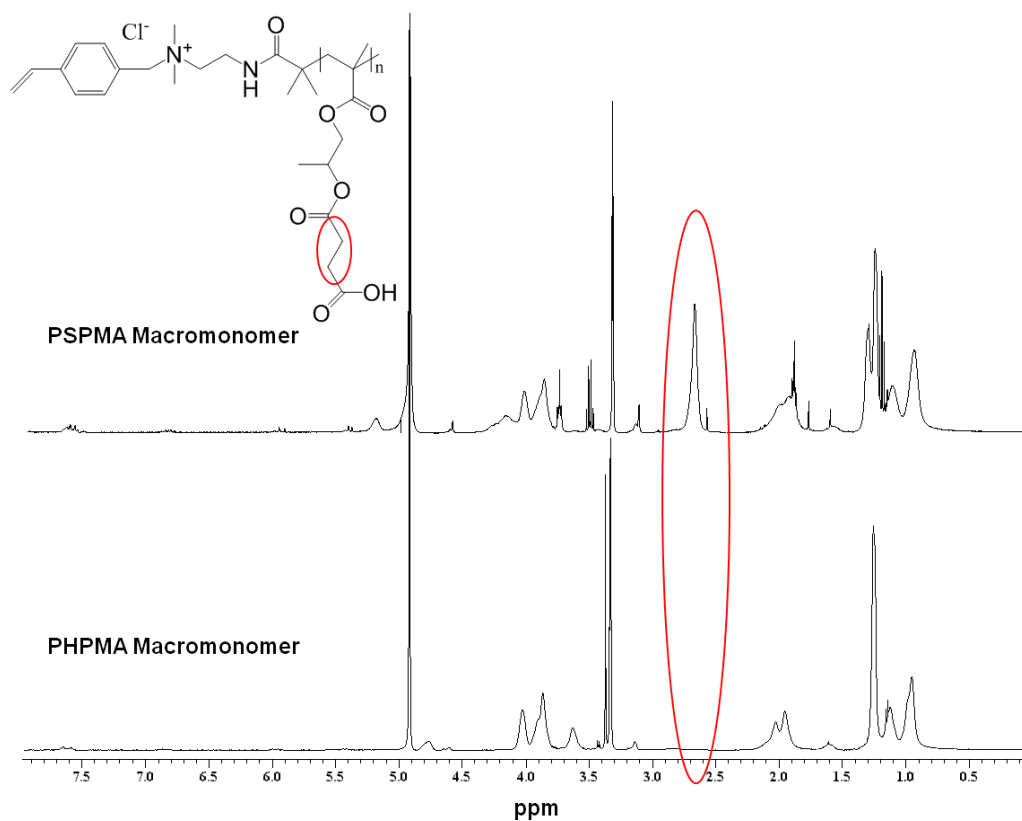
### 2. Homopolymerization of 2-hydroxypropyl methacrylate (HPMA)



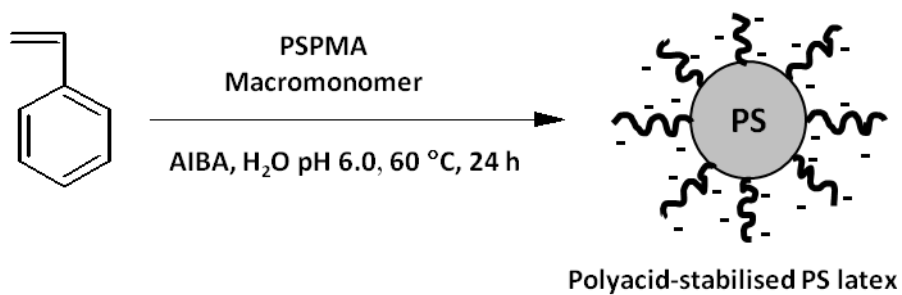
### 3. Quaternization of poly(2-hydroxypropyl methacrylate) [P(HPMA)<sub>30</sub>] using 4-vinylbenzyl chloride



**Figure S1.** Three-step synthesis of the poly(2-hydroxypropyl methacrylate) macromonomer precursor: (1) ATRP initiator synthesis; (2) ATRP of HPMA; (3) quaternisation of the macromonomer precursor using 4-vinylbenzyl chloride.

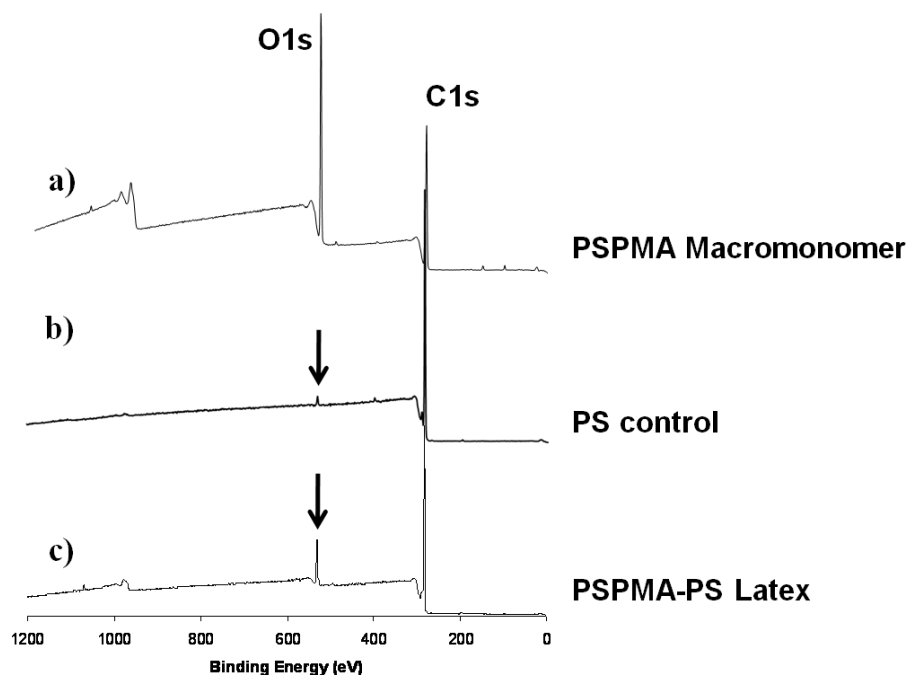


**Figure S2.** <sup>1</sup>H NMR spectra (CD<sub>3</sub>OD) of the PHPMA macromonomer precursor and the final polyacid PSPMA macromonomer after esterification using excess succinic anhydride.



**Figure S3.** Schematic representation of the formation of a polyacid-stabilised polystyrene latex (PSPMA-PS) prepared by aqueous emulsion polymerisation using a cationic azo initiator (AIBA) at pH 6.0 and 60 °C.





**Figure S4.** XPS survey spectra recorded for: (a) the polyacid PSPMA macromonomer, (b) the charge-stabilised polystyrene reference latex prepared using the AIBA initiator alone, (c) the PSPMA-PS latex. Note the presence of the O1s signal due to carbonyl groups at around 530 eV indicating the presence of the PSPMA macromonomer chains at the latex surface. A very weak signal is also present for the charge-stabilised polystyrene reference latex, but close inspection of its core-line spectrum confirms that this is not due to carbonyl oxygen..