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Controlling the Morphology of Polyurea Microcapsules Using Microfluidics

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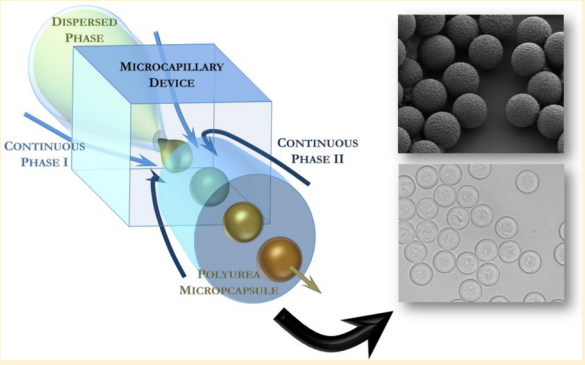
Supporting Information

ABSTRACT: We use microfluidics to continuously produce monodisperse polyurea microcapsules (PUMCs) having either aqueous or nonaqueous cores. The microcapsule shells are formed by the reaction between an isocyanate, dissolved in oil, and an amine, dissolved in water, at the surface of oil-in-water or water-in-oil drops immediately as they are formed. Different microcapsule morphologies can be generated using our approach. The thickness of the microcapsule shell increases with an increase in the amine solubility in the oil; this finding provides a simple mechanism by which the PUMC shell thickness can be controlled.



INTRODUCTION

Microcapsules are promising candidates for important applications requiring the encapsulation, delivery, and release of active materials, such as self-healing materials, catalysts, agricultural chemicals, textile chemicals, and chemicals used in paper manufacturing.[1−17] Polyurea microcapsules (PUMCs) are particularly attractive for their chemical and mechanical stability.[18−27] They are fabricated by forming drops of oil containing an isocyanate in an aqueous phase containing an amine: as they come into contact at the oil−water interfaces, the isocyanate and the amine quickly react, forming solid polyurea shells around the oil drops. Such droplet templates are typically fabricated using a variety of approaches, such as spray drying, coextrusion, and phase separation; however, because of the highly variable shear used, the sizes and morphologies of the resultant microcapsules can vary enormously.[24−27] Moreover, these fabrication approaches are typically limited to producing oil-in-water (O/W) emulsion templates and, thus, PUMCs with nonaqueous cores; this precludes the use of PUMCs to encapsulate hydrophilic actives, such as agricultural chemicals, hydrophilic drugs, or cells.

The precise flow control afforded by microfluidic technologies provides a potential means of overcoming these limitations. For example, a glass capillary microfluidic device can be used to produce highly monodisperse O/W or water-in-oil (W/O) emulsion drops.[28−32] In this approach, the PUMC shell forms by the reaction between an amine and an isocyanate at the surface of each drop immediately as it is produced. However, because of the rapidity of the shell generation, solid polyurea can form at the oil−water interface even before the emulsion drop is fully formed, ultimately clogging the microfluidic device. This prevents the unimpeded fabrication of large quantities of PUMCs. A microfluidic approach to continuously fabricating monodisperse PUMCs is thus highly desirable.

Here, we report a straightforward microfluidic approach to continuously fabricate monodisperse PUMCs, without clogging of the device, using single emulsion drops as templates. This approach is versatile, allowing us to produce PUMCs having either nonaqueous or aqueous cores. We systematically study how different PUMC morphologies can be generated using our approach. Interestingly, the PUMC shell thickness is strongly dependent on the solubility of the amine in the oil phase used; this finding provides a simple mechanism by which the PUMC shell thickness can be tuned over a broad range, spanning tens of nanometers to several micrometers.

MATERIALS AND METHODS

Materials. The isocyanates 1,6-hexamethylene diisocyanate (HDI) and 2,4-toluene diisocyanate (TDI), the amines 1,6-hexamethylenediamine (HMDA), polyethylenimine (PEI, branched; M_n = 800 g/mol), ethylenediamine (En), and tetraethylenepentamine (TEPA), the surfactant sodium dodecyl sulfate (SDS), a sodium silicate solution (water glass, ∼10.6% Na_2O, 26.5% SiO_2), and trimethoxy(octyl)silane were purchased in the highest available purity grade from Sigma-Aldrich and used without former purification. The multifunctional HDI trimer Basonat H100 was purchased from BASF SE, the

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surfactant Abil EM 90 from Evonik Industries, and 2-[methoxy(polyethylenoxypropyl)]$_{9-12}$trimethoxysilane from Gelest, Inc.

Microfluidics and PUMC Preparation. The polyurea microcapsules (PUMCs) are prepared using glass-capillary-based microfluidic devices. Round capillaries (World Precision Instruments, Inc., Sarasota, FL) with an inner diameter of 0.64 mm and an outer diameter of 1.00 mm are tapered to desired diameters by applying a micropipette puller (P-97, Sutter Instrument, Inc.). The inner capillary tip diameter is 20 μm and that of the outlet 200 μm. The round capillary is inserted inside a square glass capillary (Atlantic International Technology, Inc., Rockaway, NJ; dinner = 1.05 mm), whereas the inner fluid capillary tip is aligned centrosymmetrically with the outlet with a distance of 40 μm before it. The capillaries are sealed using a transparent epoxy resin (5 min Epoxy, Devcon, Danvers, MA). Glass capillary devices prepared after this method tend to clog at the inner fluid capillary tip region after approximately 1.5 h. To overcome this problem, an additional solvent/surfactant stream between the middle and outer fluid is integrated. By means of this technique, PUMC generation can be performed for several hours, easily. When O/W PUMCs are prepared, the round capillaries are treated with 2-[methoxy(polyethylenoxypropyl)]$_{9-12}$trimethoxysilane for 15 min; for the W/O capsule preparation, trimethoxy(octadecyl)silane is used. A photograph of the microcapillary glass device and the schematic of the work flows are shown in Figure S1 of the Supporting Information.

The inner fluid containing either the amine or the isocyanate, the middle fluid containing the continuous fluid and surfactant, and the outer fluid flow containing either the isocyanate or the amine are injected into the device at desired flow rates using syringe pumps (NE-501, New Era Pump Systems, Inc., Farmingdale, NY). The amine is always dissolved in deionized water and the isocyanate in the oil. The typical flow rates for the inner, middle, and outer fluid phases are 500, 6000, and 7000 μL h^{-1}, respectively. The contact of the outer and inner fluid material at the oil−water interface occurs by diffusive mixing. The outlet tubing leads into a container, within which the capsules are gently collected. After 18 h at room temperature, the supernatant fluid of the PUMC suspension is decanted several times and replaced with pure continuous fluid. In the case of the W/O PUMCs except from the experiments with PEI, a turbid continuous fluid was observed as a result of the bulk polyurea formation caused by the migration of the amine into the continuous media.

The liquid−liquid interfacial tension for cyclohexene and SDS (aqueous) in O/W mode is 2.78 ± 0.16 mN m^{-1} and at the cyclohexene with Abil EM 90 anc deionized water in W/O mode is 12.06 ± 0.31 mN m^{-1}, which is measured by means of the pendent drop method, using custom image processing in MATLAB.

RESULTS AND DISCUSSION

Preparation of Monodisperse PUMCs. We use a glass capillary microfluidic device to prepare monodisperse O/W emulsion drops as templates to form PUMCs; a schematic is shown in Figure 1a, and a photograph is shown in Figure S1 of the Supporting Information.[28−32] The device consists of two tapered cylindrical capillaries inserted into the opposite ends of a square capillary, whose inner dimension is slightly larger than the outer dimension of the cylindrical capillaries. This configuration allows us to accurately align both cylindrical capillaries. The dispersed oil phase is a 3 wt % solution of 2,4-toluene diisocyanate (TDI) in cyclohexane and is injected using the cylindrical capillary shown on the left in the figure. We treat this capillary with 2-[methoxy(polyethylenoxypropyl)]-trimethoxysilane; this renders its surface hydrophilic, preventing wetting of the oil on the capillary wall. The continuous phase is a 3 wt % aqueous solution of tetraethylenepentamine (TEPA) and is injected from the right; this forces it to flow in the direction that is the opposite of that of the dispersed phase, through the interstitial space between the right cylindrical capillary and the square capillary. The isocyanate reacts, forming solid polyurea, when it contacts the amine-containing aqueous phase; if this occurs too close to the tip of the left cylindrical capillary, the device clogs, preventing its further operation. We overcome this problem by injecting an additional continuous phase, a 3 wt % aqueous solution of sodium dodecyl sulfate (SDS), from the left, forcing it to flow in the same direction as the dispersed oil phase, through the interstitial space between the left cylindrical capillary and the square capillary. We operate this hydrodynamic focusing geometry in the dripping regime, causing the oil to break up at the entrance to the right cylindrical capillary. This protocol forms monodisperse O/W emulsion drops robustly for more than several hours; a representative optical micrograph is shown in Figure 1b.

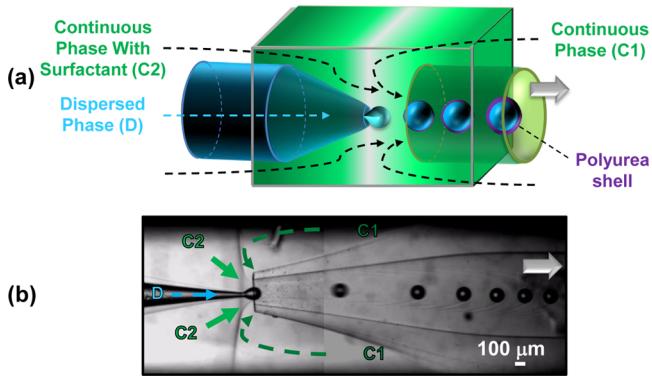

Figure 1. (a) Schematic illustration of the glass capillary microfluidic device used for polyurea microcapsule generation from emulsion drop templates. (b) Optical micrograph of the region in panel a, showing the generation of monodisperse emulsion drop templates.

We use the right cylindrical capillary to collect these emulsion drops; the capillary is treated with 2-[methoxy(polyethyleneoxy)propyl]trimethoxysilane, rendering its surface hydrophilic and preventing wetting of the oil on the capillary wall. The isocyanate within the drops and the amine in the continuous phase react at the drop surfaces, quickly forming microcapsules, with uniform polyurea shells surrounding the oil cores, over a time scale of approximately 0.1−1 s. The PUMCs thus formed are collected, and the supernatant is removed and replaced with water several times to remove any surfactant from the continuous phase. This approach generates solid microcapsules (Supporting Information); an optical micrograph is shown in Figure 2a. Because of the monodisperse nature of the drop templates used to form them, the PUMCs thus produced are highly monodisperse; the polydispersity in their sizes is ∼4−6%, as shown by the data in Figure 2b. The PUMCs are slightly wrinkled; this may result from slight evaporation of the fluid from the core or could be due to the reduction of the core volume due to the amine being used to form the shell.

The precise flow control afforded by microfluidics allows us to prepare microcapsules of varying sizes. We do this by varying the ratio between the flow rate of the dispersed oil phase, Q_D, and the sum of the flow rates of the dispersed, amine-containing continuous, and surfactant-containing continuous phases (Q_D, Q_{C1}, and Q_{C2}, respectively). The size of the emulsion drops produced and, hence, the resultant PUMCs increases with increasing $x_D = Q_D/(Q_D + Q_{C1} + Q_{C2})$, as exemplified by the green squares in Figure 2c. This provides a straightforward means of tuning the PUMC size.

Our experimental approach can be used to fabricate PUMCs of different compositions. To illustrate its versatility, we use the

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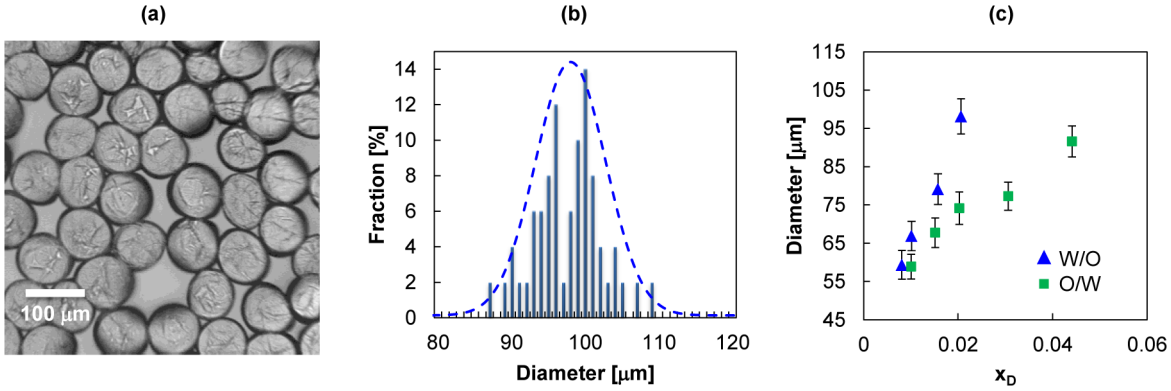

Figure 2. (a) Optical micrograph showing PUMCs with aqueous cores after collection. (b) Distribution of diameters of the PUMCs shown in panel a, with a Gaussian fit. (c) PUMC diameters increase with an increase in x_D, the fractional flow rate of the dispersed phase, for PUMCs formed from W/O or O/W emulsion drop templates. The PUMCs in all three panels are formed using cyclohexane as the oil, TDI as the isocyanate, and TEPA as the amine; we use Abil EM 90 (2.5 wt %) or SDS (5 wt %) as the surfactant for PUMCs formed from W/O or O/W templates, respectively. Error bars show one standard deviation of the microcapsule size distribution.

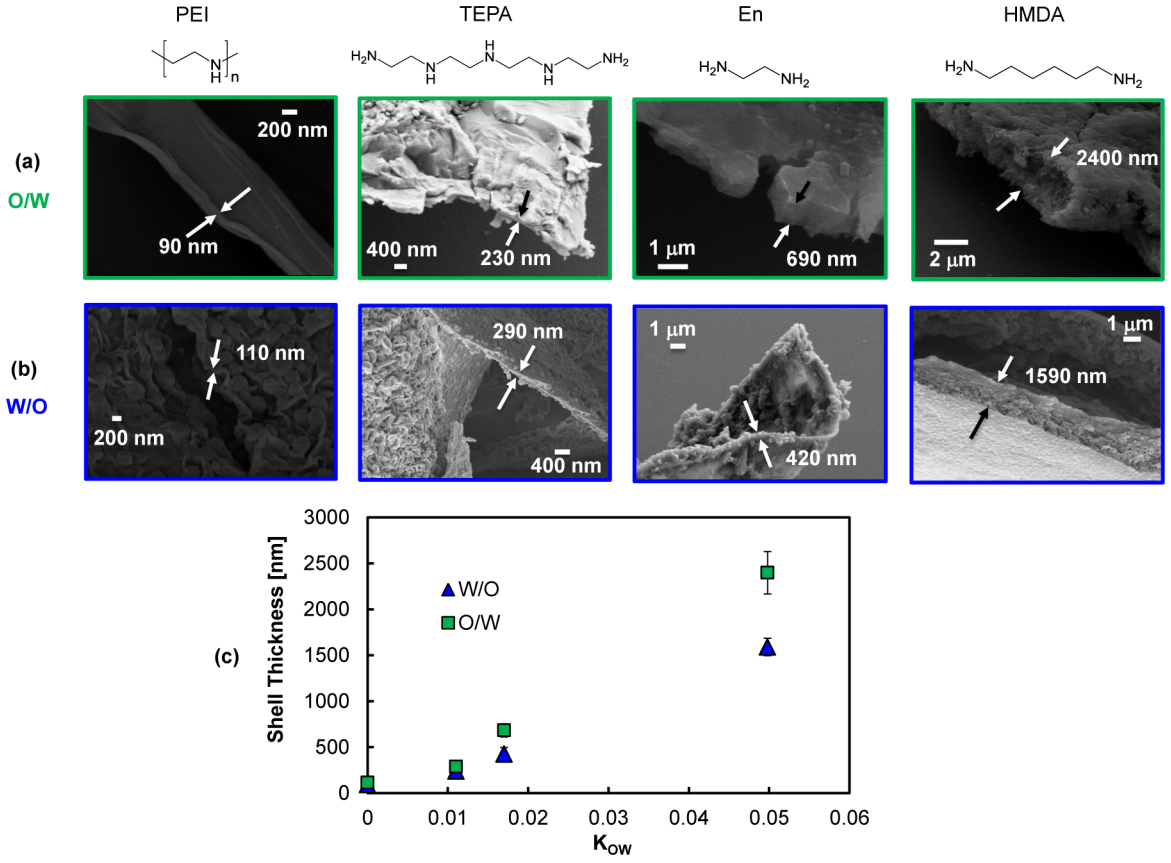

Figure 3. (a) PUMC shell thickness increases with increasing amine solubility in the oil phase, K_{OW}. We use four different amines and show their chemical structures. Toluene is the oil phase. (a and b) Scanning electron micrographs of PUMC shells formed from (a) O/W and (b) W/O emulsion templates. (c) Average microcapsule shell thicknesses for varying amines, characterized by different K_{OW} values. Error bars show one standard deviation of the microcapsule size distribution; bars for small values of K_{OW} are smaller than the symbols.

same microfluidic device, but different dispersed and continuous phases. In particular, we use this approach to prepare PUMCs with aqueous cores. To achieve this, we use a 3 wt % aqueous solution of TEPA as the inner phase and 3 wt % solutions of Abil EM 90 and TDI in cyclohexane as the surfactant- and isocyanate-containing continuous phases, respectively. The left and right cylindrical capillaries are treated with trimethoxy(octadecyl)silane; this renders their surfaces hydrophobic, preventing wetting of the water on the capillary wall. We again operate the microfluidic device in the dripping mode, thereby generating monodisperse W/O emulsion drops. The reaction between the TEPA and TDI again leads to the formation of a uniform polyurea shell; however, in this case, the microcapsule core is aqueous. As with the previous case, we use the flow control allowed by microfluidics to tune the sizes of the resultant PUMCs: by changing x_D, we can tune the PUMC diameter over the range of 50−100 μm, as shown by the blue triangles in Figure 2c.

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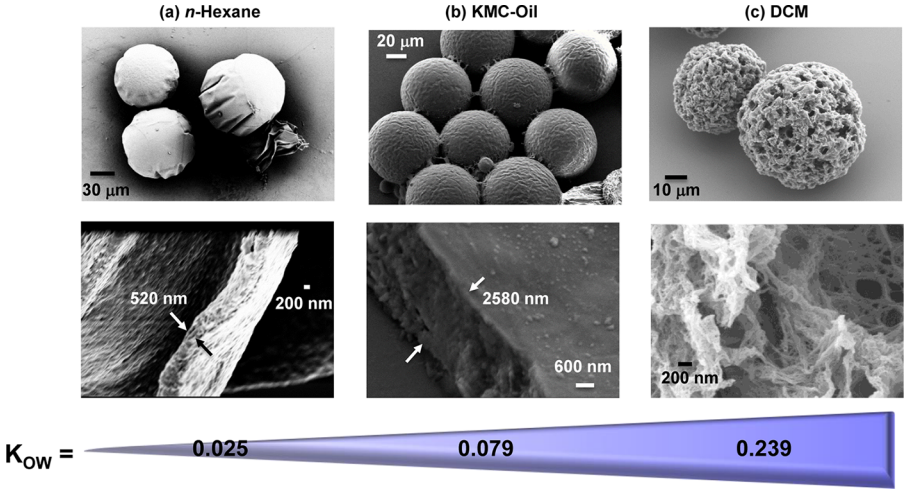

Figure 4. PUMC shell thickness increases with increasing amine solubility in the oil phase, K_{OW}. The PUMCs are fabricated from O/W emulsion templates, using three different oils, as indicated. SEM micrographs show morphologies of (top) the entire microcapsule and (bottom) the microcapsule shell.

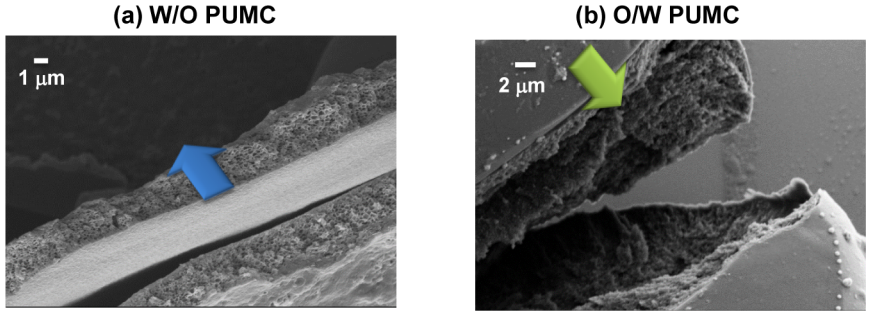

Figure 5. Scanning electron micrographs of the W/O (a) and O/W (b) PUMC shells after cutting. The shell material is 2,4-toluene diisocyanate and tetraethylenepentamine using toluene. The arrows indicate the shell growth direction. In panel a, two shell slices in opposite orientations are close to each other.

Amine Solubility Determines PUMC Shell Thickness. To elucidate how the shell thickness of the microcapsules depends on the chemical components used, we fabricate PUMCs using four different amines: TEPA, polyethylenimine (PEI), ethylenediamine (En), and 1,6-hexamethylenediamine (HMDA). We use TDI as the isocyanate and toluene as the oil phase. The amines are slightly soluble in the toluene, to varying extents. This variation can be quantified using the amine partitioning coefficient:[33] $K_{OW} = [\text{amine}]_O/[\text{amine}]_W$, where $[\text{amine}]_O$ and $[\text{amine}]_W$ are the equilibrium concentrations of the amine in the oil and water phases, respectively. We determine these concentrations using bulk experiments (details in the Supporting Information). Interestingly, the shell thickness increases with an increase in K_{OW}, as exemplified by the scanning electron micrographs shown in panels a and b of Figure 3, and summarized by the data in Figure 3c. For example, the PUMCs formed from PEI, which is insoluble in toluene and thus has a K_{OW} of ≈0, are only 90−110 nm thick; by contrast, the PUMCs formed from HMDA, which has a K_{OW} of ≈0.05, have shells an order of magnitude thicker (1.5−2.5 μm). This behavior appears to be independent of the nature of the emulsion template: we use our microfluidic approach to prepare both O/W and W/O templates, which ultimately form PUMCs having nonaqueous and aqueous cores, respectively. In both cases, the PUMC shell thickness increases with an increase in amine solubility in the oil, as shown by the squares and triangles in Figure 3c. Elucidating the exact mechanism limiting shell growth, for a given amine solubility, will be an important and interesting route for future work.

To further test the influence of amine solubility on PUMC shell geometry, we fabricate PUMCs from O/W emulsion templates, with 1,6-hexamethylene diisocyanate (HDI) as the isocyanate and HMDA as the amine, using three different oils: *n*-hexane, KMC 113 oil, and dichloromethane (DCM). The oils are characterized by K_{OW} values that vary over an order of magnitude, from 0.025 to 0.239. Consistent with our previous results, we find that the PUMC shell thickness increases with increasing K_{OW}, as shown by the scanning electron microscopy (SEM) micrographs in panels a and b of Figure 4. Intriguingly, for the case of DCM, which has the highest value of K_{OW}, we do not even observe the formation of a well-defined PUMC shell; instead, the microcapsules have a spongelike appearance, as shown by the micrographs in Figure 4c and Figure S4 of the Supporting Information. This may, for example, reflect interactions with the surfactant at the surface of the PUMC droplet template.

Our data indicate that the structure of the microcapsule shell is determined by the migration of the amine from the aqueous to the nonaqueous phase. As a final test of this idea, we use SEM to directly visualize the shell structure of PUMCs formed from either W/O or O/W emulsion templates. For both cases, the shell grows from the aqueous phase toward the oil phase, in the direction of the amine migration; this finding is exemplified by Figure 5. This observation provides further confirmation

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that the microcapsule shell structure is determined by the solubility of the amine in the oil.

We next test the influence of the isocyanate used by fabricating PUMCs from W/O emulsion templates, with PEI as the amine, using three different isocyanates (TDI, HDI, and Basonat HI100, which is a trimer of HDI). Intriguingly, there is no significant variation in the PUMC shell morphology, as shown by the SEM micrographs in Figures S2 and S3 of the Supporting Information; this likely reflects the fact that the isocyanates are insoluble in water. Our results thus suggest that the geometry of the PUMC shell is primarily influenced by the slight solubility of the amine in the oil phase.

To further elucidate the dependence of the PUMC shell geometry on the chemical components used, we vary the concentrations of the amine or the isocyanate. We prepare the PUMCs from either O/W or W/O emulsion templates, using TEPA as the amine and TDI as the isocyanate, and toluene as the oil. The shell thickness of PUMCs with aqueous cores strongly increases with an increase in amine content, as shown by the blue squares in Figure 6; this behavior highlights the

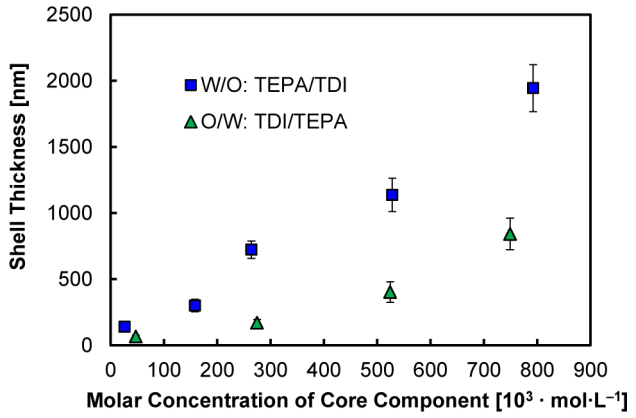

Figure 6. Microcapsule shell thickness increases with an increase in the concentration of amine (blue squares) or isocyanate (green triangles) in the core, for PUMCs prepared from W/O or O/W templates, respectively. Under the experimental conditions used here, deactivation of the isocyanate by water is negligible.

importance of the amine in determining the shell morphology, consistent with our previous results. Interestingly, the shell thickness also increases slightly with an increase in isocyanate content for the case of PUMCs with nonaqueous cores, as shown by the green triangles in Figure 6; this finding suggests that a threshold amount of the isocyanate is required for the shell to fully form.

Finally, we note that the template droplet size may also influence the amine diffusion rate and, therefore, the shell thickness, an effect not explored here. Indeed, the PUMCs used for the measurements in Figures 3 and 6 have similar diameters (57 ± 3 μm). The influence of the PUMC template size on the shell morphology will be an interesting subject for future work.

CONCLUSION

We describe a means of continuously fabricating monodisperse PUMCs, without clogging of the microfluidic device employed, using single emulsion drops as templates. Our approach is versatile and can be used to fabricate PUMCs using a variety of different chemical components; moreover, it can be used to fabricate PUMCs having either aqueous or nonaqueous cores. The geometry of the PUMC shell is primarily influenced by the slight solubility of the amine in the oil phase and can be tuned by the choice of amine used, oil phase, or the concentration of the amine or the isocyanate. Our results thus reveal a simple mechanism by which the PUMC shell thickness can be tuned from tens of nanometers to several micrometers.

ASSOCIATED CONTENT

Supporting Information

Photograph of the microcapillary glass device and verification of the outer fluid (OF), middle fluid (MF), and inner fluid (IF) flow streams (Figure S1), SEM images of the PUMCs (Figures S2–S4), and determination of K_{OW}. 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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ABBREVIATIONS

PUMC, polyurea microcapsule; O/W, oil in water; W/O, water in oil; TDI, 2,5-toluene diisocyanate; TEPA, tetraethylenepentamine; PEI, polyethylenimine; En, ethylenediamine; HMDA, 1,6-hexamethylenediamine; DCM, dichloromethane; SEM, scanning electron microscopy; D, dispersed phase; C1, continuous phase 1; CF2, continuous phase 2; SDS, sodium dodecyl sulfate

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