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Bulk Scale Synthesis of Monodisperse PDMS Droplets above 3 μm and Their Encapsulation by Elastic Shells

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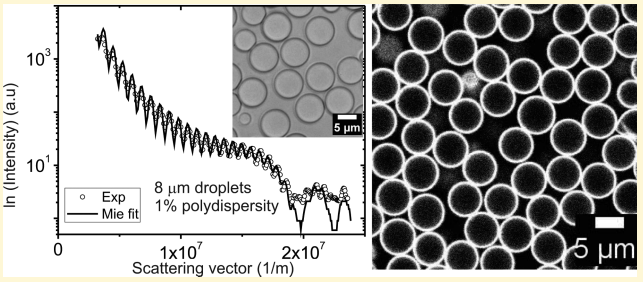
Supporting Information

ABSTRACT: We report several facile, surfactant-free methods to prepare monodisperse polydimethylsiloxane (PDMS) droplets in the size range 3−8 μm in water. These methods, of which the pros and cons are discussed, are extensions of a procedure described before by our group which focused on smaller droplet sizes. The PDMS oil droplets are formed by ammonia catalyzed hydrolysis and condensation of the monomer dimethyldiethoxysilane (DMDES) in water. One of the methods entails a seeded growth procedure in which other oils, such as lower molecular weight hydrocarbons, were found to be able to swell the PDMS droplets if their solubility in water was higher than that of the seed droplets. This way, larger droplets with mixed composition could be prepared. It also turned out to be possible to load the monodisperse droplets with an oil soluble dye. The droplets could be coated with an elastic, partially permeable, shell formed by cross-linking the PDMS with tetraethoxysilane (TES) in the presence of poly(vinylpyrrolidone) (PVP) that provided colloidal stability. Besides, the liquid interior of these shells could be changed by solvent exchange.



INTRODUCTION

Microcapsules, here loosely defined as partially permeable shells around a gaseous, liquid or solid material and with a size in the colloidal and granular domain, represent an active field of research because they can potentially encapsulate, protect, and distribute materials. As a result, there is a compelling fundamental as well as industrial interest for which the latter field is as diverse as food science, pharmaceutics, cosmetics, biotechnology, the paint industry, and advanced materials in general.[1−8] The most versatile approach for capsule synthesis is a templating technique.[9] In this technique, a shell is formed around a sacrificial particle via methods like interfacial polymerization,[10] polymer precipitation (by phase separation),[6,11,12] layer-by-layer self-assembly,[8,13] or via locking of interfacial colloids[14] followed by removal of the core. For the sacrificial core, solid particles as well as liquid droplets have been used. An important advantage of the use of solid template particles (like silica, latex, or gold colloidal particles)[15−20] is that it allows for a large scale synthesis of monodisperse cores in a wider range of sizes. However, after deposition of the shell material, relatively harsh dissolution or heating conditions are needed to remove the template. This complicates the production process and adversely affects the quality and robustness of the as-prepared particles.[21,22] On the contrary, liquid template droplets allow for a more facile removal of the core under milder conditions.[23,24] However, a combination of bulk scale synthesis and monodispersity is scarce when using liquid templating droplets.[21,25] In conventional methods like ultrasonication[26,27] and high-shear emulsification techniques,[28−30] emulsion droplets are prepared in a large amount but with a size distribution above 10% in width. The reverse is true for droplets prepared using microfluidics, which allows for an exquisite degree of control over droplet size and composition, but for which production rate, and thus yield, is low.[31−35] In general, a good control over the capsule size distribution is desirable as the particle's shell thickness and size sets the release rate as well as the mechanical breakup of shells with, for example, ultrasound.[36−40] As a result, there remains a need for efficient methods that can produce monodisperse template drops with well-controlled sizes and size distributions. Although the focus of our research is to use monodisperse emulsions droplets to arrive at monodisperse microcapsules, there are many applications, in science and industry, of monodisperse emulsions that do not involve shell growth.[41,42] For instance, monodisperse emulsions are used in food science, cosmetics, microreaction technology, as delivery vehicles in pharmacy, and even for the synthesis of bicolored droplets for electronic paper.[43−46] Many important characteristics like rheology, turbidity, texture, interparticle interactions, and shelf life are controlled by the particle size (distribution).[30,47] In addition, from a fundamental perspective, the interpretation of experimental results is easier for narrowly distributed emulsions.[47]

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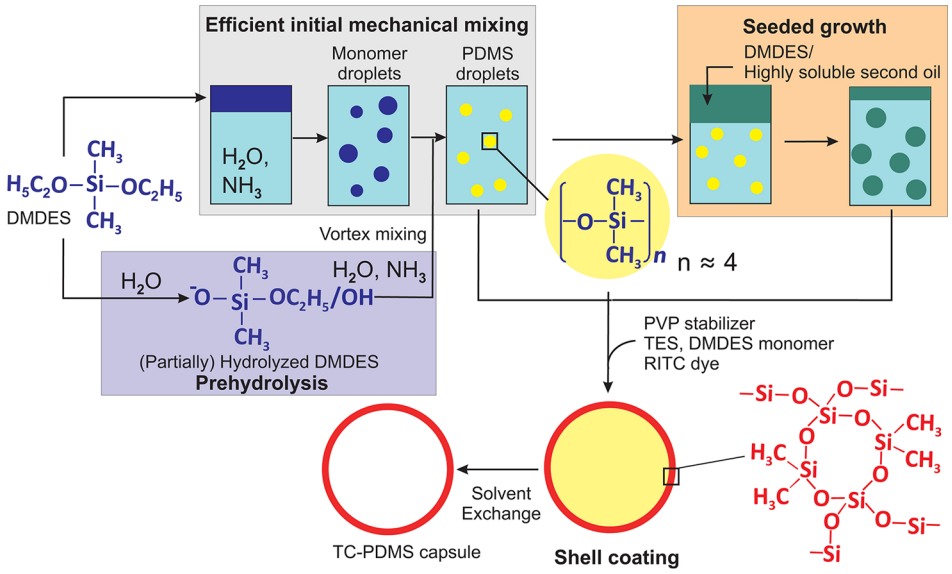

Figure 1. Schematic illustration of different synthesis procedures for PDMS droplet formation and subsequent shell coating.

An exception, where liquid droplets of high monodispersity, high yield, and without the use of surfactants can be prepared, has been described by Vincent and co-workers.[48] The process to arrive at monodisperse polydimethylsiloxane (PDMS) emulsion droplets bears a strong resemblance to the famous Stöber process, in which monodisperse silica particles are generated from tetra-alkoxysilanes, usually tetraethoxysilane (TES). Stöber synthesis is performed in a mixture of an alcohol and water to which ammonia is added as a catalyst for both the hydrolysis and condensation reactions. Nucleation in combination with early aggregation of siloxane substructures and subsequent growth, when colloidal stability has been achieved, result in monodisperse silica sphere (see for example ref 49). To create the PDMS droplets, the bifunctional monomer dimethyldiethoxysilane (DMDES) is used for which the hydrolysis and condensation reactions are, again, catalyzed by the base ammonia. Because alcohol is not added to the reaction medium, the starting monomer does not completely dissolve in the basic water and the resulting nucleation, and, most likely, early aggregation steps of siloxane substructures before growth are more complicated and less well investigated compared to the Stöber process. Hydrolysis generates slightly acidic silanol groups which make the monomers water-soluble, while subsequent condensation reactions reverse this. It has been well established that the name PDMS is actually somewhat of a misnomer as the vast majority of the condensed species are small oligomers, composed of 'chains' of only 4 units.[48,50] The fact that an important part of the monomer is initially not dissolved in the water phase, but is present as droplets, results in a dependency of the synthesis conditions on the surface area of these monomer droplets. The surface area of the initial droplets is expected to determine the rate of hydrolysis of the monomer. Via hydrolysis of silanol groups, the surface area dependency indirectly controls the increase in ionic strength and hence the final interdroplet charge stabilization. As a result, the final PDMS droplet size and polydispersity is, unfortunately, affected by the total surface area of the initial monomer droplets and therefore to stirring conditions.

Due to the high monodispersity, large scale production, and facile drop removal, the liquid PDMS droplets have been used as sacrificial templates for the production of Tetraethoxysilane-Cross-linked-PolyDiMethoxySilane (TC-PDMS) shells,[51,52] polydopamine capsules,[53] colloidosomes,[54,55] and even for polymer microspheres.[56,57] In all studies, the accessible size range was limited to about 0.6−3 μm.[51−53] However, a wider size range is preferred to be able to fully match the particle size with the application in mind. Moreover, the only alternative to monodisperse PDMS droplets is microfluidics which usually does not produce particles with sizes less than 10 μm. Related to the size dependency in the final applications, larger (micron-sized) particles allow higher loading capacity for in vitro studies.[58] Besides in drug delivery, the size of the particles (1−20 μm) controls the accessibility of certain types of cells or tissues that form the target location.[14,36] Furthermore, the size of the microcapsules dictates the frequency of the ultrasound when release of the payload is induced by acoustic cavitation.[40] Finally, the particle size determines the detection strategy that will be used during encapsulation and release studies. Ensemble assays are required for small particles based on for example UV-spectrophotometry,[59] whereas detection on a single particle level is possible for larger (micron sized) particles in real time and real space with a confocal microscope.[60−63] Attempts to further increase the size of the PDMS droplet template, which predetermines the final size of the capsule, has not produced promising results yet. In principle, the droplet size can be varied up to 5 μm by increasing the ammonia solution concentration. However, dynamic light scattering measurements on systems in which the droplet size was greater than 1 μm showed them to be more polydisperse.[48] Another way to tune the droplet size up to several micrometers is by increasing the DMDES monomer concentration.[48,50,53] However, it was found to be difficult to prepare monodisperse, intact capsules for droplet diameters above 2.4 μm, for which the initial monomer concentration had to exceed 3% v/v.[48,50,53] Another attempt to increase the capsule diameter was described in ref 64, in which both DMDES and ammonia concentrations were higher than what was used in ref 51. However, this synthesis procedure was not found to be robust as it sometimes resulted in a polydisperse system. In short, there is a lack of a reproducible synthesis procedure for monodisperse PDMS templating droplets, and hence capsules, with diameters exceeding 3 μm.

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The PDMS droplets can be coated with a tetraethoxysilane-cross-linked-polydimethoxysilane shell to form TC-PDMS microcapsules. These capsules were synthesized for the first time by Zoldesi and Imhof,[51] with sizes in the range 0.6−2 μm. One advantage of TC-PDMS capsules, next to their monodispersity and size control, is the possibility to tune their shell thickness, which is beneficial for potential encapsulation and release studies. In addition, the capsules were found to form well-defined anisotropic shapes upon drying, or via dissolution of the PDMS oil through the shell (for instance in ethanol), by simply tuning the ratio of shell thickness to droplet diameter.[50,51] From an applied point of view these capsules have already shown promise because they are permeable to small polar dye molecules.[50] Recently, our group further extended the use of these capsules as containers by efficiently encapsulating and releasing apolar liquids, which can contain fluorescent tracer molecules, via controlled and reversible buckling.[64] The capsules could even be loaded with surfactant molecules.[65] In addition, these capsules were shown to be an interesting new model system to study the physics of jammed matter.[66,67] As these capsules are highly flexible and can be fluorescently labeled and index matched easily, their jamming behavior can be quantitatively studied using real space confocal microscopy in 3D.[68]

Here, we introduce several methods to make monodisperse, stable PDMS droplets with sizes above 3 μm in a high yield. An overview of all droplet sizes and polydispersities, obtained using the various methods, can be found in Table S1 in the Supporting Information, and a schematic illustration of the various synthesis procedures is depicted in Figure 1. The first method to make larger monodisperse emulsions is based on a modification of the PDMS synthesis as described in ref 48. We used higher DMDES concentrations in combination with more efficient mechanical mixing. The second method is based on hydrolyzing the monomer under conditions where the condensation reactions are not yet important. The third procedure consists of a seeded growth technique, in which primary PDMS droplets grow through diffusion of water dissolved monomer (DMDES) molecules or oil molecules like hydrocarbons and silicone oil. We further show that oil droplets of all sizes can be used as templates for the growth of a tetraethoxysilane-cross-linked-polydimethoxysilane shell. In this way, we have extended the range of particle diameters up to more than 5 μm while maintaining the high yield, the high monodispersity, the surfactant free synthesis, and facile drop removal. The size range now nicely extends up to the micron sized capsules that can be formed using microfluidic devices.[69]

EXPERIMENTAL SECTION

Materials. Dimethyldiethoxysilane (DMDES, 97.0%), the triblock copolymer Pluronic P123 (poly(ethylene glycol)$_{20}$-poly(propylene glycol)$_{70}$-poly(ethylene glycol)$_{20}$, Mw - 5800 g/mol), Triton X-100, tetraethoxysilane (TES, 98.0%), 3-aminopropyl-triethoxysilane (APS, 99%), rhodamine B-isothiocyanate (RITC), polyvinylpyrrolidone (PVP, Mw-58000 g/mol), ammonia (25 wt % NH_3), dimethyl sulfoxide (DMSO), octamethylcyclotetrasiloxane (OMCTS, $C_8H_{24}O_4Si_4$), cyclohexane (C_6H_{12}, 99.8%), iso-octane (99%), and hexadecane ($C_{16}H_{34}$, 99.0%) were purchased from Sigma-Aldrich. The dye pyrromethene-567 was purchased from Exciton. Ethanol (100%, technical grade) was obtained from Interchema and *n*-pentane (>99% for spectroscopy) from Acros. Organically stabilized CdSe/CdS/CdZnS/ZnS nanoparticles (QD's) with a diameter of 6.9 nm were prepared by using the method of ref 70. Light is absorbed by the QD's in the 350−544 nm range, and the emission peak is located at 612 nm. The QD's contained an oleic acid capping layer and were stored in cyclohexane. All chemicals were used as received. Demineralized water (resistivity 18 MΩcm) was used in all reactions and also for cleaning of glassware.

Synthesis Methods. *Efficient Initial Mechanical Mixing and No Agitation during Growth.* (Large scale: 750 mL) We prepared monodisperse PDMS emulsion droplets by hydrolysis and condensation of the monomer DMDES, by modifying the original procedure of Vincent et al.[48] An aqueous dispersion (total volume 750 mL) of 22.7% v/v ammonia and 6.8% v/v of DMDES monomer (assuming additivity of volumes) was prepared in a 2 L beaker. Another typical sample (total volume 720 mL) was prepared at about the same ammonia concentration (23.7% v/v) but at a reduced DMDES concentration of 2.9% v/v. Directly afterward, each sample was vigorously mixed using a Turrax homogenizer (IKA's Ultra-Turrax with a S25N 10G dispersing element) at a speed of 11,200 rpm. Mixing typically continued for 8−14 min, until most of the DMDES was dispersed, and small droplets in a narrow(er) size range were seen under a light microscope. We do want to stress that all samples, especially at the high 6.8% v/v DMDES monomer concentration, always contained a layer of excess oil at the top after finishing the Turrax procedure. Despite the efficient mixing, it is therefore most likely that not all DMDES was completely dispersed. The turbid solution, including the excess layer, was poured into a 1 L flask and allowed to stand undisturbed for at least 2 days before the coating step.

(Small scale: 30 mL) Emulsion droplets were also prepared with the Turrax homogenizer on a smaller scale as compared to the above-described procedure. An aqueous solution (total volume 29.9 mL) of 22.7% v/v of ammonia and 6.7% v/v of DMDES monomer was prepared in a 40 mL glass vial. Samples were vigorously mixed using the Turrax homogenizer at a speed of 11,200 rpm for about 4−5 min. Droplets were allowed to nucleate and grow while keeping the sample static, for at least 2 days.

Based on the work described in ref 51, fluorescent shells were grown around the as-prepared emulsion droplets. Before incorporation of the RITC dye into the shells, the silane coupling agent APS and dye RITC were covalently coupled by mixing 6.5 mg of the dye and 40 μL of APS with 1 mL of anhydrous ethanol, after which this mixture was stirred for at least 12 h in the dark. The shell growth itself was modified as compared to ref 51 by introducing the steric stabilizer polyvinylpyrrolidone (PVP), which adsorbs onto the particle surface, in accordance with previous work by Graf et al.[20] An aqueous solution (total volume 1725 mL) of 2.3 wt % PVP was prepared in a 2 L flask. Hereafter, 550 mL of the as-prepared emulsion (still containing ammonia) was added while gently stirring the sample. Inspired by the postaddition method introduced by O'Sullivan et al.,[52] both TES (8 mL) and DMDES (8 mL) were added simultaneously during the shell growth step that was performed around templating droplets that were (at least) 2 days old. The monomers were added slowly over time using a syringe pump (KD Scientific, 10 μL/min). The APS/RITC dye solution (0.330 mL) was typically added 5 h after start of the shell growth. Shells were allowed to grow for at least 1−2 days, while gently stirring the sample, after which the PDMS template was removed by following the procedure below.

The dispersion containing the fluorescent shells was divided over 40 mL sample vials and centrifuged (800 g for 30 min) after which the concentrated supernatant was collected. The concentrated samples were dispersed in ethanol, which is known to penetrate the shells and to dissolve the liquid cores.[50,51] Shells were found to remain spherical in shape upon transferring about 100 mL of the concentrated dispersion to 2 L of (anhydrous) ethanol but started to buckle when the same amount of sample was dispersed in 1 L of ethanol. At this point we do not know the reason for this buckling process. In principle, buckling induced by dilution with ethanol was also reported by Zoldesi[71] for these shells when their ratio between the shell thickness and the total radius of the particle was less than 0.17. This is also the regime in which the current study is performed, as shown in the results section. However, the concentration dependency is indicative for an additional factor. Possibly, this could be electrostatics, as it was shown that the electrolyte concentration in the medium can

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alter the shape of elastic, closed shells.[72] Once shells were successfully transferred to ethanol, several washing steps with ethanol were performed in order to remove all PDMS oil during which no ethanol volume dependency was observed anymore.

Prehydrolyzed DMDES. In this method, DMDES monomer was first hydrolyzed prior to emulsion preparation by adding 2 mL of deionized water to 5 mL of DMDES monomer in a 20 mL glass vial and then stirring the solution in a vortex mixer (IKA minishaker MS2) at 2500 rpm for 5 min and thereafter on a rollerbank (Stuart SRT9D, solution was tumbled at a speed of 35 rpm) to gently homogenize the mixture. This resulted in a clear solution. By prehydrolysis, the solubility of the monomer in the reaction medium is enhanced. Two batches of monodisperse emulsion (total volume 11 mL) of PDMS oil droplets were prepared from DMDES that was prehydrolyzed for half an hour and 24 h, respectively, by adding 1 mL of prehydrolyzed DMDES (final monomer concentration 6.5% v/v) to a 22.7% v/v aqueous ammonia solution in a 20 mL glass vial. At this point the solution containing half an hour prehydrolyzed DMDES appeared clear, whereas the solution containing 24 h prehydrolyzed DMDES slightly turned turbid as a result of nucleation of oil droplets. All samples were immediately mixed with a vortex mixer for 3−4 min to completely dissolve prehydrolyzed DMDES and placed on a rollerbank during droplet growth. After 24 h of droplet growth, the droplet sizes from all samples were measured using static light scattering (SLS).

Seeded Growth - DMDES. A suspension of monodisperse PDMS seed droplets (total volume 31 mL) was prepared by shaking a mixture of 2.8 mL of DMDES (final concentration 9.0% v/v) and 28.2 mL of an aqueous solution of ammonia (concentration of ammonia 22.7% v/v) in a 40 mL glass vial for 2 min by hand. The sample was placed on a rollerbank during droplet growth. The seeds were allowed to grow for 48 h after which the emulsion was transferred to a new vial (40 mL). We would like to note here that (as an exception) this sample was prepared in a glass vial that contained a styrene−butadiene rubber capliner, manufactured by Wheaton. Synthesis of emulsions in all other methods were performed in glass bottles/vials without a capliner. Strong indications were found that chemicals, dissolved from these capliners, favorably affected the particle size distribution, most probably by acting as surface active agents, as briefly discussed in the Supporting Information. However, we do not think that the presence of the capliner influenced the droplet growth and hence believe that the results would be the same otherwise. For the seeded growth step, 2.8 mL of fresh DMDES was added at once to this seed suspension, and the sample was kept on the rollerbank (at a speed of 35 rpm) for gentle mixing. The addition of DMDES was repeated again at 120 h, 160 h, and 216 h after the emulsion synthesis using the same amount of DMDES. Each time an excess layer of oil (approximately 0.3 mL), which appeared in a matter of minutes after a sample was taken from the rollerbank, was discarded by transferring the emulsion to a new vial.

Seeded Growth - Hydrocarbons and Silicone Oil. For the seeded growth of PDMS droplets with a second oil, several seed emulsions were prepared, this time using the Turrax homogenizer, as described previously. Two samples were prepared according to the large scale mechanical mixing procedure with the Turrax but with reduced DMDES concentrations. One of these samples (sample A) was exposed to one type of oil, during which the particle size was monitored in time. The other sample (sample B) was used to investigate the change in droplet size for various types of oil. Sample A (total volume 728.9 mL) was prepared in a 2 L beaker with an ammonia concentration of 23.4% v/v and DMDES concentration of 4.1% v/v. Sample B (total volume 743.9 mL) contained 22.9% v/v ammonia and 6.0% v/v DMDES. The third monodisperse emulsion (sample C) was prepared according to the small scale mechanical mixing method based on the Turrax as described above (for an overview of all final sizes, see Table S1 in the Supporting Information). This sample was used during swelling studies with fluorescently labeled cyclohexane. In all preparations the droplets were allowed to grow, while keeping the sample without stirring or homogenization, for at least 2 days before starting the seeded growth procedure.

The preformed silicone oil droplets were grown larger using a seeded growth procedure with a second oil. The procedure for samples A and B was the following. Aqueous solutions (total volume 50 mL, 2.7 wt %) of the steric stabilizer PVP were prepared after it was found that increased particle stability was necessary during shell growth. Hereafter, 20 mL of the original emulsion (still containing ammonia) was added, as well as 10 mL of the oil, which formed a layer on top of the emulsion. The oils used were cyclohexane, pentane, iso-octane, hexadecane, and octamethylcyclotetrasiloxane (OMCTS). Swelling was found to be most successful with cyclohexane and pentane, followed by iso-octane, whereas deswelling and unstable systems were observed for the oils hexadecane and OMCTS, a point we will come back to later. The droplets in sample C were exposed to cyclohexane containing 0.28 mg/mL pyrromethene-567. For this, an aqueous solution (total volume 25 mL) of 2.7 wt % PVP was prepared. Hereafter, 5 mL of the original emulsion was added, as well as 3.5 mL of the fluorescently labeled oil phase. Droplets were allowed to grow, while keeping all samples slowly tumbling on a rollerbank for about 22 h (samples A and B) or 6 h (sample C).

The droplets resulting from the seeded growth in samples A and C were encapsulated by a solid shell by making use of the coating procedure described above for the method based on efficient initial mechanical mixing with the Turrax homogenizer. However, compared to this latter method, the current dispersion was already diluted with a PVP solution (as described above) prior to the start of the encapsulation process and even before addition of the extra oil. The dilution step with the steric stabilizer at such an early stage ensured that the continuous phase was presaturated with oil at all times and thereby facilitated a constant droplet size. Shell growth started by keeping the sample static for 5 min such that the excess oil phase creamed up. Subsequently, the turbid subnatant of the emulsion was transferred to a new vial such that the top oil phase would not be present during the coating reaction. Hereafter, the APS/RITC solution was added (4 μL for sample A and 2 μL for sample C) while gently stirring the dispersion. Then, equal amounts (0.34 mL for sample A and 0.85 mL for sample C) of the monomers DMDES and TES were added using a syringe-pump (10 μL/min). The sample was transferred to the rollerbank after all monomer had been added. Shells were allowed to grow for a maximum of 24 h (sample A) or 3 h (sample C), a time-scale set by the onset of buckling, which is a point we will come back to later. The coated emulsion droplets in sample A were transferred to ethanol within 24 h after the start of the shell growth. Shells remained stable and spherical when adding the sample drop-by-drop to (anhydrous) ethanol in a ratio of 1:8 mL, under vigorous stirring. Strangely enough, and unfortunately for unclear reasons as described above in the section for droplets prepared with the efficient mechanical mixing procedure, particles were found to buckle when using less ethanol.

Characterization. *Static Light Scattering (SLS).* The size and polydispersity of the PDMS oil droplets were determined by Static Light Scattering (SLS) experiments. The measurements were carried out in a home-built equipment using a HeNe laser as light source (632.8 nm, 10 mW). The measurements were performed on dilute suspensions in demineralized water, containing about 0.1% v/v of the original sample. The angular distribution of intensity of the scattered light was measured at scattering angles in the range 14° to 135° relative to the transmitted beam, with a photomultiplier detector mounted on a goniometer. The data were plotted against the scattering vector $k = 4\pi n\sin(\theta/2)/\lambda$, where n is the solvent refractive index and λ is the wavelength in vacuum. By comparing the scattering profiles with theoretical ones calculated with the full Mie solution for the scattering factor,[73] the radius and polydispersity were determined by fitting (by hand). The positions of the interference minima in the scattering curves give the size of the droplets, whereas the polydispersity is given by the depth of the minima: the lower the polydispersity, the deeper the minima. During the fitting, the last minima in the scattering profile were used to determine the polydispersity. By doing so, the effect of multiple scattering at low angles (the first minima) could be avoided for these micron-sized particles. The value of the refractive index used to fit the experimental

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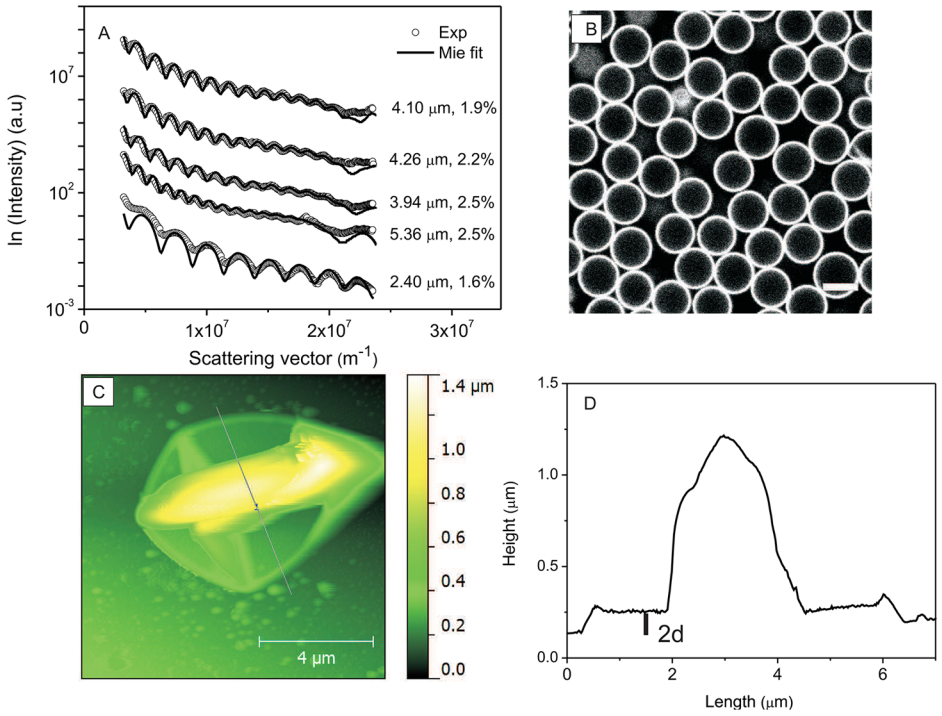

Figure 2. (A) SLS experimental data (scatter) fitted by theoretical calculations with full Mie solution of the form factor (lines) for different series of PDMS droplets prepared using the Turrax homogenizer. The values of droplets size and polydispersity are obtained from the fit (described in the Characterization section). (B) Confocal micrograph of the 5.36 μm microcapsules in an index matching solvent (mixture of ethanol and 52.6% v/v DMSO), the scale bar represents 5 μm. (C) AFM image of a dried capsule, after removing the PDMS core by washing with ethanol. (D) The height profile taken along the line drawn through the collapsed capsules from which we obtained a shell thickness of d = 56 nm.

data for the oil droplets was n_D^{25} = 1.394, corresponding to a low molecular weight silicone oil,[74] and for water was n_D^{20} = 1.333.[75]

Confocal and Optical Microscopy. The fluorescently labeled shells were imaged using an inverted Leica, TCS-SP2 Confocal Scanning Laser Microscope (63 × NA 1.4 oil immersion confocal objective). A 543 nm green HeNe laser was used for the excitation of rhodamine (RITC) labeled shells, and a 488 nm blue argon laser was used for the excitation of pyrromethene-567 dye and of CdSe/CdS/CdZnS/ZnS QD's. Samples were put in a capillary (Vitrocom) either 0.1 × 1 mm or 0.1 × 2 mm for imaging. Unlabeled oil droplets were observed using a Leica optical microscope (63× NA 0.7 air objective).

Atomic Force Microscopy (AFM). The thickness of the microcapsules was measured using Atomic Force Microscopy (AFM, Digital Instrument, Nanoscope) 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, due to drying, leads to plateaus in the height profile that correspond to twice the thickness of the shell.

Refractive Index of the Shells. The refractive index of the solid shells (after removing the PDMS oil template) was obtained by adding dimethyl sulfoxide (DMSO, n_D^{20} = 1.47) drop by drop to a dispersion of shells in ethanol (n_D^{20} = 1.36) up to a point where the solution became almost transparent. Initially, shells in pure ethanol scattered light as the solution was slightly turbid, and the particles were also visible with an optical microscope. The concentration of DMSO in the final volume was approximately 52.6% v/v, and the refractive index of the solvent mixture (without shells, shells were removed by centrifugation) was n_D^{20} = 1.42, measured using a refractometer (Abbe Refractometer Atago NAR-3 T).

■ DISCUSSION

A number of approaches was used to prepare monodisperse, large polydimethylsiloxane (PDMS) oil droplets by hydrolysis and condensation of dimethyldiethoxysilane (DMDES) in an aqueous ammonia solution, based on variations of the method of ref 48. The droplets were then encapsulated by a thin tetraethoxysilane-cross-linked-polydimethoxysilane (TC-PDMS) shell. A schematic illustration of the newly developed synthesis procedures which are presented in this paper is shown in Figure 1.

Efficient Initial Mechanical Mixing and No Agitation during Growth. We modified the synthesis procedure, by introducing a Turrax homogenizer for mixing and by using higher ammonia and DMDES monomer concentrations than what was reported before by Zoldesi et al.[50,51] The Turrax homogenizer helped to speed up the hydrolysis of the added monomer by increasing the surface area. As a result, the nucleation time for PDMS droplets was reduced, so that the droplets became more monodisperse. Samples prepared in this way became turbid about 8−14 min after start of the mixing, indicative for the formation of PDMS droplets. This happened faster when compared to the 1 h time-scale described in refs 48 and 51. The position of the homogenizer-probe in the flask was found to strongly affect the monodispersity of the droplets, because mixing variations affect the homogenization and hence the nucleation and growth (by early aggregation of siloxane substructures and growth with monomer) details. A probe position close to the interface of the two immiscible liquids was found to be most successful. Despite the efficient mixing with the Turrax homogenizer, all samples contained an excess layer of oil directly after stopping the homogenization. It was also found out that the samples had to be kept static after mixing. Samples that were kept on the rollerbank became polydisperse. This problem can be attributed to the unreacted DMDES monomer which would be mixed in during the tumbling motion on the rollerbank and could, upon hydrolysis, increase the ionic strength and hence affect the charge stabilization of

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the as formed emulsion. It is known,[76] that these PDMS droplets are typically stabilized both by surface ionized groups (resulting in a zeta potential of −69 mV) and by the linear chains in the synthesized oil that act as surfactants. In addition, sensitivity to the way the system was agitated could originate from the increased surface area of the dispersed DMDES droplets by using the Turrax homogenizer, which leads to an increase of the hydrolysis rate. For both reasons, the higher concentration of silanol groups by hydrolysis would result in a higher ionic strength which reduces the charge stabilization of droplets present and makes them less stable against shear induced aggregation. Apparently, the tumbling motion caused by the rollerbank already produced enough shear to induce aggregation compared to unagitated growth. A further indication that the system is indeed really sensitive to changes in the amount of hydrolyzed DMDES is that both methods (agitated/unagitated) resulted in polydisperse systems when the overall monomer concentration was increased to higher values than what has been reported in the Experimental Section. When taking this restriction into account, the method resulted in a high yield of highly monodisperse and micron sized oil droplets. Four batches of droplets were prepared at an ammonia concentration of 23% v/v and DMDES concentration of 6.8% v/v, and one more batch was prepared at a reduced DMDES concentration of 2.9% v/v. The many well-defined minima in the static-light-scattering (SLS) curves in Figure 2A are indicative of the high monodispersity in these large scale (750 mL) suspensions. The size and polydispersity of the droplets could be obtained by comparing the scattering profiles with theoretical ones calculated using the full Mie solutions for the scattering form factors.[73] The fits showed that the droplet diameters and polydispersities varied slightly between the four different batches (with a DMDES concentration of 6.8% v/v) after 3 days of droplet growth, in the range 4−5.4 μm and 2−2.5%, respectively. See Table S1 in the Supporting Information for an overview of all droplet diameters and polydispersities for this and all other synthesis methods. On a side note, we would like to mention that these droplets typically became 3 μm already within the first 24 h. Hence, the synthesis procedure generates droplets that are similar in size to the upper limit that was achieved so far[48](∼5 μm). However, the deep minima in the SLS profiles prove that the polydispersity remains significantly lower in the current system. When reducing the DMDES monomer concentration from 6.8 to 2.9% v/v, the droplet diameter decreased to 2.4 μm, Figure 2A and Supporting Information Table S1. Earlier studies have also shown a similar relationship between droplet size and monomer concentration.[48,50,53] This decrease is probably affected not only by the total amount being less but also by the reduced ionic strength during nucleation and early aggregation of the siloxane subunits, as was observed before for the Stöber growth.[49]

All samples prepared with the smaller scale method also resulted in monodisperse emulsions. Using SLS, the droplet sizes were determined for two batches after 2 days of droplet growth. The droplet diameter and polydispersities were found to be 2.8 and 1.7 μm and 1.9% and 1.8% (see Supporting Information Table S1), respectively. One can conclude that these sizes were reduced when compared to the large scale procedure that uses the same concentration of ammonia and DMDES. The absence of an excess DMDES phase after mixing as well as a more effective homogenization in general for smaller amounts of emulsions are most likely the cause of this difference. As mentioned already, the consequence of using a pure water phase which does not dissolve the unhydrolyzed monomer makes that the latter changes in the effectiveness of the mixing will alter the surface area of the (unhydrolyzed) monomer and hence also alter the size of the final droplets. A strong influence of the emulsion amount and the mixing procedure on the particle size was also reported in ref 50.

Tetraethoxysilane-cross-linked-polydimethoxysilane shells were grown around the monodisperse, template droplets prepared with the large scale Turrax procedure. The cross-linked network of silica and siloxane units formed upon addition of both the monomers DMDES and TES, in accordance with previous work done by O'Sullivan et al.[52] However, shells were found to form aggregates consisting of a small number of up to 10 particles during the coating step, likely caused by van der Waals attractions between these micron sized particles. In order to prevent this, we modified the procedure slightly by diluting the emulsion with a solution of the steric stabilizer PVP prior to addition of the monomers as described in the Experimental Section. In addition, PVP is known to facilitate silica growth on surfaces.[20] A concentration of PVP of 2.3 wt % was found to reduce aggregation considerably.

Shell growth typically continued for about 2 days, after which the liquid templating drop could be removed by transferring the coated droplets to ethanol. In pure ethanol, the TC-PDMS microcapsules were found to have a zeta potential of −40.5 mV (Zetasizer Nano ZS, Malvern), indicating that these dispersions are stabilized by surface charges. A confocal micrograph of shells formed around 5.36 μm templating droplets, dispersed in an index matched solvent mixture of ethanol and DMSO (n_D^{20} = 1.42), is given in Figure 2B. The shell thickness of the capsules in this sample was measured by taking cross-sectional profiles through Atomic Force Microscopy (AFM) height images, as shown in Figure 2C and D. Using this procedure, the shells were found to be about 56 nm thick. We can therefore conclude that we can grow stable TC-PDMS capsules around PDMS template droplets with diameters exceeding the limit of about 3 μm reported before.[50,52]

Prehydrolysis. Another method that we used to synthesize monodisperse PDMS oil-in-water emulsions is using prehydrolyzed DMDES. A similar procedure has been reported in refs 77 and 78 for the preparation of lock and key colloids, where the trialkoxysilane 3-methacryloxypropyltrimethoxysilane (TPM), instead of DMDES, was solubilized in water and used as a precursor of monodisperse silicone oil droplets. Prehydrolysis of DMDES makes the monomer readily soluble in the reaction medium, so that the nucleation time may be reduced, leading to monodisperse droplets. Prehydrolysis, prior to emulsion preparation, was done by mixing 28.5% v/v of deionized water and 71.5% v/v DMDES. Before mixing, the solution formed two phases, as DMDES is less soluble in water; but within half an hour it became a clear single phase, indicating the hydrolysis of the monomer. Note that the formation of a clear single phase did not necessarily mean that the monomer is completely hydrolyzed in water. Previously, Zoldesi et al.[50] already confirmed from NMR studies on solutions of PDMS oil in water, after 10 h of emulsion preparation, that a significant amount of DMDES was only hydrolyzed at one end. Besides, we also checked the conductivity (Radiometer Analytical, CDM230) of the prehydrolyzed solution after half an hour and 24 h of sample preparation. We measured an increase in the conductivity value from 1.0 ± 0.1 μS/cm to 2.2 ± 0.1 μS/cm in

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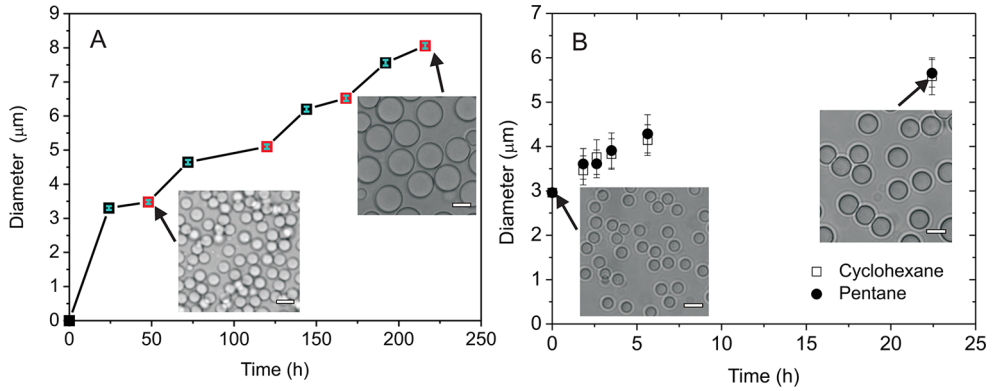

Figure 3. Increase of the droplet diameter with time using a seeded growth procedure with (A) DMDES (data points marked in red denote the time at which more of the monomer was added), and (B) cyclohexane or pentane. Please note that the error bars in these figures are not the errors in the measurement of the particle size but indicate the polydispersity of the size distributions. Sizes and polydispersities were determined with SLS (A) and from optical micrographs (B), making the systematic deviation in B larger due to the poor resolution. Inset pictures are the optical micrographs of droplets before and after addition of DMDES and hydrocarbons. Scale bars represent 5 μm.

24 h of prehydrolysis, caused by an increase in the concentration of acidic silanol groups in the solution as a result of hydrolysis of DMDES.

We prepared four batches of emulsions using this hydrolyzed DMDES solution, two batches each, after half an hour and 24 h of prehydrolysis. Emulsions were prepared by adding 9% v/v of prehydrolyzed DMDES (final concentration of DMDES was 6.5% v/v) to an aqueous solution of 22.7% v/v of ammonia, followed by shaking in a vortex mixer for 3−4 min to dissolve prehydrolyzed DMDES in the solution. Thereafter, the samples were placed on a rollerbank to gently tumble the mixture during droplet growth. After 24 h of synthesis, two batches prepared from half an hour prehydrolyzed DMDES contained monodisperse PDMS oil droplets of diameter 5.6 and 5.0 μm, respectively, with polydispersities 2% and 1.9% (see Supporting Information Table S1). These sizes were comparable to those obtained using the Turrax homogenizer. However, two batches of emulsions, each prepared using a 24 h old prehydrolyzed DMDES, contained droplets of only 1.7 and 2.0 μm diameter with polydispersity 2.9% (see Supporting Information Table S1). Although still monodisperse, the average droplet size was reduced approximately by 60% compared to the droplets prepared from a half hour old prehydrolyzed DMDES. This could be due to the fact that the aging of prehydrolyzed monomer results in a gradual increase in the concentration of hydrolyzed monomer, confirmed from the conductivity measurements. As a result the nucleation rate is increased in the sample, leading to smaller droplets.

On the contrary, we found that emulsions made without prehydrolysis of monomer under otherwise identical conditions often became polydisperse. This result is therefore also in agreement with the adverse effect of the excess unreacted DMDES phase that was described above for samples prepared with the Turrax homogenizer, which were gently tumbled during droplet growth instead of being kept static. Apparently, prehydrolysis reduces the amount of unreacted DMDES in the sample that would otherwise adversely affect the size distribution of droplets.

Seeded Growth - DMDES. Multiple additions of DMDES were used as an alternative means to increase the size of the PDMS droplets, in a way similar to the seeded growth of silica colloids.[79] The total amount of DMDES that was added during the seeded growth step was the same as what had been used during the preparation of the seed/original suspension. Seeded growth was performed for 9 days during which the monomer was added four times with time intervals of 48 h, except for the second addition which was done after 72 h. The sample was placed on a rollerbank (at a speed of 35 rpm), after each addition, during droplet growth. In previous systems with an excess DMDES phase in the reaction medium even the slight agitation caused by a rollerbank often resulted in a polydisperse emulsion. This was probably due to an increase in ionic strength (by the hydrolysis of excess monomer) and hence a decrease in stability of droplets against shear induced aggregation. However, in the present system PDMS droplets remained stable and monodisperse, even in the presence of excess unreacted DMDES. Apparently, the stability of the droplets here can be attributed to factors like the increase in surface area and hence surface charge,[48] as the seed droplets are a lot larger than the PDMS nuclei formed during emulsion synthesis, and the surfactant-like behavior of linear PDMS chains.[76] The growth profile of the DMDES seeded growth study is shown in Figure 3A, where the points marked in red represent the time of addition of monomer. The data point at 0 h represents the time of preparation of the seed emulsion. A major increase in size of the seed droplets, approximately 1 μm in diameter occurred during the first 24 h of growth; in the next 24 h the droplets grew approximately another 0.5 μm. The droplets were found to remain stable and monodisperse up to 8.00 μm (the SLS curve is shown in the graphical abstract). However, after the last addition of monomer the emulsion became unstable and underwent coalescence. Thus, although the size of the droplets can be increased by feeding with DMDES monomer, the size increase occurred relatively slowly due to the slow condensation reaction of hydrolyzed monomer.[50] So it would be interesting to search for oils where a similar, or even larger, size increase can be achieved in a shorter time period.

Seeded Growth - Hydrocarbons and Silicone Oil. It was found that PDMS emulsions could be grown larger, at a faster rate and without the need of successive addition steps, by using a seeded growth procedure with hydrocarbon oils instead of DMDES. Preformed PDMS emulsions were used that were at least 2 days old as the droplets are known to increase slowly in time within the first 48 h.[50] An elapse of at least 2 days therefore allowed us to attribute any further changes in droplet

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size to the exposure to the oil. The original PDMS droplets (sample A), 3 days old, were found to be 2.96 μm in diameter with a polydispersity of 2% as determined with SLS. One batch of these droplets was exposed to cyclohexane, and another batch was exposed to pentane. After 22 h, the droplet diameter in both samples had increased to 5.4 μm as shown in Figure 3B, where sizes were measured from optical micrographs instead of via SLS as a dilution step was not possible since the reaction medium had to be saturated with oil at all times, as discussed later. As a result, the resolution was poor, resulting in a larger standard deviation than what was typically seen with SLS but which remained almost constant for increasing sizes. The similar increase of the particle diameter is caused by the fact that the solubility of pentane in water is similar to that of cyclohexane,[80] a point we will come back to. Compared to the seeded growth with DMDES (Figure 3A), the droplet size increase after 24 h was more rapid for cyclohexane and pentane.

In order to investigate the seeded growth procedure for a wider variety of oils, preformed PDMS emulsions were not only exposed to cyclohexane but also to iso-octane, hexadecane, and the silicone oil OMCTS for 22 h. For this experiment, 2 days old PDMS droplets were used with a diameter of 4.2 μm and polydispersity of 2.1% (sample B). The optical micrographs of the original droplets and the droplets exposed to various oils are shown in Figure 4. A significant size increase was observed in the presence of cyclohexane, resulting in monodisperse droplets of about 8.2 μm in diameter. This indicates that swelling with cyclohexane is a highly efficient process as seeded growth with 100% of the added oil would have resulted in droplets of about 8.9 μm in diameter, (roughly) estimated from the volume fraction and size of the initial PDMS droplets. A smaller increase, resulting in diameters of about 4.9 μm, was observed for the sample with iso-octane. Droplets in both samples remained stable for a couple of days. With OMCTS (result not shown) and hexadecane, the droplet size was found to decrease and the number of oil droplets to reduce. Besides, these systems became polydisperse. From these observations, one can conclude that the various oils affect both the size and the stability of the original PDMS seed droplets.

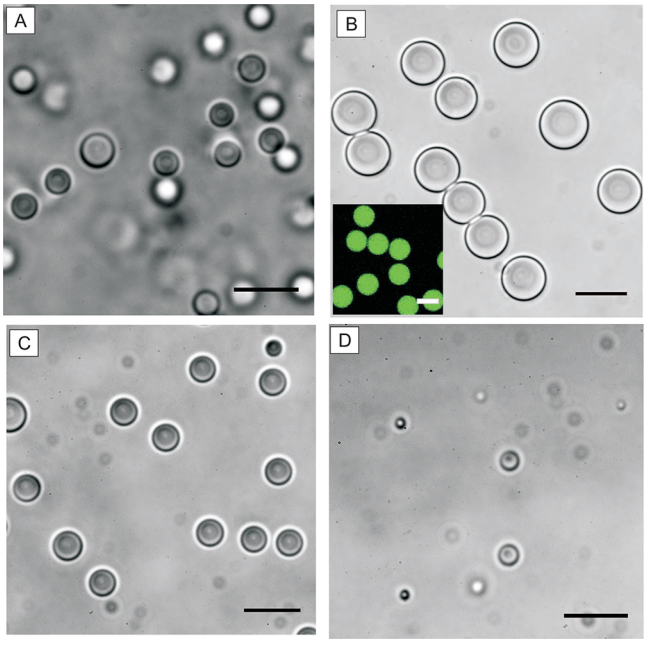

Figure 4. Optical micrographs of the (A) original PDMS seed droplets and of these droplets after 22 h of exposure to (B) cyclohexane, (C) iso-octane, and (D) hexadecane. The droplet size was found to vary, depending on the solubility of the hydrocarbon oil in water. Scale bars denote 10 μm. The appearance of a core−shell structure is caused by the refractive index mismatch. Inset figure in (B) represents a fluorescence micrograph of pyrromethene-567 loaded droplets, swollen with cyclohexane.

The droplet size is most likely related to the solubility of the added oil in water. The threshold for successful swelling of the preformed emulsion will be set by the solubility of the synthesized PDMS oil itself. Oils that are more soluble in water than PDMS resulted in a droplet size increase. Also note that the largest, and similar, size increase was seen for cyclohexane and pentane (Figure 3B) which are equally well soluble in water, whereas iso-octane, for which the solubility is significantly reduced, but still larger than PDMS, resulted in a smaller size increase. The reverse, a decrease in droplet size, occurred for oils poorly soluble in water (like hexadecane[81]). The stability of the swollen droplets is most likely brought about by the linear chains in the synthesized PDMS oil which can act as surfactants.[76] The presence of these linear chains could explain the stability of droplets swollen with cyclohexane, pentane, and iso-octane in the present study even though the volume fraction of PDMS within the swollen droplets (down to 0.12 in the present system) is lower than what has been described in ref 76. In this context, it is surprising that droplets exposed to OMCTS were found to deswell and to become unstable as indicated by the polydispersity and the reduced number of droplets. In principle, stable droplets were expected as the interfacial tension of OMCTS is lower than that of *n*-heptane, which is known to result in stable droplets when mixed with synthesized PDMS.[76] About 80% of the total material in the synthesized PDMS oil is comprised of the cyclic tetramer OMCTS.[48] Deswelling with OMCTS therefore suggested that the linear oligomers, present in the synthesized PDMS oil, raise the water solubility of the preformed emulsion to values above that of OMCTS. Along the same line of reasoning, it is possible that these linear chains were withdrawn first from the as-prepared emulsion during the deswelling process. A reduction in the number of these surface active molecules could also clarify why droplets did not only become smaller but also became unstable in the presence of poorly soluble oils, as indicated by the polydispersity and by the reduction in the number of droplets. Hence, the interplay between the solubility of the oils in water and the presence of linear PDMS oligomers sets the success rate for swelling.

On a final note, we would like to mention that, apart from swelling, also loading with a fluorescent dye was possible when using the seeded growth procedure. Such loading of chemicals is clearly of importance in many applications. Preformed PDMS droplets (sample C) (3.2 μm in diameter, polydispersity 2%, 5 days old) were swollen to 5.5 μm within 6 h by exposure to cyclohexane stained with pyrromethene-567. A confocal micrograph of this dyed emulsion is shown in the inset of Figure 4B. Unfortunately, emulsion preloading in the present system was not found to be successful when using cyclohexane in which 6.9 nm quantum dots were dispersed ($0.5 * 10^{-7}$ mol/mL). Even though the droplets did swell, the quantum dots were apparently not water-soluble enough and remained dispersed in the phase separated (excess) cyclohexane phase. Future work has to show if a slightly more polar capping molecule, making the solubility of the quantum dots in water

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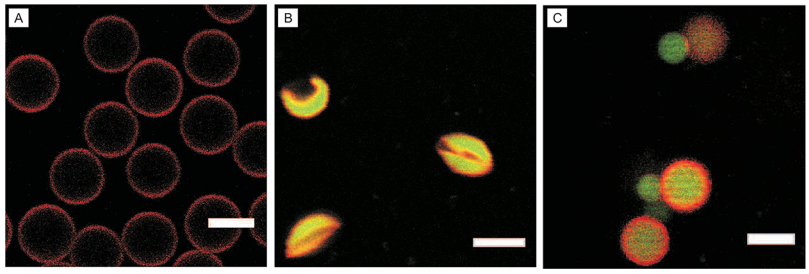

Figure 5. (A) Confocal micrograph of shells formed around cyclohexane swollen PDMS droplets, 24 h after the start of shell growth. (B) The preformed PDMS emulsion could be swollen with fluorescently labeled cyclohexane. After encapsulation, shell buckling indicated that the volume of the templating droplets is not conserved anymore, even though the water was initially presaturated with this oil. This suggests that loss of oil possibly occurred via evaporation. (C) Shells unbuckled, and then budded secondary droplets, in the presence of excess cyclohexane due to overloading, similarly as reported in ref 64. Scale bars denote 5 μm.

higher, could overcome this negative result. As a result, loading with quantum dots such as described by Cui et al.[53] could not be achieved in the present study.

The hydrocarbon swollen droplets could also be encapsulated by a solid shell. In principle, we used the same procedure as described for the method based on efficient initial mixing with the Turrax homogenizer, including the addition of PVP. Addition of PVP was required to ensure stability of the swollen droplets under the conditions of the shell growth step. However, addition of a PVP solution would undo part of the swelling, as some cyclohexane or pentane would dissolve back in the added quantity of water. To prevent this, a PVP stock solution was already added before swelling with cyclohexane or pentane. The same effect also made it necessary to determine the drop size in the reaction medium using an optical microscope, rather than using the SLS for which dilution of the suspension is needed. With this presaturation step, shells could for example be successfully grown around the 5.4 μm cyclohexane swollen droplets (sample A, Figure 3B) as can be seen in Figure 5A.

Spherical, ethanol-filled capsules could be obtained with this seeded growth procedure when shells were transferred to ethanol according to the procedure described in the Experimental Section. The shell thickness was found to be only 20 nm with AFM. We expect that by increasing the amount of DMDES and TES during shell growth, thicker shells could be formed.[52] However, the present study focused on the increase in the capsule diameter rather than control over the shell thickness as the latter has already been achieved.[50−52] Besides, capsules with high diameter-to-wall thickness ratios can be interesting for potential applications.[7]

Unfortunately, shells that were formed around the seeded grown droplets were found to buckle in time in the reaction medium. Often this was observed within about 24 h of shell growth. An example of the buckling behavior is shown in Figure 5B, for shells formed around the droplets swollen with stained cyclohexane (sample C, inset Figure 4B). Buckling indicated that the volume of the templating droplet was not conserved anymore. In principle, such a decrease in volume should be prevented if the continuous aqueous phase is kept saturated with oil during the whole process of shell growth. These results therefore suggest that loss of oil possibly occurred via evaporation, even though the samples were sealed with a cap. An indication for this hypothesis is that samples swollen with pentane, which has an even higher vapor pressure than cyclohexane, buckled in a more pronounced way and already within the first 24 h. Leakage of oil might be prevented in further studies by exposing the aqueous dispersion to oil vapors. Alternatively, the formation of other solutes during the coating step could affect the solubility of the added oil in the continuous phase. Finally, also a reduction in the ionic strength might be the cause,[72] due to slow disappearance of silanol groups in the aqueous phase.

When transferring buckled shells from the reaction medium to ethanol, a deformed capsule was obtained. These capsules were slightly dimpled, and their shape did not change 24 h after transfer to ethanol. This therefore suggests that the particles had become fixated in this shape, possibly because shell growth proceeded while the volume of the template had already decreased. To prevent this, shells could be transferred to ethanol before the onset of buckling. Unfortunately, this also limits the time for shell growth and hence the achievable shell thickness.

Interestingly, unbuckling of the buckled capsules was possible by exposing the sample, in water, again to an excess phase of (dyed) cyclohexane. We visualized this by filling half a capillary with the buckled shells from the reaction medium (Figure 5B) and the rest of the capillary with the (fluorescent) cyclohexane phase. Confocal micrographs of this system were taken near the oil−water interface soon after preparation of this sample. As can be seen in Figure 5C, shells fully relaxed back to spheres and even became overloaded with the oil phase[64] resulting in the formation of snowman-like particles. The relaxation of the buckled capsules indicated that the shells are still highly permeable to both oil and dye molecules, even though the particle synthesis is slightly altered when compared to procedures used in refs 50, 51, 82, and 52 by introducing the polymer PVP and using the seeded growth procedure.

■ CONCLUSIONS

In the present study, we have shown that we can synthesize monodisperse PDMS droplets with sizes significantly above 3 μm. In addition, we showed that it is possible to grow an elastic shell of TES-cross-linked-PDMS around these droplets. The templating droplets were prepared via various methods, for which an overview of the achieved final particle sizes and polydispersities is given in Table S1 in the Supporting Information. In one method, a Turrax homogenizer was used to enhance mixing of the immiscible monomer DMDES and to increase the rate of hydrolysis and solubilization of the as formed hydrolyzed species. This procedure resulted in droplets (and hence capsules) with diameters above 5 μm on a bulk (750 mL) scale. In the second technique, the monomer DMDES was prehydrolyzed, creating readily hydrolyzed and

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water-soluble species. By doing so, the nucleation time was reduced when compared to emulsions prepared under otherwise identical conditions, leading to more monodisperse droplets. In the third method, preformed PDMS templates were swollen with DMDES monomer or with low-molecular weight hydrocarbons during a seeded growth procedure, resulting in the largest monodisperse droplets formed in this study of up to 8.2 μm. Besides, we have shown that along with swelling, oil soluble chemicals (like a pyrromethene dye) can be loaded into the droplets. For swelling with a second oil, the solubility of the added oil in water has to be higher than that of the synthesized PDMS, which for the oils we tried was valid when using cyclohexane, pentane, and iso-octane. A drawback when using swelling with second oils is that encapsulation of the mixed oil droplets resulted in buckled capsules even after presaturating the aqueous phase, possibly because the solubility changes over time due to formation of other solutes or due to evaporation of oil affecting the equilibrium concentration. To prevent this, the spherical capsules had to be transferred to ethanol before buckling started in the reaction medium, limiting the duration of shell growth.

In short, this paper presents several robust and surfactant free synthesis procedures that yield highly monodisperse PDMS droplets above 3 μm. In addition, we have shown that these large particles can also be used as sacrificial templates and allow facile drop removal. When comparing all procedures, it can be stated that the efficient initial mechanical mixing with the Turrax homogenizer currently allows for the largest scale synthesis of droplets up to about 5.5 μm in diameter. When aiming for even larger droplets, the seeded growth procedures with DMDES or hydrocarbons are preferred. The main advantages of the hydrocarbon method are that the droplet size increases faster, and no successive addition steps are required. Finally, also the droplet size up to 5.6 μm of the prehydrolysis method can compete with the efficient initial mechanical mixing of the Turrax homogenizer even though the synthesis scale is smaller. Overall, we think that the increased PDMS drop diameters broaden the horizon for potential applications and also allow the use of elastic shells for granular jamming/contact force studies not only when the sub-10 μm PDMS droplets are used as templates for shell synthesis, a topic we focused on, but also in general for synthesis of monodisperse emulsions that find applications in food science, cosmetics, and drug delivery.

■ ASSOCIATED CONTENT

Supporting Information

Information and characterization data on the contaminants released by the styrene−butadiene capliner that were found to favorably affect the particle distribution in the samples prepared for the seeded growth study with DMDES. An overview of PDMS droplets size and polydispersity obtained from all different synthesis methods. 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.

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