

RAPID COMMUNICATION

Thermo-responsive liquid marbles

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Aussillous and Quéré used the term liquid marbles to refer to non-stick droplets coated with micro- or nano-scale hydrophobic powder particles.¹ A liquid droplet is encapsulated by a hydrophobic powder at the liquid–air interface. Liquid marbles have been prepared using powders such as lycopodium powder,² silica,³ carbon black,⁴ poly[2-(perfluorooctyl)ethyl acrylate],⁵ polytetrafluoroethylene,⁶ polyvinylidene fluoride,⁷ aerogels,⁸ graphite⁹ and others.^{10–12} The surface wettability of the powder is an important parameter for the preparation of liquid marbles. The hydrophobic liquid marble shell prevents direct contact between the liquid core and surfaces outside the marble shell. Liquid marbles are spherical and retain a stable shape while on the surface of a solid or liquid. Liquid marbles have shown particular promise for applications in water surface pollution detection,¹³ gas detection¹⁴ and microreactors.¹⁵

Recent reports have described various stimulus-responsive liquid marbles with stability that can be controlled by external stimuli. For example, liquid marbles stabilized by particles containing pH-responsive polymers such as deprotonated hydrophobic poly((2-dimethylamino)ethyl methacrylate)¹⁶ and poly(2-vinylpyridine) (P2VP),¹⁷ which can float on the surface of water, disintegrate upon the addition of acid to the bulk water because the particle surface becomes hydrophilic owing to the protonation of the pH-responsive polymers. Wang *et al.*¹⁸ reported the preparation of magnet- and ultraviolet (UV)-responsive liquid marbles using Fe₃O₄/SiO₂ particles with a pH-responsive block copolymer containing P2VP and a photo acid generator. The movement of these particles can be controlled by an external magnetic field. Upon UV irradiation, the photo acid generator-generated acid, which induces ionization of the P2VP chains on the particle surface, leads to the disintegration

of the liquid marble. Recently, UV-responsive liquid marbles were prepared using a water droplet covered with photochromic spiropyran powder.¹⁹ These UV-responsive liquid marbles disintegrated upon UV irradiation because the hydrophobic spiropyran was transformed into hydrophilic merocyanine, which has a betaine structure. The development of stimulus-responsive liquid marbles may expand their area of application. It is interesting to investigate new stimulus-responsive liquid marbles, including thermally responsive liquid marbles.

An aqueous solution of poly(*N*-isopropylacrylamide) (PNIPAM) undergoes a thermally reversible phase separation.²⁰ At room temperature (<32 °C), PNIPAM is hydrophilic and dissolves in water, adopting a random coil conformation because of hydrogen bonding between the pendant amide groups and water molecules. However, PNIPAM separates from the aqueous phase when heated to temperatures higher than 32 °C, a lower critical solution temperature (LCST). This finding indicates that PNIPAM powder may exhibit hydrophilic properties below the LCST and may become hydrophobic above the LCST. The LCST for PNIPAM is influenced by the type and concentration of salts added to the aqueous solution.^{21,22}

In the current study, thermo-responsive liquid marbles (Figure 1) were prepared using PNIPAM powder. It was difficult to maintain precise control of the temperature for the liquid marbles because room temperature (~22 °C) was below the LCST. To simplify the experiments, a stable liquid marble floating on the surface of bulk water in a Petri dish disintegrated when the temperature of bulk water decreased below room temperature. This strategy involved the preparation of stable liquid marbles using PNIPAM powder at room temperature followed by a decrease in the LCST below room

temperature. To decrease the LCST, salt (Na₂SO₄) was added to the water droplet and the bulk water.

EXPERIMENTAL PROCEDURE

NIPAM from Kohjin Holdings Co. (Tokyo, Japan) was purified by recrystallization from a mixture of benzene and *n*-hexane (3/7, v/v). *N,N*-dimethylformamide (DMF, 99.0%) was dried over 4 Å molecular sieves and purified by distillation under reduced pressure. 2,2'-Azobis(isobutyronitrile) (98%) from Wako Pure Chemical (Tokyo, Japan) was recrystallized from methanol. Sodium sulfate (Na₂SO₄, >99.0%), iron(III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 99.9%), potassium hexacyanoferrate(II) trihydrate (K₄[Fe(CN)₆]·3H₂O, 99.5%) and safranin were purchased from Wako Pure Chemical and were used as received.

PNIPAM was prepared by conventional free radical polymerization as follows. NIPAM (3.00 g, 26.5 mmol) and 2,2'-azobis(isobutyronitrile) (21.7 mg, 0.133 mmol) were dissolved in DMF (15 ml). The solution was heated at 60 °C for 16 h under an Ar atmosphere. After reaction, the reaction mixture was poured into a large excess of diethyl ether/*n*-hexane (5/5, v/v) to precipitate the polymer. The PNIPAM was obtained as a white powder and was dried under vacuum at 60 °C for one day (2.59 g, 86.3%). The chemical structure was confirmed by ¹H nuclear magnetic resonance (Supplementary Figure S1). The number-average molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) were 1.93 × 10⁴ and 3.80, respectively, estimated from gel-permeation chromatography (Supplementary Figure S2).

¹H Nuclear magnetic resonance spectra were obtained using a DRX-500 spectrometer (Bruker Biospin Co., Kanagawa, Japan). The gel-permeation chromatography measurements were performed using an instrument equipped with an RI8021 refractive index detector (Tosoh Co., Tokyo, Japan)

and two Shodex LF-804 polystyrene mixed gel columns (Showa Denko K.K., Tokyo, Japan; bead size = 7 μm , pore size = 20–200 \AA) operated at 40 $^{\circ}\text{C}$ under a flow rate of 0.5 ml min^{-1} . A DMF solution containing 10-mM LiBr was used as the eluent. M_n and M_w/M_n were calibrated using standard polystyrene samples. The values of % T for PNIPAM aqueous solutions at a constant polymer concentration (C_p) of 1.0 g l^{-1} were measured using a V-530 spectrophotometer (Jasco Co., Tokyo, Japan) with a 1.0 cm path length quartz cell at various temperatures. The temperature was adjusted from 0 to 40 $^{\circ}\text{C}$ at a heating rate of 1.0 $^{\circ}\text{C min}^{-1}$ using an ETC-505T thermostat system (Jasco Co.). The fine structure of the powder was observed using a Keyence Co. (Tokyo, Japan) VE-9800 scanning electron microscope (SEM) at 12 kV. Samples were prepared for SEM by placing powder directly onto electrically conductive tape. The sample was treated by Pt sputtering using a Quick Coater Sc-701 MKII (Sanyu Electron Co., Tokyo, Japan). The surface temperature of the liquid marbles was monitored using a CPA8000 infrared camera (Chino Co., Tokyo, Japan). Digital photographs of the liquid marbles were obtained using an EOS Kiss X5 digital camera (Canon Inc., Tokyo, Japan).

RESULTS AND DISCUSSION

Liquid marbles can be prepared using PNIPAM powder and hot pure water at 60 $^{\circ}\text{C}$, which is above the LCST. The marbles were prepared as follows. First a ground PNIPAM powder bed was prepared in a polytetrafluoroethylene dish. A 10- μl hot water droplet was deposited on the PNIPAM powder bed using a syringe. Gentle rolling of the hot water droplet on the powder bed led to the complete encapsulation of the droplet by the powder, resulting in a liquid marble. When the temperature was maintained above 60 $^{\circ}\text{C}$, the liquid marbles were stable and remained intact after transfer onto a glass slide or onto the surface of bulk hot water at 60 $^{\circ}\text{C}$. To decrease the LCST, Na_2SO_4 salt was added to the water droplet and the bulk water. The LCST of PNIPAM depends strongly on the type and concentration of added salt. In general, the LCST for PNIPAM in water decreased with increasing salt concentration because of salting out effects. Supplementary Figure S3 shows the percentage transmittance (% T) at 600 nm for aqueous PNIPAM solutions as a function of temperature from 0 to 40 $^{\circ}\text{C}$ in the presence of varying concentrations of Na_2SO_4 . Without Na_2SO_4 , the LCST for PNIPAM in pure water was 32 $^{\circ}\text{C}$, which is similar to the

values reported in the literature.²⁰ The LCST decreased with increasing Na_2SO_4 concentration. The LCST for PNIPAM was 8 $^{\circ}\text{C}$ in the presence of Na_2SO_4 (0.5 M). This observation suggests that the wettability of the PNIPAM powder with aqueous Na_2SO_4 (0.5 M) solutions was low at room temperature.

A liquid marble was prepared using aqueous 0.5 M Na_2SO_4 covered with ground PNIPAM powder (Figure 2). The liquid marble was prepared at room temperature. The liquid marbles exhibited significant

surface roughness, suggesting that they were coated with irregular powder clusters. The PNIPAM powder may trap air, thus resulting in a Cassie-Baxter wetting regime at the powder-liquid interface inside the liquid marble.⁴ The shape of the irregular PNIPAM powder clusters, which is non-uniform and indeterminate, can be observed by SEM (Supplementary Figure S4).

The liquid marbles were prepared by rolling a 10- μl droplet of aqueous 0.5 M Na_2SO_4 containing safranin dye over a ground PNIPAM powder bed, which was then transferred

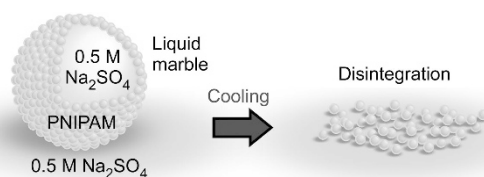


Figure 1 Conceptual illustration of a liquid marble consisting of a droplet of 0.5 M Na_2SO_4 aqueous solution covered with poly(*N*-isopropylacrylamide) (PNIPAM) floated on the surface of aqueous 0.5 M Na_2SO_4 , followed by the disintegration of the liquid marble by cooling. A full color version of this figure is available at *Polymer Journal* online.

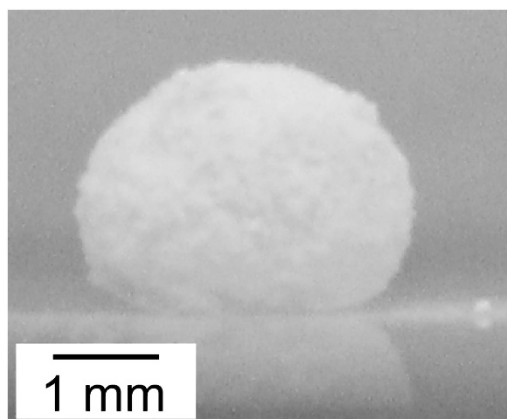


Figure 2 A digital photograph of a liquid marble containing aqueous 0.5 M Na_2SO_4 (10 μl) covered by poly(*N*-isopropylacrylamide) powder on a glass substrate at room temperature. A full color version of this figure is available at *Polymer Journal* online.

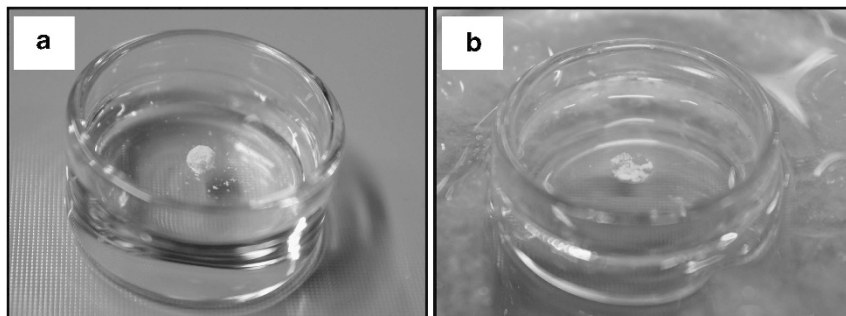


Figure 3 Digital photographs of a floatable liquid marble made from an aqueous safranin dye solution containing 0.5 M Na_2SO_4 covered with poly(*N*-isopropylacrylamide) powder on bulk water containing 0.5 M Na_2SO_4 (a) at room temperature and (b) after cooling to 0 $^{\circ}\text{C}$ using an ice bath for 5 min. A full color version of this figure is available at *Polymer Journal* online.

to the surface of bulk water containing 0.5 M Na_2SO_4 at room temperature (Figure 3). The bulk water was not colored when the liquid marble containing safranin dye was stable on the surface. However, when bulk water was cooled using an ice bath, the liquid marble disintegrated and leaked safranin dye from the interior of the liquid marble to the bulk water because the PNIPAM powder that formed the liquid marble dissolved in the water below the LCST. A video of the thermo-responsive behavior of the liquid marble is provided as Supplementary Video 1.

Figure 4a reports the disintegration temperatures of liquid marbles formed from PNIPAM powder and water droplets containing various Na_2SO_4 concentrations floated on bulk water containing the same concentration of Na_2SO_4 as in the liquid marble. The surface temperatures of the liquid marble were monitored using an infrared camera (Supplementary Figure S5). Measurements were performed five times for each Na_2SO_4 concentration, and the average destabilization temperatures were plotted against Na_2SO_4 concentration (Figure 4b). The disintegration

temperature of the liquid marble decreased with the increasing Na_2SO_4 concentration. At an Na_2SO_4 concentration of 0.5 M, the LCST value decreased to 6 °C. The stability of the liquid marbles was enhanced above room temperature, indicating that PNIPAM powder was sufficiently hydrophobic to adsorb strongly at the air–liquid interface under these conditions. In contrast, liquid marbles containing 0.5 M Na_2SO_4 were always unstable and disintegrated when the surface temperature of the liquid marble decreased below 6 °C, because of the dissolution caused by hydrated PNIPAM, followed by the disintegration of the liquid marble. The liquid marble formed from PNIPAM powder and a water droplet containing 0.5 M Na_2SO_4 remained stable for longer than a day at room temperature under humid conditions. Therefore, the liquid marble of an aqueous Na_2SO_4 solution coated with PNIPAM powder placed on bulk water containing Na_2SO_4 disintegrated in response to cooling. The disintegration temperature of the liquid marble was close to the LCST of PNIPAM at the same Na_2SO_4 concentration.

These results suggested that thermo-responsive liquid marbles could be used to induce chemical reactions unrelated to temperature changes by floating a liquid marble containing one reactant on bulk water containing another reactant. Cooling the bulk water could lead the liquid marble to disintegrate, thereby allowing the two reactants to come into contact and triggering the reaction. This behavior was demonstrated using a liquid marble prepared from PNIPAM powder and a water droplet containing both 0.5 M Na_2SO_4 and 0.01 M $\text{Fe}(\text{NO}_3)_3$, which was floated on the surface of bulk water containing 0.5 M Na_2SO_4 and 0.2 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ (Figure 5). $\text{Fe}(\text{NO}_3)_3$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$ reacted to generate water-insoluble $\text{KFe}[\text{Fe}(\text{CN})_6]$, Prussian blue.²³ To verify the chemical reaction, the precipitate of Prussian blue was observed after cooling the liquid marble (Figure 5b and Supplementary Video 2 in the Supporting information).

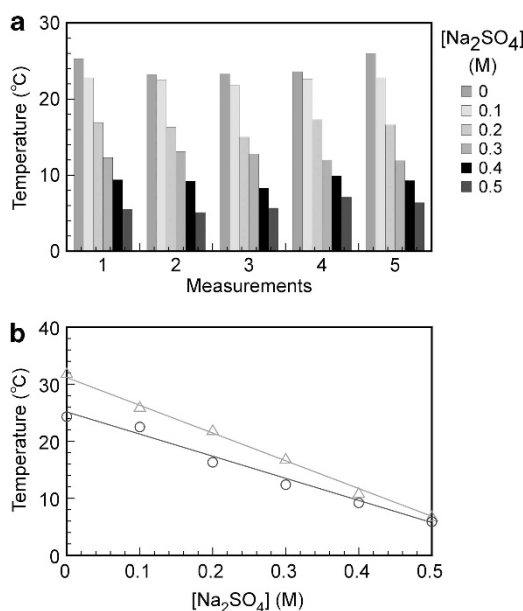


Figure 4 (a) Disintegration temperatures of the liquid marble prepared from poly(*N*-isopropylacrylamide) (PNIPAM) powder and 10 μl water containing various concentrations of Na_2SO_4 floated on bulk water with the same Na_2SO_4 concentration as in the liquid marble. Measurements were performed five times for each Na_2SO_4 concentration. (b) The effect of Na_2SO_4 concentration on the disintegration temperature of the liquid marble (\circ) and on the lower critical solution temperature of the aqueous PNIPAM solution (Δ). A full color version of this figure is available at *Polymer Journal* online.

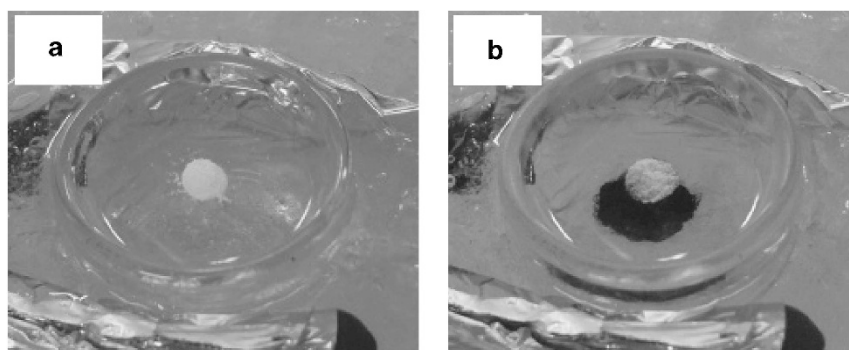


Figure 5 Digital photographs of a temperature-triggered chemical reaction using a poly(*N*-isopropylacrylamide) (PNIPAM) liquid marble consisting of a water droplet containing 0.5 M Na_2SO_4 and 0.2 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ covered with PNIPAM floating on bulk water containing 0.5 M Na_2SO_4 and 0.01 M $\text{Fe}(\text{NO}_3)_3$ (a) before and (b) after cooling in an ice bath. A full color version of this figure is available at *Polymer Journal* online.

CONCLUSIONS

This report described the preparation of thermo-responsive liquid marbles composed of PNIPAM powder and water droplets containing salts. The liquid marbles were transferred to the surface of bulk water containing salts, where they remained stable for longer than a day under humid conditions at room temperature. When the bulk aqueous solution was cooled, the liquid marbles disintegrated because the wettability of the PNIPAM powder increased. The remote triggering of chemical reactions using

liquid marbles can be achieved by cooling. It is important to develop various external stimuli to disintegrate liquid marbles. We attempted to prepare thermo-responsive liquid marbles using powders of ureido polymers that exhibit upper critical solution temperatures in water.²⁴ However, we could not obtain these liquid marbles because the ureido polymer powders wetted independent of temperature.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)