Langmuir

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Unloading and Reloading Colloidal Microcapsules with Apolar Solutions by Controlled and Reversible Buckling

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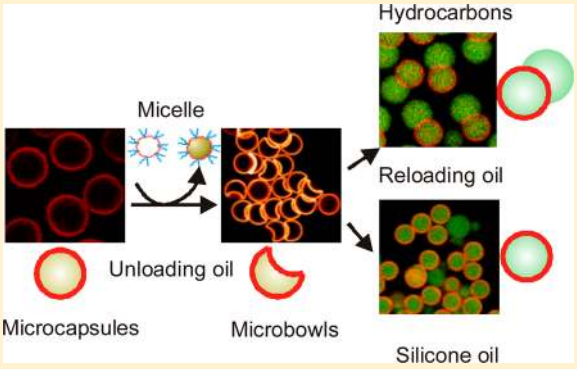
Supporting Information

ABSTRACT: We introduce a new experimental method to encapsulate and release oils and fluorescent molecules into preformed elastic colloidal microcapsules of polydimethylsiloxane (PDMS)-filled siloxane shells, which are cross-linked with tetraethoxysilane. The method uses controlled buckling, where the volume of the capsule is reduced by dissolving the PDMS oil inside the capsule by surfactant micelles. This results in a change in the morphology of the capsule that depends on the ratio of shell thickness to total particle radius (d/R_t). Microcapsules of d/R_t in the range 0.007−0.05 formed microbowls upon decreasing the inner volume. The amount of oil released or dissolved by the micelles can be directly related to the concentration of surfactant. By tuning the amount of oil released, we can make microbowls of variable depth. In addition, we demonstrate that the microbowls can be further used to load different oils like silicone oil, hydrocarbons, and apolar dyes. The elasticity of the capsule wall and the leftover PDMS oil inside the capsule provide the principal driving forces by which one can promote the uptake of different oils, including dissolved dye molecules.



1. INTRODUCTION

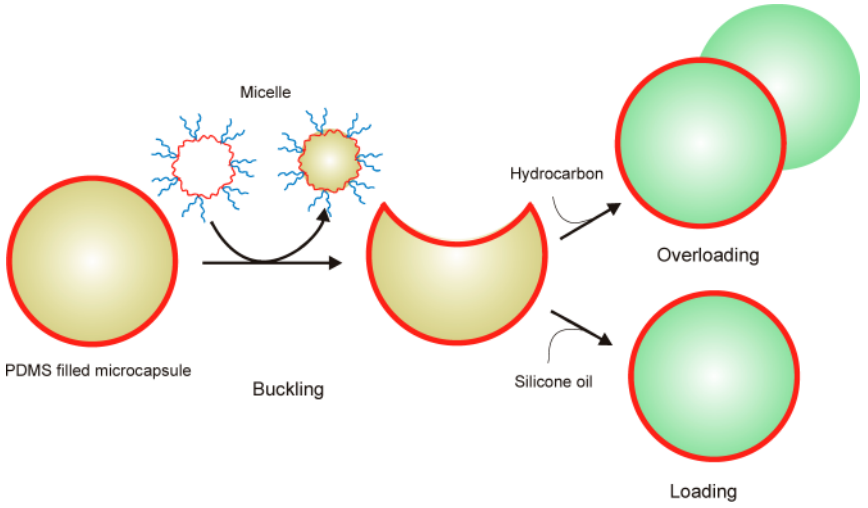
In recent years polymer microcapsules have gained huge attention in fields as diverse as food science, pharmaceutics, cosmetics, biotechnology, the paint industry, and advanced materials.[1−7] To date, different routes are available to fabricate a range of polymer capsules. Among them, the templating technique is a well-known synthesis route. In this technique material is deposited on to a sacrificial template via methods such as interfacial polymerization[8,9] and layer-by-layer self-assembly.[5,10] Various templates, including solid particles (e.g., silica, latex, or gold colloidal particles)[11−14] and emulsion droplets,[15,16] have been used for this purpose. One main advantage of emulsion droplets as templates over solid particles is that the former can be removed under relatively mild conditions. In recent years there has been an increasing demand for microcapsules that can encapsulate and release cargo as desired, especially in the medical field for drug delivery. Polyelectrolyte microcapsules are a versatile system studied intensively in biotechnology and medicine for the controlled and targeted delivery of therapeutic molecules.[17−20] They are made by layer-by-layer adsorption of polyelectrolytes onto charged colloidal templates, followed by decomposition of the templates. One advantage of these microcapsules compared to other polymer capsules is the tunability of both capsule interior and wall using external triggers like a change in pH, temperature, ionic strength, etc.[21−23] Moreover, the capsule wall can be functionalized with nanoparticles and biomolecules for targeted delivery.[24] In microcapsules available today chemicals are mostly encapsulated in the template during the synthesis. Alternatively, chemicals are allowed to diffuse through the permeable wall, but the amount loaded will be limited by the bulk concentration and the encapsulation efficiency will be low. Accumulation inside preformed capsules has been observed to a certain extent in polyelectrolyte capsules.[25,26] But it remains a challenge to design capsules that can reversibly load and release their cargo above the level at which it is present in the solvent.

Microcapsules generally undergo a deformation when materials are released from their interior. This deformation results in interesting shapes depending on several factors like composition and thickness to radius ratio of the capsule, rate of deformation, wall permeability, etc.[27,28] It is also important to have a good release mechanism for different types of microcapsules. In polyelectrolyte microcapsules the deformation of the capsule was achieved by osmotically induced buckling.[29] Also recently atomic force microscopy (AFM) in combination with fluorescence microscopy was used to quantify the release of materials from polyelectrolyte capsules.[30] Moreover, an osmotic pressure difference has been used to investigate the folding pathways of polymer capsules of inhomogeneous thickness, upon release of inner material.[31] Another way to release the core and to induce buckling was

Received: January 7, 2014
Revised: February 18, 2014
Published: February 19, 2014

 © 2014 American Chemical Society dx.doi.org/10.1021/la500070s | *Langmuir* 2014, 30, 2385−2393

Scheme 1. Schematic Illustrating the Release of Core Material through Micelle Induced Buckling of a TC-PDMS Microcapsule and Subsequent Loading and Overloading in the Presence of Silicone Oil and Hydrocarbons



reported in microcapsules made of Pickering emulsion droplets.[32] There the deformation was induced by dissolving the inner core in an unsaturated continuous phase resulting in different morphologies.

In this paper we focus on a new type of polymer capsule, recently developed in our group by Zoldesi et al.[33,34] using an emulsion templating technique. They are highly monodisperse, elastic tetraethoxysilane-cross-linked-polydimethylsiloxane (TC-PDMS) colloids. The sacrificial templates used for microcapsule preparation were emulsion droplets of polydimethylsiloxane (PDMS). By now, several groups have used these droplets as templates for making different microcapsules because of their high monodispersity and relatively easy removal.[35−37] The PDMS droplets are obtained by the base-catalyzed hydrolysis and condensation of the difunctional silane monomer dimethyldiethoxysilane (DMDES) into short linear oligomers approximately four units long.[38] The droplets are then coated with a solid shell which is formed by cross-linking of a small percentage of the silicone oligomer with tetraethyl orthosilicate (TEOS). If desired, the template can be easily removed by transferring the capsules to ethanol or even by evaporation, leading to hollow TC-PDMS capsules. One main advantage of these microcapsules is the tunability of the shell thickness. It was found that, depending on the ratio of the shell thickness to the total particle radius (i.e., droplet radius and shell thickness) (d/R_t), solvent-filled TC-PDMS capsules formed different shapes upon drying: microspheres, microbowls, and microballoons.[34] Therefore they are also a good candidate for making anisotropic colloids. For many applications, the most important properties of a capsule are its wall permeability, adhesion, and mechanical behavior. Mechanical properties of the solvent-filled TC-PDMS capsules were investigated using AFM and buckling experiments.[39] The deformation of the capsules strictly followed a macroscopic continuum theory derived to describe the elasticity of thin shells.[40,41] This was true both for the regime where the capsules were slightly flattened by the AFM's tip and the regime where a dimple is formed in the capsule wall. The Young's modulus (E) of the shell was found to be 200 MPa, indicating that the material is somewhere between a soft polymer and a stiff rubber.[39] Qualitative experiments showed the permeability of hollow shells to polar molecules but excluded apolar chemicals.[33] No studies were done on the controlled release and loading of chemicals in these microcapsules, as far as we know.

Herein, we report a novel method which enables these microcapsules to be emptied and then reloaded with an oil that could contain functional compounds, like surfactants, dyes, or drugs. If needed, they can even be loaded and unloaded multiple times. This adds functionality for use in, for example, drug delivery. In the proposed method we utilize two aspects of TC-PDMS microcapsules that drive these processes: the elasticity of the shell and the apolar nature of the emulsion template. Release by buckling is first induced by micelles, which gradually dissolve the PDMS oil template inside the microcapsule by forming a microemulsion. This transforms the shape of the microcapsules to bowls. This shape provides an elastic restoring force to drive the reloading of the capsule when exposed to excess oil, like low molecular weight silicone oil or hydrocarbons that may also contain, for example, a hydrophobic dye. This process was helped by the mixing of the added hydrophobic chemical with some remaining PDMS template, which provided an additional driving force. The loading of hydrocarbons also led to interesting particle morphologies which depended on the kinetics at which the content was able to pass through the shells. Scheme 1 shows the whole process of release of PDMS oil and subsequent loading of different oils.

2. EXPERIMENTAL SECTION

Materials. Dimethyldiethoxysilane (DMDES, 97.0%) was obtained from Fluka Analytical. Tetraethyl orthosilicate (TEOS, 98.0%), 3-aminopropyltriethoxysilane (APS, 99%), rhodamine B isothiocynate (RITC), pyrromethene 546, triblock copolymer Pluronic P123 ($(PEG)_{20}-(PPG)_{70}-(PEG)_{20}$, M_w = 5800), ammonia (25 wt % NH_3), octamethylcyclotetrasiloxane (OMCTS, $C_8H_{24}O_4Si_4$), cyclohexane (C_6H_{12}, 99.8%), decane ($C_{10}H_{22}$, 99.0%), and hexadecane ($C_{16}H_{34}$, 99.0%) were purchased from Sigma-Aldrich. CdSe QD's were prepared using the recipe from ref 42. All chemicals were used as received. Demineralized water (resistivity ∼18 MΩ cm) was used in all reactions and also for cleaning of glassware.

Preparation of PDMS Contained Tetraethoxysilane-Cross-Linked-Polydimethylsiloxane (TC-PDMS) Microcapsules. PDMS-filled microcapsules were prepared by the emulsion templating method reported by Zoldesi et al.[34] The synthesis was performed in two steps. In the first step monodisperse, PDMS an oil-in-water emulsion was prepared by base-catalyzed hydrolysis and partial

dx.doi.org/10.1021/la500070s | Langmuir 2014, 30, 2385−2393

condensation of the DMDES monomer ($(CH_3)_2Si(OC_2H_5)_2$). To make the microcapsule suspension (11 mL), DMDES monomer (1 mL) and 25 wt % ammonia solution (2.5 mL) were added to deionized water (7.5 mL). The reaction mixture was then mixed by shaking either in a vortex mixer or by hand for few minutes. By this time the nucleation of PDMS droplets had started, and the sample was placed on a roller bank to gently stir the mixture during droplet growth. The concentrations of DMDES and ammonia used were higher than what was used in ref 34. Droplets were grown for 3−8 days. In the second step PDMS oil droplets were coated with a tetraethoxysilane-cross-linked-polydimethylsiloxane (TC-PDMS) shell by adding TEOS (0.018 M) in steps with 5 min intervals and then placing on rollers after each addition. The sample was diluted with deionized water (3 mL) prior to the addition of TEOS. To incorporate dye in the sample, a solution of RITC (6.3 μL), prepared by mixing overnight RITC powder (6.5 mg) in ethanol (1 mL) and APS (coupling agent) (40 μL), was added to the sample after the addition of TEOS. The shell is formed by the co-condensation of TEOS and unreacted DMDES left over from the PDMS droplet synthesis. From previous studies[33] it was clear that the main contribution to the thickness of the shell is from the unreacted DMDES in the sample. By tuning the days of droplet growth (3−8 days) and shell growth (1−5 days), we prepared microcapsules of different shell thickness/total particle radius (d/R_t). We note that this procedure sometimes leads to more polydisperse shells. We did our experiments only on those batches that turned out monodisperse.

Characterization. The size and polydispersity of the PDMS oil droplets were determined by static light scattering (SLS) experiments. The measurements were carried out using home-built equipment using a He−Ne laser as light source (632.8 nm, 10 mW). The thickness of the shell was measured using atomic force microscopy (AFM) in tapping mode. Samples for AFM were prepared by applying a drop of the hollow shells in ethanol onto a glass cover slide. The collapse of the shells leads to plateaus in the height that correspond to twice the thickness of the shell (Supporting Information Figure S4). To study the postbuckling morphologies of the microcapsules and the relaxation of the microbowls in real space, an inverted Leica TCS-SP2 confocal scanning laser microscope in fluorescence mode was used. A 543 nm green He−Ne laser was used for the excitation of rhodamine-labeled shells, and the 488 nm blue argon laser was used for the excitation of pyrromethene 546 dye and CdSe QD's. Samples were taken in a capillary either 0.1 × 1 or 0.1 × 2 mm for imaging.

Controlled Buckling of Capsules. PDMS oil from inside the microcapsule was released by adding a surfactant. A stock solution of Pluronic P123 (15 wt %) in water was prepared. The total radius (R_t) of the particle and the thickness (d) of the shell of two microcapsules used to study the variation of the depth of the dimples with surfactant concentrations were R_t = 2225 and 2133 nm and d = 88 and 16 nm, respectively. This corresponds to a (d/R_t) of 0.04 and 0.0075. Different concentrations of P123 were added to a suspension of d/R_t = 0.04 (0.52% v/v) microcapsules and a suspension of d/R_t = 0.0075 (1.53% v/v) microcapsules. After addition, the sample was shaken well and left to equilibrate for 30 min. Then a capillary (Vitrocom, 0.1 × 1 mm/0.1 × 2 mm) was filled with suspension to image the morphology of the microbowls. To study the evolution of the morphology upon surfactant addition of thin microcapsules with d/R_t = 0.006 and d/R_t < 0.005, a capillary was partly filled with microcapsule suspension. Then slowly a P123 solution was injected into the remaining space of the capillary, such that a concentration gradient of P123 built up in the capillary. In this way we could see individual buckling events of microcapsules in the confocal or optical microscope.

Reversed Buckling of Microbowls. Microbowls obtained from buckling experiments were used to encapsulate different oils like silicone oil and hydrocarbons. The microbowls were therefore already placed in a Pluronic surfactant solution. The shell thickness to total particle radius (d/R_t) of these microbowls was 0.04. For the encapsulation of OMCTS and cyclohexane bowls of depth to particle radius, δ/R_t = 0.78 were used and for hexadecane δ/R_t = 0.56. The oil was dyed by dissolving pyrromethene 546 (oil soluble dye) (2 mg) in oil (1 mL) prior to addition, except for decane. The dyed oil (100 μL) was added to microbowl suspension (100 μL), and the sample was put on the roller bank for mixing. Capillaries were filled with this suspension at different times, always avoiding the bulk oil phase. For the swelling experiment of microcapsules with cyclohexane spherical PDMS-filled shells (d/R_t = 0.04) dispersed in water were used. These did not contain any surfactant. For loading of CdSe quantum dots (QD) of size 3 nm microbowls of δ/R_t = 0.56 and d/R_t = 0.04 were used. The QD's were dispersed in toluene stabilized by oleic acid and made according to a literature procedure.[42]

3. RESULTS AND DISCUSSION

Controlled Buckling/Release. Monodisperse TC-PDMS microcapsules of sizes around 4 μm containing low molecular weight PDMS were prepared using an emulsion templating technique as described in the Experimental Section. The TC-PDMS shell was labeled with the dye rhodamine B isothiocyanate (RITC) to be able to observe the morphology of the capsules after release of the PDMS oil using confocal microscopy. Shell thicknesses were measured using atomic force microscope (AFM), and the PDMS droplet radii were obtained from static light scattering (SLS). To release the PDMS oil template from inside the microcapsules, we used a surfactant. The surfactant used in the present study was the nonionic block copolymer Pluronic P123 ($(PEG)_{20}-(PPG)_{70}-(PEG)_{20}$), but we expect that our methodology is not dependent on the exact nature of the surfactant used. The concentration of surfactant used was always above the critical micelle concentration (CMC) (0.004 wt % at 20 °C[43]). We started with microcapsules with a ratio of shell thickness to total particle radius (d/R_t) of 0.04. To release the PDMS oil, we initially added 0.5 mL of an aqueous solution of P123 to 0.02 mL of microcapsules to give a final concentration of 0.48% v/v of P123 and 0.52% v/v of microcapsules. A precise number for the latter was obtained by counting the number of microcapsules in a volume measured with confocal microscopy. After addition, the suspension was left for about 30 min to equilibrate and then observed with the confocal microscope. Figure 1a shows that the spherical microcapsules had developed a bowl-like shape with a small dimple. The presence of the dimple clearly indicates the release of PDMS oil contained in the microcapsule. We recorded a movie of this phenomenon of the increase in depth of such a dimple, or the decrease in the capsule volume in time, in a capsule that was stuck to wall of

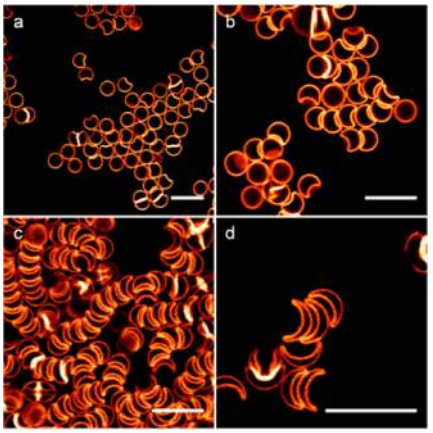


Figure 1. Confocal microscope images of microbowls (d/R_t = 0.04) partly filled with PDMS obtained at different concentrations of Pluronic P123: (a) 0.48, (b) 1.44, (c) 5.3, and (d) 6.3% v/v. All scale bars represent 10 μm.

dx.doi.org/10.1021/la500070s | Langmuir 2014, 30, 2385−2393

the capillary during the equilibration period (Supporting Information Movie S1). Similar shapes were observed in water-filled polyelectrolyte capsules that were buckled osmotically when exposed to a polyelectrolyte solution.[29] Here the release of PDMS oil from the capsules was triggered by the Pluronic micelles in the solution. The micelles in the suspension solubilize PDMS oil in the aqueous medium. This uptake of oil by micelles causes the capsule volume to decrease for as long as the tendency to solubilize oil exceeds the elastic restoring force of the shells, resulting in the buckling of the spherical capsule and the formation of a bowl-like shape. In Figure 1a, some capsules appear to be spherical because the dimple is out of the focal plane, but it was observed by analyzing 3D confocal data sets that all capsules possessed a dimple of similar depth. Since we started with monodisperse spherical microcapsules the resultant microbowls were also monodisperse. To release even more PDMS oil, we further increased the concentration of P123 for the same concentration of microcapsules (0.52% v/v). The confocal pictures of microcapsules at concentrations 1.44, 5.3, and 6.3% v/v of P123 is shown in Figure 1b,c,d. The depth of the dimple increased, i.e., the microbowls became deeper, with increasing concentration of P123. This indeed shows that we can release the oil inside the capsule in a very controlled way by simply tuning the surfactant concentration above the CMC. For surfactant concentrations below the CMC there was no release of PDMS and hence no change in the shape of capsules. In addition to the release of oil, the micelles also serve as a depletant.[44] The microbowls were found to self-assemble into stacks by depletion force (Figure 1a–d). This is similar to the lock and key self-assembly of colloidal particles described in ref 45.

From the mechanical theory of elasticity of shells,[40,41] the critical pressure at which a spherical capsule becomes unstable and buckles is given by the relation

$$P_c = \frac{4E}{\sqrt{12(1-\nu^2)}}\left(\frac{d}{R_t}\right)^2 \quad (1)$$

Assuming the values of E = 200 MPa[39] and ν = 0.3, for microcapsules of d/R_t = 0.04 the critical buckling pressure that must be overcome to induce buckling is P_c = 0.3873 MPa (eq 1). For the thinner capsules of d/R_t = 0.0075 the calculated value of P_c = 0.0136 MPa is lower by about 96%.

Since the orientations of the microbowls in the stacks were mostly restricted, we could easily quantify the average depth of the dimples from confocal images for different P123 concentrations. We compared the variation of the depth of dimple to particle diameter ($\delta/2R_t$) with the ratio of surfactant to capsule concentration ($\phi_{surf}/\phi_{capsules}$) for capsules of d/R_t = 0.04 and 0.0075 as shown in Figure 2. As expected from eq 1, $\delta/2R_t$ is higher for d/R_t = 0.0075 compared to 0.04, but only by about 50%. Also, $\delta/2R_t$ is found to have approximately a square root dependence on $\varphi_{surf}/\varphi_{capsules}$ for both d/R_t = 0.04 and 0.0075 (inset of Figure 2).

High-resolution confocal images of microbowls of different capsule volume also gave us the possibility to investigate the precise shape of the dimple. For small to moderate depth the dimple was always an inverted sphere with the same radius of curvature as the original capsule. This way a strongly curved region was formed near the cusp. This curvature is related to the shell thickness and can thus be used to find an approximate, independent value of d/R_t of the capsules, which in other

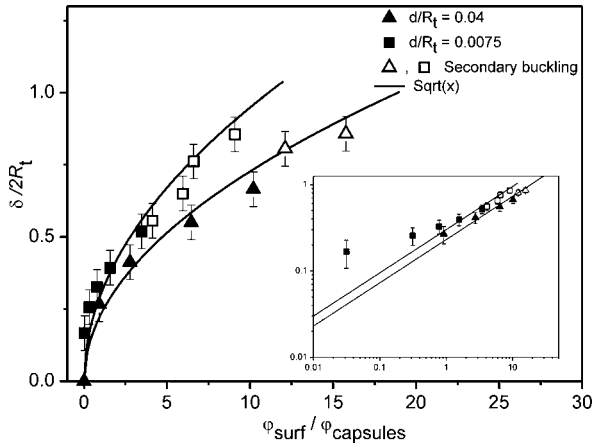


Figure 2. Plot of the ratio of dimple depth to particle diameter ($\delta/2R_t$) against the concentration ratio of P123 surfactant to capsules ($\varphi_{surf}/\varphi_{capsules}$) for two different d/R_t. Open symbols indicate samples in which secondary buckling into a polygonal shape was observed. Inset shows the double-logarithmic plot with lines of slope 0.5.

studies was determined by light scattering and atomic force or electron microscopy.[5] The estimation is done by using the relation between the radius of curvature at the cusp of the dimple, r_{edge}, and the Föppl–von Kármán number, $\gamma = 12(1-\nu^2)(R_t/d)^2$, described in ref 46

$$\frac{r_{edge}}{R_t} = \frac{c}{\gamma^{1/4}}\left(1-\frac{V}{V_0}\right)^{-1/4} \quad (2)$$

The numerical prefactor c is only weakly volume dependent. The radius of curvature r_{edge} for different capsule volumes V/V_0 was measured by fitting an osculating circle at the cusp of a capsule as shown in Figure 3a. The logarithm of this power law was indeed found to be a straight line with slope −0.25 and y-intercept $\ln(c/\gamma^{1/4})$. Figure 3b shows the logarithmic plot of r_{edge}/R_t against $(1-V/V_0)$ for two capsules of d/R_t = 0.04 and 0.0075. Assuming c = 0.7 from ref 46, we find the Föppl–von Kármán number, $\gamma = (3.6 \pm 0.5) \times 10^3$ and $(64 \pm 5) \times 10^3$ (eq 2) for d/R_t = 0.04 and 0.0075. From this we find d/R_t = 0.055 ± 0.004 and 0.0130 ± 0.0005, respectively, which is in reasonable agreement with the measured values.

Simulations and experiments[27,28,47] have indicated that for a large deformation of thin elastic shells the smooth circular rim of the indentation undergoes a secondary buckling and forms a polygonal shape within the buckled dimple. This is a spontaneous way of minimizing the elastic energy of the shell caused by in plane stretching, which is energetically costly. Earlier buckling experiments performed on these shells, where the PDMS was completely dissolved in the solvent, have shown these polygonal shapes with four to eight regularly spaced wrinkles in the inner surface of microbowls.[28] These shapes were also reproduced in simulation.[27,28] We also observed these polygonal shapes when the volume of the capsule was sufficiently reduced. Cases where this happened are shown by the open symbols in Figure 2. For capsules of d/R_t = 0.04, at a reduced volume, V/V_0 = 0.28, the rim of indentation is a smooth polygon with four wrinkles as shown in Figure 4a. Whereas for d/R_t = 0.006, at a reduced volume of V/V_0 = 0.34, the rim of indentation was found to possess prominent sharp edged wrinkles, as shown in Figure 4b. These well-defined polygonal internal structures would be quite interesting to combine with the recently developed depletion-induced lock-

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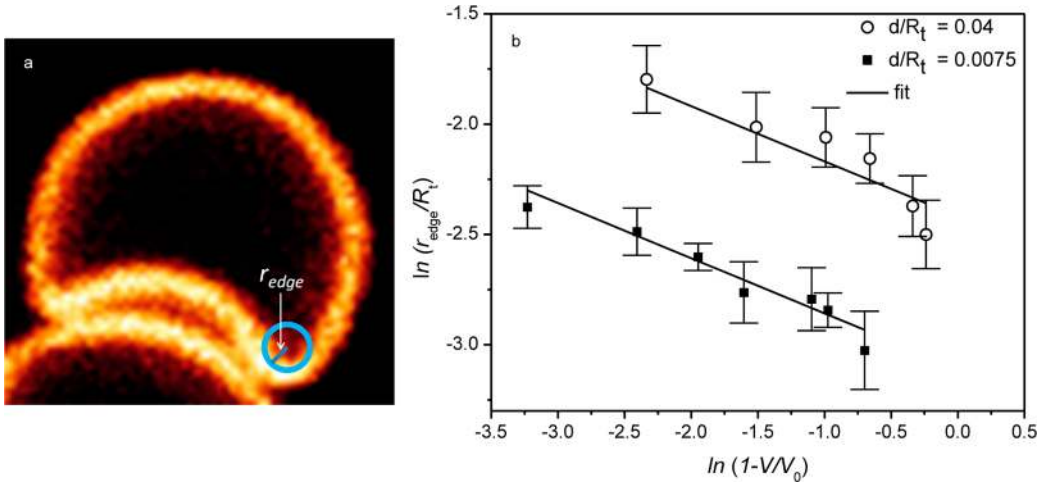

Figure 3. (a) Confocal picture of a microbowl (d/R_t = 0.04) of reduced volume V/V_0 = 0.93, with a radius of curvature at the edge of the circular rim, r_{edge}. (b) Logarithmic plot of ratio of radius of curvature to radius of capsule (r_{edge}/R_t) vs capsule volume for microcapsules of d/R_t = 0.04 and 0.0075. The lines are fits with a slope of −0.25.

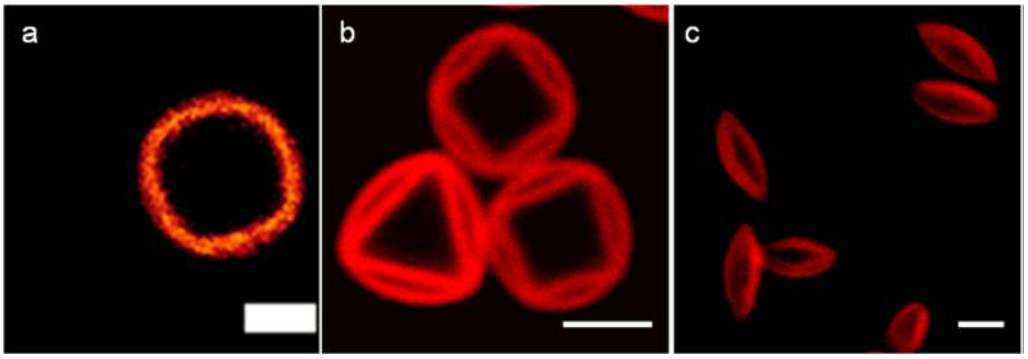

Figure 4. Confocal pictures of (a) smooth polygonal rim of indentation for d/R_t = 0.04 and V/V_0 = 0.28, (b) polygonal shape with three to four sharp wrinkles for d/R_t = 0.006 and V/V_0 = 0.34, and (c) subsequent collapse of microbowls with sharp wrinkles to a coffee bean shape with elongated depression. All scale bars represent 2 μm.

and-key interactions.[45] In the picture there is also a capsule with three wrinkles, which was not observed before in these microbowls. For d/R_t = 0.006 the maximum number of wrinkles observed was five; after that, instead of an increase in the number of wrinkles with decreasing inner volume, surprisingly the microbowls transformed into a shape with a single elongated depression, like that of a coffee bean (Figure 4c). We recorded a movie of this transition of capsules from bowl to coffee bean configuration and noticed that it happened rather suddenly (Supporting Information Movie S2). Coffee bean shapes were observed before in various experimental systems.[32,36,48] But then these shapes were not formed by a collapse of an initially bowl-like conformation. They also have not been predicted theoretically for uniform shells[27,28] but appeared when elongated apertures were introduced in the shells.[49] This might suggest that the coffee beans were induced by slight rupturing or weakening of the shells in their polygonal conformation. For capsules of low value of d/R_t < 0.005 we observed a series of morphological changes during the release of inner oil: from multiple small dimples to a single large dimple and finally to a coffee bean shape (Supporting Information Movie S3 and Figure S1). The transition from multiple dimples to a single dimple followed an Ostwald ripening pathway rather than a merging of dimples as reported in simulations.[27]

Reversed Buckling/Loading. Here we introduce an efficient way to load hydrophobic chemicals including fluorescent dyes into preformed TC-PDMS microcapsules by reversing the buckling process. Microbowls (d/R_t = 0.04) obtained by controlled buckling were used for loading with an apolar liquid (oil). Loading of buckled shells with oil was done by making use of the elasticity of the shell. We did this by adding a small excess of the oil to a suspension of microbowls already present in surfactant solution from a buckling experiment. We started with the silicone oil octamethylcyclotetrasiloxane (OMCTS, $C_8H_{24}O_4Si_4$). It was confirmed earlier that 90% of the PDMS oil inside the spherical microcapsule is OMCTS, and the rest includes slightly longer linear oligomer chains and cyclic trimers.[33,38] Thus, most of the oil already present inside the capsules is OMCTS. The microbowls used for loading had a dimple to diameter ($\delta/2R_t$) ratio of 0.78. OMCTS was dyed with an oil soluble dye, pyrromethene 546, for identifying its presence inside the capsule. Confocal snapshots at different stages of encapsulation of OMCTS by the microbowls is shown in Figure 5a–d. Over a period of 6.5 h, the depression in the microbowls slowly decreased until they finally became spherical (Figure 5d). Not only the OMCTS but also the dye was encapsulated in the microcapsule. Both oil and dye are poorly soluble in water, making this process of diffusion of oil and dye through the aqueous phase slow. The presence of

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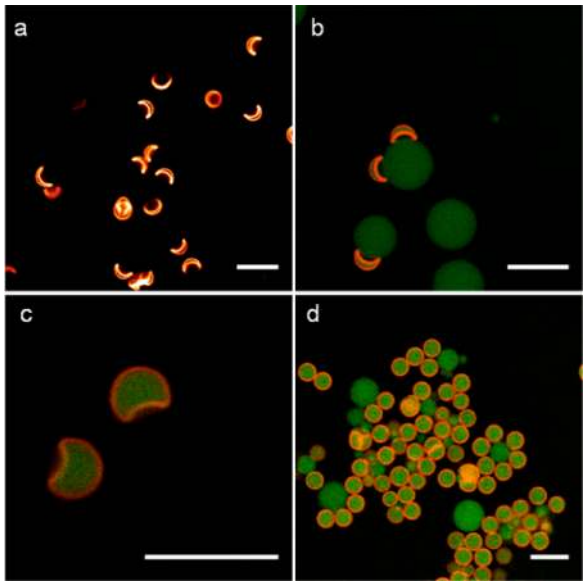

Figure 5. Confocal pictures of (a) microbowls (d/R_t = 0.04 and $\delta/2R_t$ = 0.78) before loading and (b) 0.5, (c) 2.5, and (d) 6.5 h after addition of silicone oil, OMCTS. Red color indicates the shell, and the green color shows the dyed oil. The green droplets without shell in (b) and (d) represent excess OMCTS droplets in the sample. All scale bars represent 10 μm.

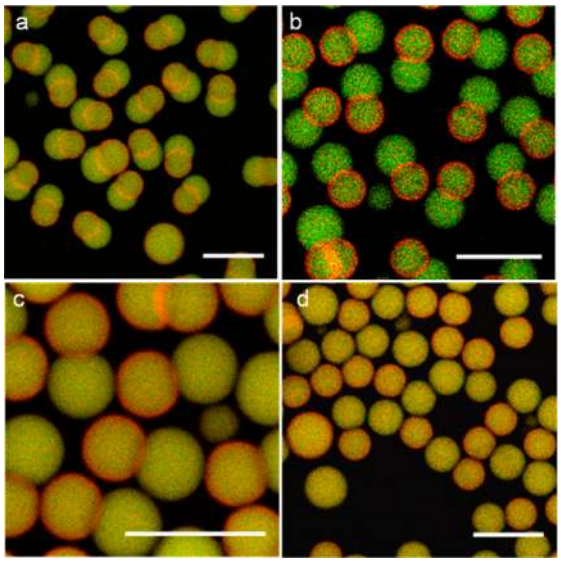

Figure 6. Confocal pictures of microbowls (d/R_t = 0.04 and $\delta/2R_t$ = 0.78) after addition of cyclohexane (a) 25 min, (b) 4 h, (c) 8 h, and (d) 10 h. The oil droplet sticking to the shells slowly detaches from the shell in time. Red color indicates the shell, and the green color shows the dyed oil. All scale bars represent 10 μm.

surfactant micelles probably helped speed up this process. We recorded a confocal movie of the encapsulation and full relaxation of a microbowl to a sphere by the diffusion of OMCTS into the capsule (Supporting Information Movie S4). Once the shell was fully relaxed, no further change in shape was observed. Apparently, the elasticity of the shell prevented further uptake of oil.

Similarly, we tested whether hydrocarbons of different carbon chain−length or molecular weight could also be encapsulated in the microcapsules. For hydrocarbons, the solubility of the oil in water plays an important role in the speed of encapsulation. In general, the solubility of hydrocarbons in water decreases with increasing chain length.

We started with a lower cyclic hydrocarbon cyclohexane (C_6H_{12}). The microbowls used for encapsulation and the method of preparation were similar to that of OMCTS. Confocal images of microbowls at different stages after addition of cyclohexane are shown in Figure 6a−d. We observed that the bowls fully relaxed to spheres already within minutes, probably due to the relatively high solubility of cyclohexane in water. But in addition to elastic recovery, the microcapsules surprisingly continued absorbing oil forming dumbbell-like particles. In Figure 6a−c, one part of the dumbbell is the spherical microcapsule (with a red shell) and the other part is the oil droplet (without a red shell). The images were taken from a capillary, prepared soon after mixing, by avoiding the presence of any excess cyclohexane phase. This prevented further growth of oil droplets from that shown in Figure 6a. Over the next several hours, in the same capillary we observed the slow detachment of the oil droplet from the microcapsules, increasing the contact angle between the oil and the capsule from $\theta = 63.1 \pm 2.8°$ to 180° (Figure 6a−d). The detachment possibly could have happened due to the slow adsorption of Pluronic surfactant, already present in the sample, to the oil−water interfaces causing a dewetting of the oil droplet from the shell. However, in the suspension with excess cyclohexane the droplets continued to grow larger while staying attached to the shells.

Apparently, in the cyclohexane case, apart from elasticity of the shell, there was an additional force that drove the uptake of cyclohexane by the bowls. Since $\delta/2R_t$ = 0.78, the bowls still contained about 32% of the original PDMS at the start of the experiment. The difference in the composition of oil inside and outside the bowls creates an osmotic pressure difference. Because of the entropy of mixing, even after the shell had reached its original spherical shape, more and more cyclohexane molecules continued to diffuse into the shell. We hypothesize that this leads to the swelling of the capsule and consequent stretching of the TC-PDMS shell. However, since stretching is energetically costly elastic energy is minimized by pushing out the oil through the pores in the shell and nucleating a liquid droplet on the outside of the shell. In these experiments with microbowls we were not able to observe the initial swelling of the capsules because the dumbbell structure was formed too soon after mixing, as micelles enhanced the transport of oil. We therefore repeated the swelling experiment with fully PDMS filled TC-PDMS shells ($\delta/2R_t$ = 0), in the absence of any surfactant. The capsules were therefore still spherical (Supporting Information Figure S2). We measured a maximal average increase in the size of the capsule by 0.8 μm in diameter from the initial size just before a droplet was formed on the outside of the shell. It has been shown that the relation describing the stretching of a spherical shell due to a positive pressure P is[46]

$$R^2 - \frac{2Ed}{P(1-\nu)}(R - R_t) = 0 \tag{3}$$

Using this, we find $P(1-\nu)/E$ = 0.01. Assuming values of E = 200 MPa[33] and ν = 0.3, we calculate the pressure exerted on a capsule wall to be P = 2.98 MPa, a reasonable value for an osmotic pressure. The magnitude of this osmotic pressure is higher than the critical buckling pressure P_c = 0.38 MPa for

dx.doi.org/10.1021/la500070s | Langmuir 2014, 30, 2385−2393

these capsules. This indicates the major role of the osmotic pressure in the overloading of capsules with cyclohexane.

For a longer chain hydrocarbon, hexadecane ($C_{16}H_{36}$), rather than overloading, the microbowls ($\delta/2R_t$ = 0.56) formed deeper dimples than the original as shown in Figure 7a,b.

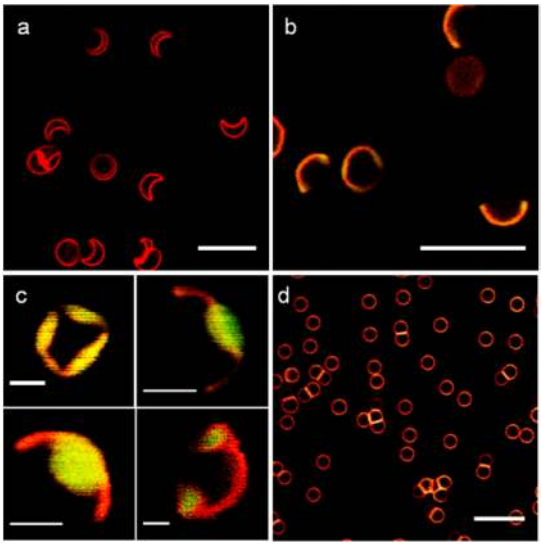

Figure 7. Confocal pictures of microbowls (d/R_t = 0.04 and $\delta/2R_t$ = 0.56): (a) before addition of hexadecane, (b) one day after addition, when the dimple has grown deeper, and (c) after a period of two years where the bowls are loaded with a small amount of hexadecane. (d) Spherical microcapsules (d/R_t = 0.05) one year after addition of decane. Scale bars in (a), (b), and (d) represent 10 μm and (c) represent 2 μm.

Apparently, this time the PDMS was completely extracted from the capsules by the hexadecane rather than the reverse. This indicates that the rate of diffusion of PDMS in water exceeds that of hexadecane. This is possible because the PDMS contained in the capsules consists of small oligomers with on average four monomer units. Even after a period of two years these microbowls did not fully relax to spheres, but there was a slight change in the shape of the bowls, due to a slight loading of hexadecane. Figure 7c is the confocal image of the microbowls in different orientations, loaded with a little hexadecane that concentrated near the cusp or in the center. Note that this figure shows some representative shapes; not all the bowls had the same morphology. This image was only taken two years after addition, and so we do not know how long this slight shape transformation took, but probably much less than two years. That the microbowls did not fully relax back is most likely because of the strong van der Waals forces at regions where the inner walls of the bowl touch. The presence of hexadecane was only detected from regions where the walls were not in contact. Thus the amount of hexadecane loaded in the capsules was low compared to OMCTS and cyclohexane.

From the theory of Ostwald ripening we know that the ripening rate is proportional to the product of the solubility (C_∞) of the oil and its diffusion coefficient (D_0), both of which decrease with increasing molecular weight. Of the other hydrocarbon oils we tested, hexane, 2,2,4-trimethylpentane, decane, dodecane, and tetradecane, we qualitatively found that the product of solubility and diffusion coefficient of decane ($C_{10}H_{22}$) was more or less the same as the PDMS oil inside the capsule (predominantly OMCTS). In the presence of dodecane and tetradecane microbowls formed deeper dimples, whereas with 2,2,4-trimethylpentane and hexane they formed dumbbells. Figure 7d shows a confocal image of spherical microcapsules (d/R_t = 0.05) taken about one year after addition of decane to PDMS-filled spherical capsules. Even after one year the capsules had not changed their shape. The shells remained spherical because the rate of diffusion was almost the same in both directions, and the elasticity of the shell was also strong enough to withstand small volume changes. Meanwhile, for a much thinner shell, d/R_t = 0.006 the elasticity of shell proved not strong enough to slight volume changes. This caused buckling, even with decane. The difference in the behavior of the shells in the presence of hydrocarbons lead to selective encapsulation of oils, which is most likely a general feature related to solubility and is of interest to explore further in future work.

The range of materials that can be loaded/released into/from microcapsules highly depends on the permeability of the shell. To roughly estimate the upper size limit of cargo, we used a fluorescent marker, for example quantum dots (QD's) of average size 3 nm. The QD's were CdSe particles dispersed in toluene and stabilized with oleic acid.[42] The experiment was performed in the same way as for other oils (Supporting Information Figure S3). The microbowls fully relaxed to spheres within minutes, but there was no fluorescence from the interior of the capsules. This indicated that the capsules can be loaded with toluene but that the shells are not permeable to the QD's of size 3 nm. This sets a threshold to the maximum size of materials than can be loaded in these capsules.

4. CONCLUSIONS

We demonstrated a new method to encapsulate and release hydrophobic liquids and dissolved molecules like a fluorescent dye in and from elastic tetraethoxysilane-cross-linked-polydimethylsiloxane (TC-PDMS) microcapsules. With the addition of surfactant micelles it is possible to solubilize the encapsulated oils, which leads to controlled buckling of the capsules. This buckling leads to the formation of anisotropic colloidal microbowls with a uniform and tunable dimple depth. For certain parameters the bowl shape underwent a further transition to well-defined shapes of interest for e.g. creating unique lock-and-key interactions. Additionally, there was a parameter range where a final transition to a coffee-bean shape was observed. The slow dissolution of oil, on the order of several minutes, allowed us to observe the morphology changes of the shells and hence the individual buckling events for different d/R_t. Elasticity of the shell and leftover PDMS oil inside the capsule provided two driving forces for the uptake of hydrophobic oils and dye placed in contact with an aqueous suspension of microbowls, thereby efficiently encapsulating them in the capsules. We found that low molecular weight oils were readily encapsulated, whereas higher ones caused the capsules to empty even further and the amount loaded was rather low. Failure to load capsules with quantum dots of 3 nm size revealed the approximate upper limit for materials that can be loaded into the capsules in this manner. The proposed method of controlled buckling and subsequent loading from/into preformed TC-PDMS capsules can be further extended to drug molecules, provided they are hydrophobic and small enough to pass through the shell of the capsules.

dx.doi.org/10.1021/la500070s | *Langmuir* 2014, 30, 2385−2393

■ ASSOCIATED CONTENT

Supporting Information

Several movies showing the buckling and unbuckling of microcapsules and figures that characterize these processes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to M. P. Boneschanscher for his help in AFM measurement on capsules, W. H. Evers for providing the CdSe QD's, and N. A. Elbers for careful reading of the article. This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse organisatie voor Wetenschappelijke Onderzoek (NWO)".

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