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Shape-Designable Polyhedral Liquid Marbles/Plasticines Stabilized with Polymer Plates

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Polyhedral liquid marbles/plasticines are prepared using (sub)millimeter-sized polymer plates as a stabilizer and water as an inner liquid. Precise control of size and shape can be successfully performed by tuning the size ratio of the water droplet and the plate, number of plates adsorbed to the droplet, coalescence (jointing) of multiple polyhedral liquid marbles/plasticines, and application of external mechanical stress. Thanks to interfacial jamming of the plates, plastic deformation of the liquid marbles/plasticines is achieved. The authors are able to fabricate liquid marbles/plasticines with various shapes including A–Z letters of alphabet. Liquid marble/plasticine with an aspect ratio exceeding 800, the largest aspect ratio ever reported, is also successfully prepared; the length of the liquid marble/plasticine exceeded 1.5 m. The liquid marbles can be picked up and be piled up on top of each other using tweezers or fingers. Furthermore, Janus-type liquid marbles/plasticines with different curvatures and different stabilizers in a single liquid marble/plasticine can be fabricated by coalescence (jointing) of near-spherical and cuboid liquid marbles/plasticines stabilized by plates with different sizes. An internal liquid flow from the near-spherical liquid marble to the cuboid liquid marble/plasticine immediately after jointing is observed, making this system act as a micropump.

1. Introduction

Liquid droplets covered by a monolayer or multilayer of solid particles, which are known as liquid marbles (LMs), have gained great interest ever since they were brought into the limelight in 2001 by Aussillous and Quéré.[1] LMs possess unique characters which cannot be attained by bare liquid droplets.[2–7] LMs show non-wetting and non-sticky natures, because the solid particle layer on their surfaces prevents the liquid core from contacting the supporting substrates, and they can move on solid and liquid surfaces without any trails. The particle layer can protect the inner liquid against contamination from outer world. Furthermore, the inner liquid can be released by disruption of the LMs via application of external stimuli, such as pH, temperature, magnetic field, and mechanical stress.[5] Thanks to these characters, researches on LMs have yielded various promising applications such as carriers of materials in microfluidics,[6,8–12] sensors,[13–17] miniature reactors for chemical and biological reactions,[3,7,18–24] and powdered pressure-sensitive adhesives.[25]

In spite of the fascinating character and applications of LMs, there are still limitations which need to be tackled in order to expand the opportunities and diversity of the LMs as a functional system. LMs are usually stabilized with solid particle aggregates with ill-defined shapes and wide size distributions. The particles with sizes ranging between a few micrometers and a few hundred micrometers scatter visible light, and therefore the particle layers on the LMs are opaque, which hinders clear observation of inner liquids from outside. The size of the LMs is between millimeters and a few centimeters, and their shapes are near-spheres and oblates, which are thermodynamically stable under gravity. In many cases, the LMs are too soft to be handled by fingers and are easily disrupted by mechanical stress. In particular, LMs larger than the capillary length (2.7 mm for water) are susceptible to mechanical stress.

In recent years, studies on shape-designable LMs have been started. Li's[26–29] group and Liu's[30] group demonstrated that LMs stabilized with SiO_2 nanoparticles showed plastic deformation; they could be mechanically formed into various shapes. Here, the strong adhesion of the nanoparticles to the droplet surfaces provided mechanical stability. These shape-designable LMs were named liquid plasticines (LPs).[26] It is noteworthy that the LMs/LPs developed by these two groups are near-transparent because of the attenuated light scattering due to the nano-sized particles. Salehabad et al.[31] succeeded in the fabrication of shape-designable LMs/LPs using stearic

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DOI: 10.1002/admi.202001573

acid powder as a stabilizer. It forms a gel layer on the LM/LP surfaces. Although several methods for fabricating shape-designable LMs/LPs have been proposed, the repertoire is still limited and there is a need to develop further methods to control the surface curvature, morphology, and transparency of the LMs/LPs. In addition, an interesting question is how large the LMs/LPs could be prepared. Therefore, fine design of shape and size of the LMs/LPs are still challenging research topics.

Recently, we succeeded in the fabrication of polyhedral LMs/LPs stabilized with millimeter-sized polymer plate monolayers.[32] The LMs/LPs could be stably deformed to shapes with convex and concave areas, which were kinetically stable. These shapes could not be attained with bare liquid droplets and general LMs. The polyhedral LMs/LPs were optically transparent. The inner liquid phase could be clearly observed, because the millimeter-sized polymer plates on the LM/LP surfaces hardly scattered visible light. In order to increase the range of possible applications of polyhedral LMs/LPs, it is crucial to gain detailed insight in the controllability of the shapes, sizes, and morphologies of these LMs/LPs.

In this study, we investigate the designability of highly transparent polyhedral LMs/LPs. In particular, curvature, shape, and size of the LMs/LPs are extensively explored. The handling ability of the LMs/LPs using pipette tips, fingers, and tweezers is demonstrated. Furthermore, we fabricate >1.5 m-sized LM/LP with an aspect ratio exceeding 800 and Janus LM/LP consisting of two sides covered by solid particles with different sizes by jointing method.

2. Results and Discussions

The size ratio ($D_{wd}/2S$) between the water droplet (diameter D_{wd}) and the size of the plates ($2S$) plays an important role in predicting the shape and size of the resulting LMs (**Figure 1**). In the case of conventional LMs, D_{wd} is larger than $2S$. Polyhedral LMs can be fabricated when the sizes of D_{wd} and $2S$ are comparable. In this study, transparent hexagonal poly(ethylene terephthalate) (PET) plates with three different sizes (S = 0.2, 1, and 2 mm) and the same thickness ($T \approx 38$ μm) were used to stabilize the LMs (Figure S1, Supporting Information). The PET plates did not form aggregates in air, because each PET plate was 0.2 mm or even larger. Therefore, gravity dominated rather than the attractive force between PET plates. The pristine PET plates were relatively hydrophilic; water formed a contact angle of 73°. Therefore, pristine plates could not stabilize stable LMs; only meta-stable LMs could be prepared using water droplets, which were easily broken by application of weak external mechanical stress. To render the PET plates suitable as an LM stabilizer, surface modification was conducted with trichloro(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane, as previously reported.[32] The contact angle of water droplets was measured to be 107°, indicating a hydrophobic surface.

Water droplets of 2–100 μL volume were placed onto the fluorinated and dried PET plate bed, and then slowly rolled on the bed. The hydrophobic PET plates (0.2, 1, 2 mm) spontaneously adsorbed to the surface of the water droplets, resulting in formation of LMs (**Figure 2**a). The size ratios ($D_{wd}/2S$) of water droplet diameter (D_{wd}, calculated assuming spherical droplet) to long diagonal length of the hexagonal PET plate ($2S$) are

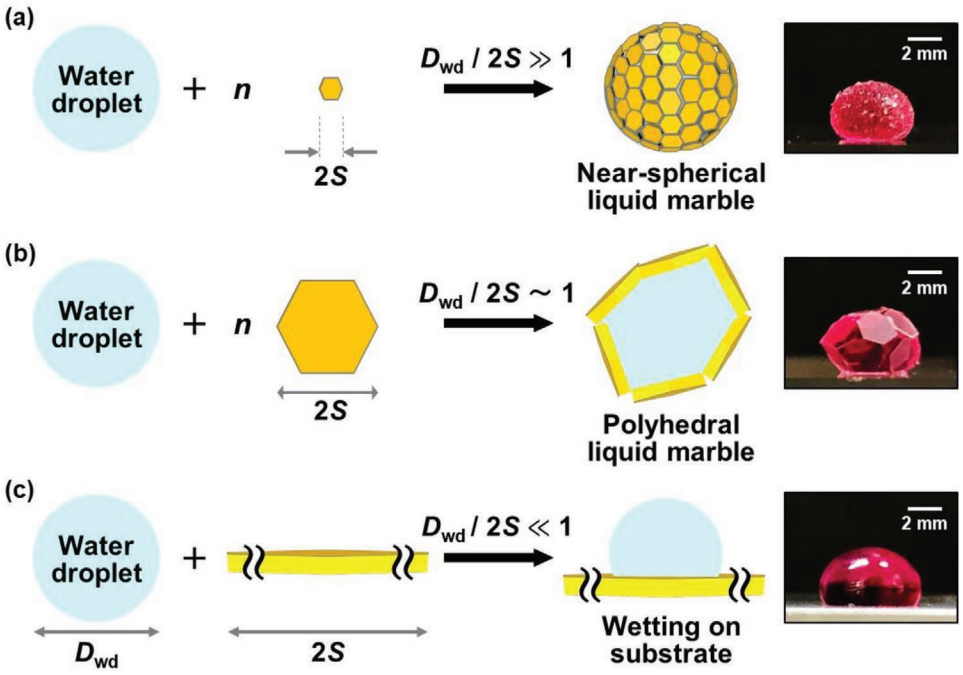

Figure 1. Relationship between water droplet size (D_{wd}) and solid plate size ($2S$). a) $D_{wd}/2S \gg 1$, near-spherical liquid marble (LM) is formed, b) $D_{wd}/2S \approx 1$, polyhedral LM is formed, and c) $D_{wd}/2S \ll 1$, wetting phenomenon described using Young's equation. Optical photographs of LMs stabilized with hydrophobic polyethylene terephthalate (PET) plates: a) 0.2 mm- and b) 2 mm-sized PET plates. c) Optical photograph of water droplet (50 μL) placed on hydrophobic PET film.

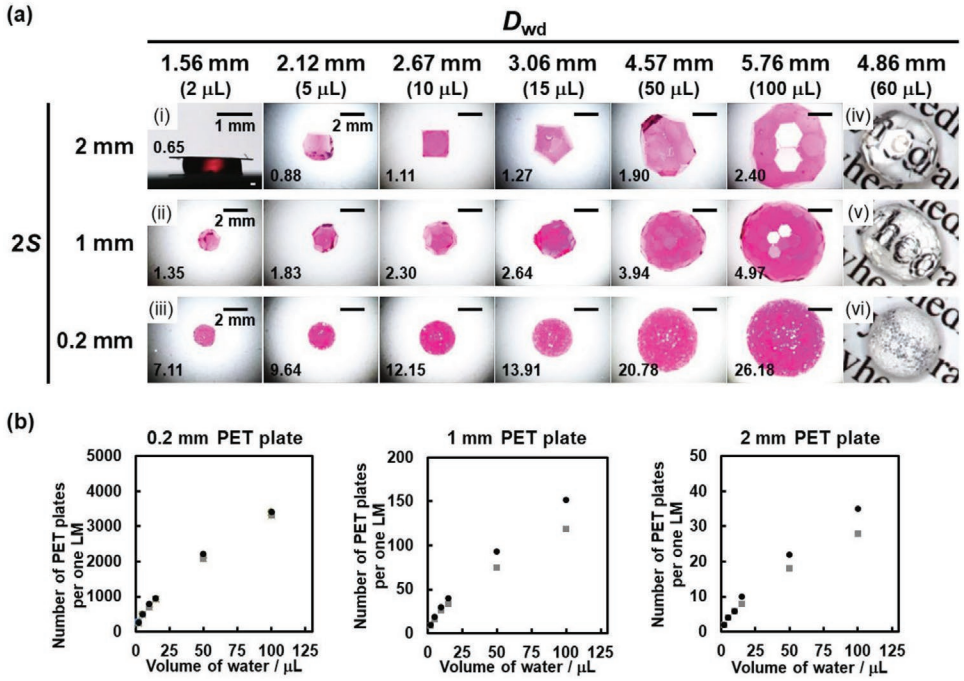

Figure 2. a) Optical photographs of polyhedral LMs with various amounts of internal liquid (dyed with 0.3 wt% Powder Sun Red YM) stabilized with hydrophobic PET plates with various plate sizes: (i,iv) 2 mm-, (ii,v) 1 mm-, and (iii,vi) 0.2 mm-sized PET plates. Lower left values are size ratio of water droplet/plate size ($D_{wd}/2S$). b) Relationship between internal water volume and number of adsorbed hydrophobic PET plates per one LM: (●) experimental and (■) theoretical values. The theoretical values were calculated assuming spherical water droplets.

shown in the lower left of the images. When the $D_{wd}/2S$ values exceeded 8, spherical or oblate-shaped LMs were formed as in the cases of conventional LMs.[2–5,33] When the $D_{wd}/2S$ values were between 2 and 8, mirror ball-like polyhedral LMs were fabricated. In the cases of the $D_{wd}/2S$ values between 0.8 and 2, polyhedral LMs with sharp edges were prepared. It is worth noting that it is even possible to form LMs, having a droplet size significantly below the size of the plates. Recently, these polyhedral structures have been also observed in particle-stabilized emulsion systems.[34] Interestingly, sandwich-like LMs were fabricated when the $D_{wd}/2S$ values were less than 0.8.

Figure 2b shows the relationship between the volume of internal water and the number of hydrophobic PET plates adsorbed to a single LM. Experimental adsorbed plate numbers were gravimetrically determined and the theoretical numbers (n) were calculated under assumption that the shape of the internal liquid is spherical using Equation (1) (also see Supporting Information).

$$n = 4.83\left(\frac{D_{wd}}{2S}\right)^2 \quad (1)$$

When the $D_{wd}/2S$ values of LMs stabilized with PET plates of different sizes were close, the shape of the LMs and the experimental number of PET plates adsorbed to the LMs were similar. For example, the number of PET plates adsorbed to an LM (2 μL) stabilized with 1 mm-sized PET plates ($D_{wd}/2S$ = 1.35, 10 plates) and that adsorbed to an LM (15 μL) stabilized with 2 mm-sized PET plates ($D_{wd}/2S$ = 1.27, 10 plates) were equal, the shape of the LMs was mirror ball-like polyhedron. The experimental plate number accorded relatively well with theoretical numbers (9 and 8 plates). It is interesting to note that the number of PET plates adsorbed to an LM (50 μL) stabilized with 2 mm-sized PET plates ($D_{wd}/2S$ = 1.90, 22 plates) was a little bit larger than that adsorbed to the LM (5 μL) stabilized with 1 mm-sized PET plates ($D_{wd}/2S$ = 1.83, 19 plates), even though the $D_{wd}/2S$ values were close. And the experimental numbers of adsorbed plates were a little bit larger than the theoretical numbers (17 and 16 plates). These are because the internal liquid volume increased and the shape of LM changed from sphere to oblate due to gravity, and the surface area of the droplet became a little bit larger than a spherical one (note that the capillary length of water is 2.7 mm; the capillary length is $(\gamma/g\rho)^{1/2}$, where γ is the surface tension of water, g = 9.81 m·s^{-2}, and ρ is the density of water). An LM (60 μL water) stabilized with 2 mm-sized PET plates showed excellent transparency and the transparency of the LMs decreased as the size of PET plates became smaller (Figure 2aiv–vi) (note that light scatters at air–PET plate and water–PET plate interfaces; refractive index of air, water, and PET are 1.0003,[35] 1.33,[35] and 1.57,[36] respectively). The small PET plates have larger specific surface areas compared to large ones, thus the light scattering area increased and the transparency of the LM was lowered.

The shape of the LMs could also be controlled by changing the number of adsorbed PET plates while keeping the volume of liquid constant. When 2 to 6 hydrophobic 2 mm-sized PET plates adsorbed to 10 μL water droplets, polyhedral LMs such as sandwich, trihedron, tetrahedron, pentahedron, and hexahedron (cube) could be prepared (**Figure 3**a). The surface area of the bare air–water interface decreased with increasing number of plates. Notably, cube-shaped LMs can be picked up with tweezers

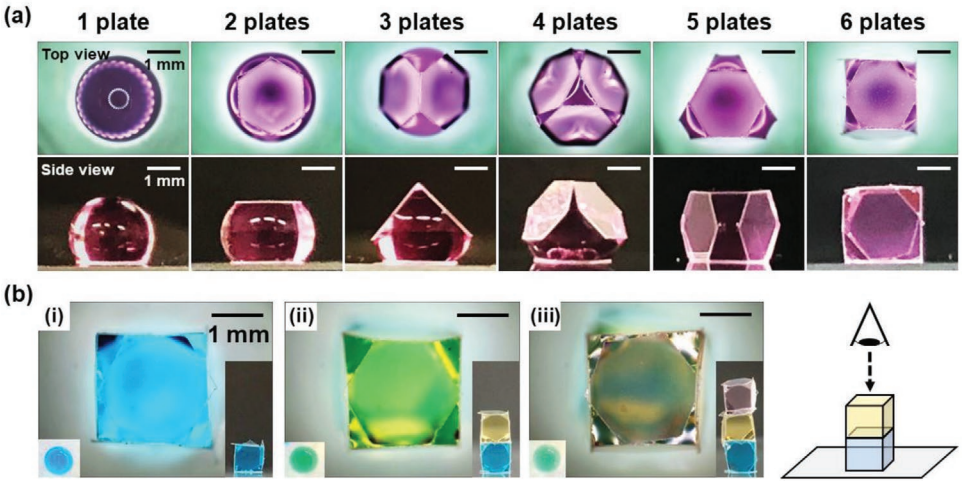

Figure 3. a) Polyhedral LMs with various shapes (e.g., sandwich-, trihedral-, tetrahedral-, pentahedral-, and cube-shaped LMs). Hydrophobic 2 mm-sized PET plates were adsorbed to water droplet (10 μL, dyed with 0.3 wt% Powder Sun Red YM). b) Optical photographs of piled cube-shaped LMs (10 μL) stabilized with hydrophobic 2 mm-sized PET plates, observed from top. Insets show side views. Internal liquids were dyed with 3×10^{-3} wt% Food Blue, 3×10^{-3} wt% Food Yellow, and 5×10^{-2} wt% Powder Sun Red YM. The illustration explaining how to observe the piled cube-shaped LMs is also shown.

or fingers (Figure S2, Supporting Information). This renders it possible to pile them up on top of each other. The color of light transmitted through a stack of LMs could be tuned when LMs of differently colored internal phase were used. For example, in Figure 3b, blue, yellow, and red colored cubes were piled up on top of each other. The reservoirs of the piled-up LMs were not connected; dye from one LM did not enter the other LMs. Since the polyhedral LMs were stabilized with millimeter-sized plate-shaped stabilizer, light scattering could be extensively attenuated compared to those fabricated using solid particles with diameters of tens of nanometers to micrometers. Therefore, it was easy to observe the internal liquid of the polyhedral LM.

The size as well as the shape of the LMs could be controlled by coalescence (jointing) of multiple LMs and by application of external mechanical stress to them. **Figure 4**a shows two LMs stabilized with 2 mm-sized PET plates that were jointed using pipette tips. The joint LM/LP could be shaped with the pipette tips and an LM/LP with 90° edges could be prepared. The same method was utilized to prepare LMs/LPs stabilized with 0.2 and 1 mm-sized PET plates having angles of <45° to 360°. The sharpness of the angle decreased with a decrease of plate size (Figure 4b). This is because the sizes of the plates were smaller than those of water droplets.

Surprisingly, an LM/LP with a length of 1.7 m could be fabricated using 2 mm-sized PET plates (**Figure 5**a). This extraordinary long LM/LP was fabricated by jointing ≈300 near-spherical LMs (50 μL). Please note that it took more than 10 h to fabricate the meter-sized LM/LP and additional water was added to

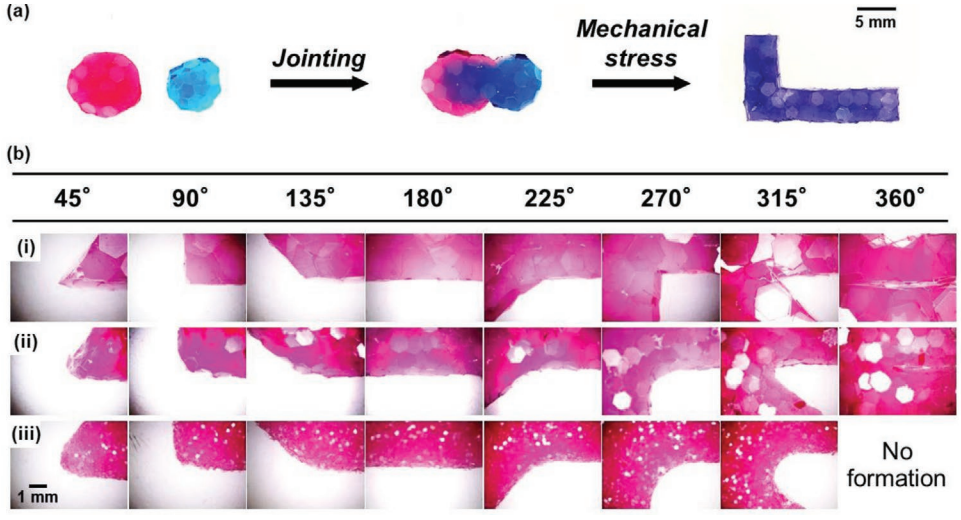

Figure 4. a) Optical photographs demonstrating joint process of two LMs, followed by shape designing via application of external mechanical stress in the presence of additional free PET plates. b) Optical photographs of parts of polyhedral LMs/LPs with various angles stabilized with hydrophobic PET plates: (i) 2 mm-, (ii) 1 mm-, and (iii) 0.2 mm-sized PET plates. Internal liquid was dyed with 0.3 wt% Powder Sun Red YM.

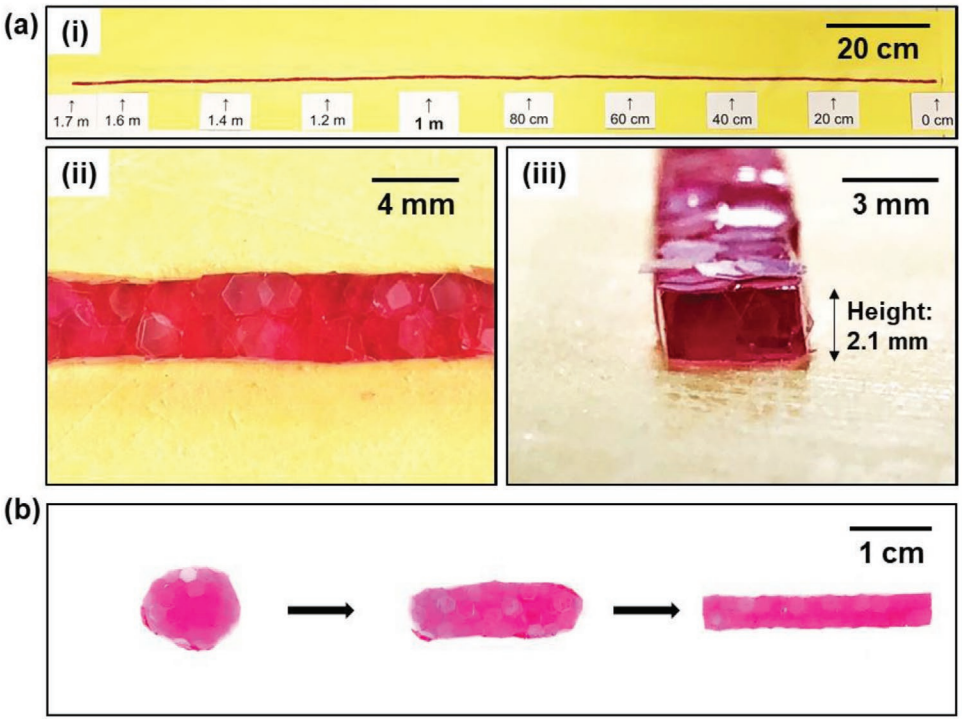

Figure 5. a) Optical photographs of extraordinarily long LM/LP with a length of 1.7 m (aspect ratio: 810 (side view), 354 (top view)). The LM/LP was prepared by jointing LMs (50 µL) stabilized with hydrophobic 2 mm-sized PET plates: (i,ii) Top views and (iii) side view. Internal liquid was dyed with 0.3 wt% Powder Sun Red YM. b) Shape manipulation from spherical LM to cuboid LM/LP by application of external physical stress in the presence of additional free PET plates.

the LM/LP, because water evaporated during fabrication. The length of the worm-like LM/LP could be extended without any limit by additional jointing. The aspect ratios of the 1.7 m-long LM/LP were estimated to be 810 and 354 from side and top views. To the best of our knowledge, this is the largest aspect ratio for an LM/LP which has ever been reported. Such a cuboid LM/LP could also be prepared by applying external stress on a polyhedral LM/LP using pipette tips in the presence of free hydrophobic 2 mm-sized PET plates (Figure 5b). Here, the free hydrophobic PET plates adsorbed to the newly exposed air–liquid interface on the LM/LP surface during shape designing.

To find out where precisely the PET plates are positioned at the air–water interface, ethyl-2-cyanoacrylate vapor treatment was conducted on an LM, followed by scanning electron microscopy (SEM) observation.[37,38] A poly(ethyl-2-cyanoacrylate) film was formed on the bare air–water interface of the LM stabilized with hydrophobic PET plates, trapping the plates at the interface (**Figure 6**a). The obtained capsules were broken and the cross section was observed using an optical microscope and SEM (Figure 6a,b). Only the inner sides of the PET plates were in contact with water. The contact lines were pinned at the inner edge of the plates. Thus, the internal water was confined inside the hydrophobic PET plates. The position of the contact line also explains why polyhedral LMs/LPs were stable on hydrophilic glass. The plates were ≈38 µm thick, creating an air layer of roughly the same thickness.

After clarifying the adsorption position of the PET plates at the air–water interface, the adsorption energies can be calculated using Equation (2) (also see Supporting Information):[32]

$$\Delta G = \frac{3\sqrt{3}}{2} S^2 \left(\gamma_{WS} - \gamma_{AS} - \gamma_{AW}\right) \quad (2)$$

where γ_{WS} is the solid–water interfacial tension, γ_{AS} is the air–solid interfacial tension, and γ_{AW} the is air–water interfacial tension. The adsorption energies of 0.2, 1, and 2 mm-sized PET plates were calculated to be -3.87×10^{11}, -1.08×10^{13}, and -4.61×10^{13} kT, respectively. Here, ΔG is negative, indicating spontaneous adsorption of the plate to the interface. Due to these extremely high adsorption energies compared to those of molecular-level surfactants (≈a few tens kT), the adsorption of the plate to the air–liquid interface is irreversible at room temperature. Therefore, the LM/LP surfaces showed plastic character due to steric jamming.[27,39,40]

When changing the volume by injection and suction of inner water of an LM/LP while keeping the plate number fixed, morphological changes of a cuboid LM/LP (200 µL) were observed (Figure S3, Supporting Information). The shape of the LM/LP gradually changed from cuboid to oblate during water injection (1000 µL) using a needle, which relaxed the jammed interface because of an increase of droplet surface area (Figure S3i,ii, Supporting Information). From the water-added oblate LM/LP, the inner water was then sucked out (900 µL) using the needle, which resulted in a decrease of LM/LP size, keeping its oblate shape and eventually buckling occurred on the LM/LP surface (Figure S3iii, Supporting Information), rather than going back to the original non-equilibrium jammed cuboid shape. Then, the water (900 µL) was again injected to the buckled polyhedral LM/LP, which led to its previous oblate shape (Figure S3iv,

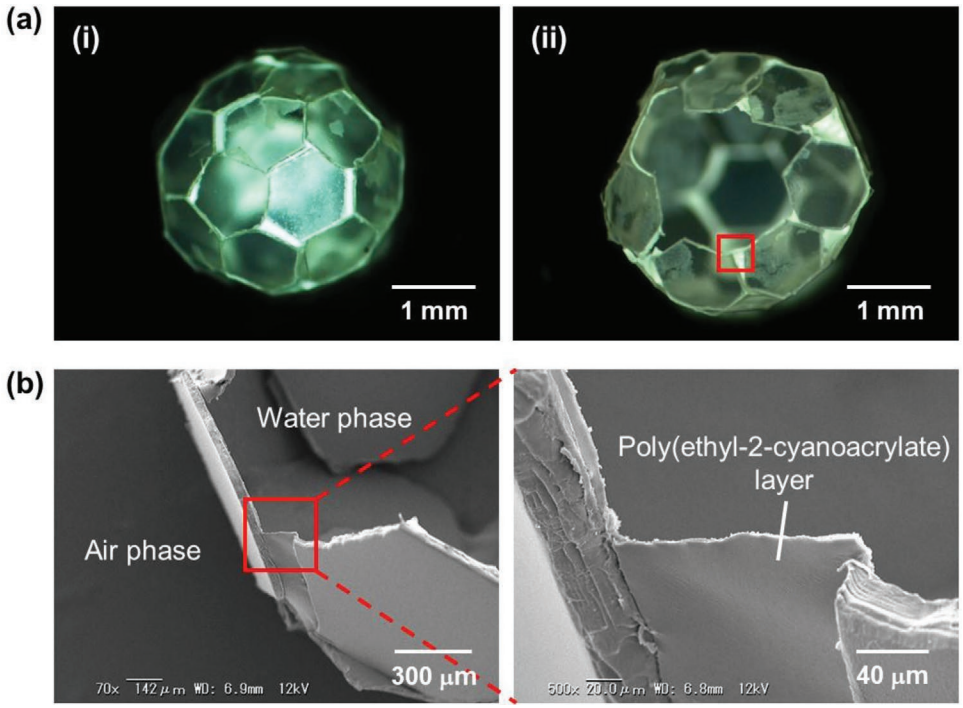

Figure 6. a) Optical photographs and b) scanning electron microscopy images of polyhedral LM (10 μL) stabilized by hydrophobic 1 mm-sized PET plates after interfacial anionic polymerization of ethyl-2-cyanoacrylate, followed by evaporation of water. (i) Before and (ii) after breakage using spatula.

Supporting Information). These results also indicate that the non-spherical LMs/LPs were realized due to steric surface jamming.

Different shapes of polyhedral LMs/LPs with different curvatures could be fabricated (**Figure 7**a). It was possible to prepare stable LMs/LPs carrying convex and concave areas with various shapes. Figure 7b shows the alphabet table made from LMs/LPs. It is worth noting that the letters of alphabet with hole(s) (e.g., B, D, O, Q, and R) could be prepared. The font

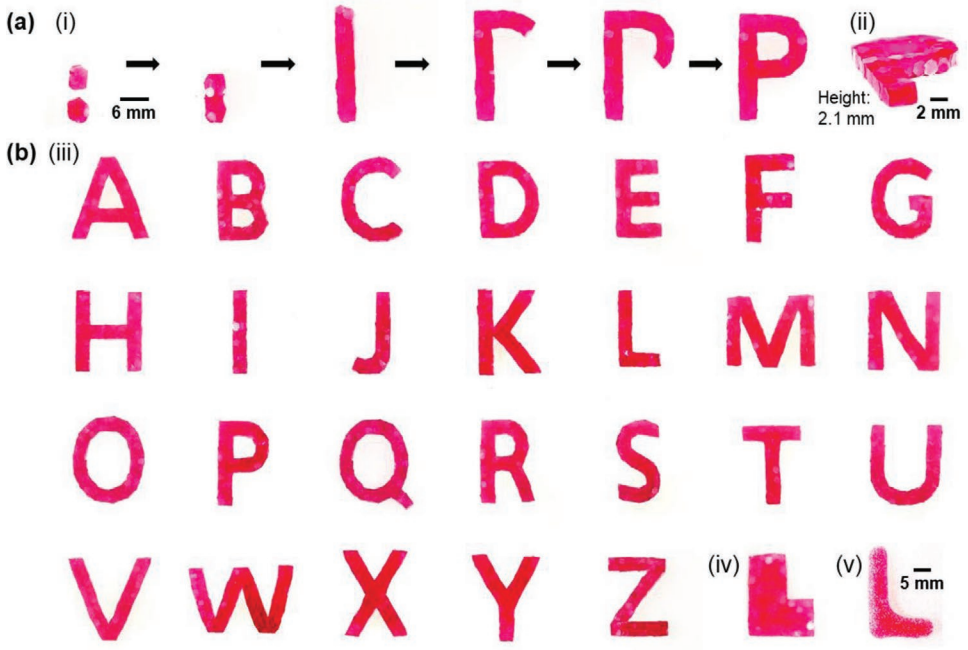

Figure 7. a) Optical photographs showing process of preparing "P"-shaped LM/LP stabilized with hydrophobic 2 mm-sized PET plates. "P"-shaped LM/LP was prepared via application of external physical stress after jointing polyhedral LMs (50 μL): (i) Top views and (ii) side view. b) Optical photograph of LM/LP alphabet table. The LMs/LPs were stabilized with hydrophobic (iii,iv) 2 mm- and (v) 0.2 mm-sized PET plates.

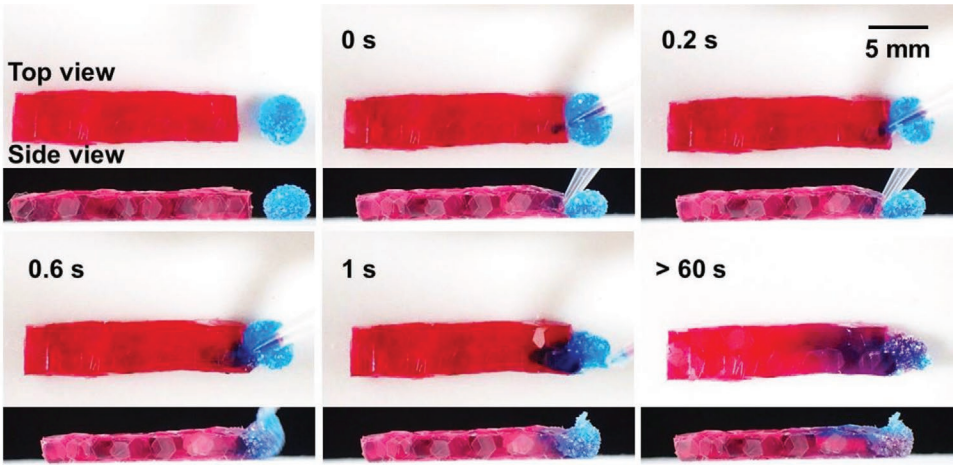

Figure 8. Optical photographs showing process to fabricate Janus-type LM/LP by jointing of cuboid LM/LP (200 µL) and spherical LM (25 µL). Cuboid LM/LP was stabilized with hydrophobic 2 mm-sized PET plates (dyed with 0.3 wt% Powder Sun Red YM). Spherical LM was stabilized with hydrophobic 0.2 mm-sized PET plates (dyed with 5×10^{-3} wt% Food blue).

weight of the letters could be also changed (Figure 7biv and Figure S4a, Supporting Information); the width of the line could be controlled to 1, 2, 3, and 5 plate sizes in a stepwise fashion. Additionally, font of the letters could be controlled by varying plate size (Figure 7bv and Figure S4b, Supporting Information). L-shaped LM/LP stabilized with 2 mm-sized PET plates had sharp edges, but the edges became softer as the size of the PET plate decreased. The L-shaped LM/LP stabilized with 2 mm-sized PET plates could retain its shape even after placement in *n*-dodecane for over 2 days (Figure S5, Supporting Information).

Finally, a Janus-type LM/LP with different curvatures and different stabilizers in a single LM/LP was prepared by jointing a near-spherical LM stabilized with 0.2 mm-sized PET plates and a cuboid LM/LP stabilized with 2 mm-sized PET plates (**Figure 8**). Simple jointing led to the formation of a Janus-type LM/LP. We confirmed that the internal liquid of the spherical LM flowed into the cuboid LM/LP immediately after jointing. Gravimetric study after cutting the Janus LM/LP at the connection point confirmed that 59 ± 6% inner water of the near-spherical LM stabilized with 0.2 mm-sized PET plates flowed into the cuboid LM/LP. This phenomenon can be discussed from a viewpoint of Laplace pressure.[41]

The Laplace pressures of near-spherical LM stabilized with 0.2 mm-sized PET plates and cuboid LM/LP stabilized with 2 mm-sized PET plates were estimated using the capillary method.[42–44] First, the tip of the glass capillary was plugged into pure water, and the height (H) to which the water has risen inside the capillary was measured. The surface tension of pure water (γ_{AW}) was determined from the H value using Jurin's law (Equation 3).

$$\gamma_{AW} = \frac{\rho g R_{cap} H}{2} \tag{3}$$

Here, R_{cap} (0.3 mm) is the inner radius of the glass capillary. The calculated γ_{AW} values were 72.2 ± 0.2 mNm^{-1} (Table S1, Supporting Information). Since these measured γ_{AW} values were close to those of pure water, it was confirmed that the measurement accuracy was high. Subsequently, the same glass capillary (containing water) was plugged into the near-spherical LM and cuboid LM/LP, and the additional heights (ΔH) of water rising in the glass capillary were measured. The Laplace pressures were calculated by substituting ΔH into Equation (4).

$$\Delta P = \rho g \Delta H \tag{4}$$

Based on Equation (4), the Laplace pressures of near-spherical LM and cuboid LM/LP were estimated to be 65.9 ± 6.9 and 2.3 ± 1.1 Pa. The Laplace pressure of near-spherical LM was larger than that of cuboid LM/LP. From these results, it can be concluded that the internal liquid of the near-spherical LM flowed into the cuboid LM/LP due to the difference in Laplace pressure of the inner water.

3. Conclusion

In conclusion, we demonstrated that polyhedral LMs/LPs can be prepared by rolling water droplets on a hydrophobic PET plate bed. The shape and size of the LMs/LPs was precisely controlled by tuning the size ratio of the water droplet compared to the PET plate size and number of plates adsorbed to the droplet. Coalescence (jointing) of multiple polyhedral LMs/LPs and application of external mechanical stress could also work to design the shape of the LMs/LPs. It was possible to pick up and pile up LMs onto each other using tweezers or fingers. Notably, we could design an LM/LP with an aspect ratio exceeding 800, the largest aspect ratio ever reported. Janus-type LM/LP with different curvatures and different stabilizers in a single LM/LP was successfully fabricated by coalescence of near-spherical and cuboid LMs/LPs stabilized by PET plates with different sizes. It was confirmed that the internal liquid of the near-spherical LM flowed into the cuboid LM/LP immediately after jointing and the system could be used as a micropump. Handling of liquid droplets has received great interest in a broad range of research areas including microfluidics, enabling chemical reactions, medical analysis, separation and extraction of target analytes,

triboelectric generation, and water harvesting.[8,45–50] The shape-designable polyhedral LMs/LPs developed in this study show unique handling abilities and should attain great interest due to possible applications including high-performance microreaction containers and sensors.[51,52]

4. Experimental Section

Materials: The following chemicals were used without further purification: Trichloro(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane (96%, TCI), *n*-hexane (96%, Wako), ethanol (95%, Sigma-Aldrich), ethyl-2-cyanoacrylate (> 95%, Toa Gosei Co., Ltd.), *n*-dodecane (≥ 99%, Sigma-Aldrich), Powder Sun Red YM (San-Ei Gen F.F.I Co., Inc.), Food Blue (San-Ei Gen F.F.I Co., Inc.), and Food Yellow (San-Ei Gen F.F.I Co., Inc.). Water purification was performed using an Advantec MFS RFD240NA (GA25A-0715), and the doubly distilled water was used for all experiments. Transparent PET plates with sizes of 0.2 mm ($S = 0.11 \pm 0.01$ mm, $T = 36.6 \pm 9.0$ μm), 1 mm ($S = 0.57 \pm 0.03$ mm, $T = 38.5 \pm 9.1$ μm), and 2 mm ($S = 1.2 \pm 0.1$ mm, $T = 37.8 \pm 8.8$ μm) were obtained from Nakajima Metal Leaf, Powder Co., Ltd., (Figure 1 and Figure S1, Supporting Information) (here, 2*S* and *T* are the long diagonal length and thickness of the hexagonal plate, respectively). Glass capillaries (FPT-100, Fujiston) with inner and outer diameters of 0.60 and 1.0 mm, respectively, were obtained from Fujirika Co., Ltd., Osaka, Japan.

Hydrophobization of Polymer Plates: Hydrophobization was conducted using hydrophobic silane coupling agent as reported previously.[32] The pristine PET plates (50 g) were sonicated in ethanol (300–400 mL) for 10 min and the supernatant was discarded. This cycle was repeated three or four times. The washed PET plates were first dried in ambient atmosphere for 24 h and then left under vacuum overnight. The dried PET plates (10 g) were dispersed in *n*-hexane (40 mL), followed by addition of trichloro(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane (40 μL). During the reaction time of 30 min, the dispersion was shaken every 5 min for ≈20 s to ensure homogeneous surface modification of the PET plates. Subsequently, the modified PET plates were rinsed three times with *n*-hexane. The hydrophobized PET plates were first dried in atmosphere for 24 h and then left under vacuum overnight.

Preparation of Polyhedral Liquid Marbles: The near-spherical and oblate-shaped polyhedral LMs were prepared by dropping water using a micropipette (00-NPLO2, Nichiryo Co., Ltd.) on the PET plate bed placed on surface-roughened perfluoroalkoxy alkane (PFA) petri dish (Sanplatec Co., Ltd.) and subsequent rolling on the bed. The prepared LMs could be transferred to other substrates including hydrophilic glass slides using a glass/plastic spoon. The internal liquids were dyed using Powder Sun Red YM, Food Blue, or Food Yellow. Observation of PET plates and LMs were conducted using a stereo microscope (TG300PC, Shodensha Co., Ltd.) and an SEM (Keyence Co., VE-8800, 12 kV).

Encapsulation of Polyhedral Liquid Marbles: Ethyl-2-cyanoacrylate can react with water and initiate its polymerization. This polymerization proceeds rapidly upon exposure to water surface. By exposure of a polyhedral LM (10 μL) stabilized with hydrophobic 1 mm-sized PET plates to the ethyl-2-cyanoacrylate vapor generated at ≈50 °C in an enclosed box for 30 min, bare air–water surface of LM, where no plate was adsorbed, was covered with poly(ethyl-2-cyanoacrylate) and the PET plates were trapped at the air-water interface

Shape Control of Polyhedral Liquid Marbles/Liquid Plasticines: To fabricate kinetically stable non-spherical LMs/LPs, external mechanical stress was applied using pipette tips (00-BMT2-SG, Nichiryo Co., Ltd.) to joint near-spherical LMs. Alternatively, oblate-shaped LMs/LPs were deformed by rolling them in horizontal direction on the PET plate bed. During rolling, the surrounding free PET plates adsorbed to the free air–water interface newly generated by the deformation to lower the surface energy. To obtain the Janus-type LM/LP, near-spherical LM (25 μL) and cuboid LM/LP (200 μL) were jointed on the surface-roughened PFA substrate and. The smaller near-spherical LM was stabilized with hydrophobic 0.2 mm-sized PET plates. The larger cuboid LM/LP was stabilized with hydrophobic 2 mm-sized PET plates. The internal liquid was dyed with Powder Sun Red YM and Food Blue.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors thank Prof. D. Vollmer (Max Planck Institute for Polymer Research) for stimulating discussions. San-Ei Gen F.F.I. is thanked for the kind donation of dyes. This work was supported by JSPS-DAAD Bilateral Joint Research Project, a Grant-in-Aid for Scientific Research (B) (JSPS KAKENHI Grant Number JP20H02803) and Scientific Research on Innovative Areas "Engineering Neo-Biomimetics (JSPS KAKENHI Grant Number JP15H01602)" and "New Polymeric Materials Based on Element-Blocks (JSPS KAKENHI Grant Number JP15H00767)", Private University Research Branding Project (Type A: Osaka Industrial Technology Platform) and ERC Advanced Grant No. 340391 "SUPRO" (H.-J.B. and F.G.), the German Research Foundation (DFG) with the Collaborative Research Center 1194 (H.-J.B. and F.G.).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

interfacial jamming, Janus, liquid marbles, liquid plasticines, shapes

Received: September 7, 2020
Revised: October 8, 2020
Published online: November 4, 2020

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