

Monodisperse Emulsions through Templating Polyelectrolyte Multilayer Capsules

Sri Sivakumar,^{†,§} Jugal K. Gupta,^{‡,§}
Nicholas L. Abbott,^{*,‡} and Frank Caruso^{*,†}

Centre for Nanoscience and Nanotechnology, Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia, and Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, Wisconsin 53706

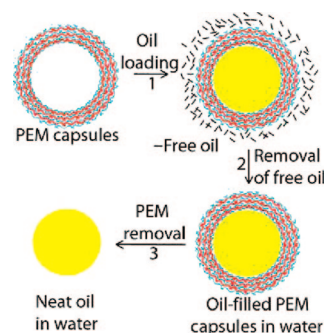
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General and facile methods that permit precise control over the size and surface chemistry of micrometer-scale oil droplets will broadly enable both fundamental studies of confined condensed phases (e.g., effects of confinement on order) as well as advance a range of promising technologies that revolve around the control of dispersed phases (e.g., sensor and optoelectronic technologies). Previous studies have shown that emulsion droplets can be prepared by various techniques, such as photopolymerization,¹ ultrasonication,² shearing of droplets and subsequent crystallization fractionation,^{3,4} droplet break-off in a coflowing stream (microfluidics),⁵ and dispersion polymerization.^{1,6,7} Although most of these approaches result in polydisperse emulsions, emulsion droplets with limited control over interfacial properties, or the formation of polymerized droplets, the microfluidic approach enables the preparation of monodisperse emulsion droplets with sizes larger than approximately 2 μm .^{4,5} Typical quantities of emulsion droplets prepared by microfluidics are on the order of 1–5 s⁻¹ for a single junction.⁸ Recent, more elaborate multiple-device systems can produce 100–1000 particles s⁻¹.⁹ Despite these advances, there is still a need for a general and scalable, highly parallel synthesis strategy that permits the formation of monodisperse emulsions with fine control over their size (even below 1 μm) and surface chemistry.

Herein, we report a versatile method, based on templating polyelectrolyte multilayer (PEM) capsules formed by the layer-

Scheme 1. Schematic Representation of the Procedure Used To Prepare Monodisperse Emulsion Droplets



by-layer (LbL) adsorption of PEs on sacrificial particles, to produce a range of emulsions of a predetermined size and surface chemistry (Scheme 1). Both nonporous and mesoporous (MS, ~ 8 nm pore size SGX) silica particles were used as sacrificial particle templates. The silica particles (5 ± 0.5 μm) were first amine-functionalized by grafting 3-aminopropyltriethoxysilane (APTS) to the particle surface.^{10,11} The APTS-functionalized silica particles were next coated with PEMs, and the coated particles were exposed to hydrofluoric acid (HF) to etch the silica core, resulting in the formation of PEM capsules. Two types of polyelectrolyte capsules were investigated: electrostatically coupled poly(sodium-4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) and hydrogen-bonded poly(methacrylic acid) (PMA) and poly(vinylpyrrolidone) (PVPON). These PEMs have been well-studied^{11–13} and were chosen because the PSS/PAH capsules are highly stable under different conditions, whereas the PMA/PVPON capsules can be readily disassembled as a result of weakening of the hydrogen bonding between the layers by changing the pH. The thickness of each polymer layer in these systems is approximately 2–3 nm. APTS-functionalized silica is positively charged; hence, the anionic PE (PSS or PMA) was deposited as the first layer, followed by either PAH or PVPON as the second layer. As described in detail in the Experimental Section (see Supporting Information), after etching of the silica cores with HF, oil was infiltrated through the semipermeable walls of the PEM capsules, and excess oil was removed from outside of the PEM capsules by contacting the capsules with water. This procedure resulted in the formation of monodisperse PEM-coated oil droplets (denoted as oil-(PSS/PAH)₄ or oil-(PMA/PVPON)₄). Naked oil emulsion droplets were prepared by disassembling the PMA/PVPON layers upon exposure to pH 7.5 solutions. The above-described technique was shown to be successfully applied to a range of oils, including silicone oil, paraffin oil, and thermotropic liquid crystals (LC). The size of capsule templates was also varied (3, 8, and 10 μm) to produce monodisperse emulsions of various sizes. This method is robust and can be potentially applied to routinely produce large

* Corresponding authors. E-mail: fcaruso@unimelb.edu.au (F.C.), abbott@engr.wisc.edu (N.L.A.).

[†] The University of Melbourne.

[‡] University of Wisconsin-Madison.

[§] These authors contributed equally to this work.

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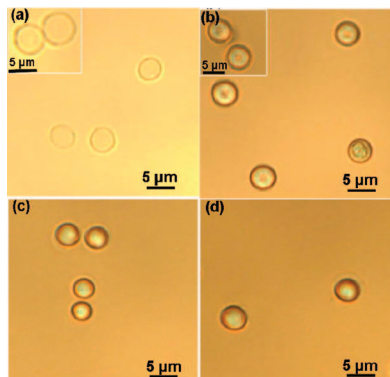


Figure 1. Bright field optical micrographs of (a) water-filled (PSS/PAH)₄ capsules made using MS templates (inset, water-filled (PSS/PAH)₄ capsules prepared from nonporous silica templates); (b) 5CB-filled (PSS/PAH)₄ capsules prepared from MS templates (inset, 5CB-filled (PSS/PAH)₄ capsules made from nonporous silica templates); (c) silicone oil-filled (PSS/PAH)₄ capsules made from MS templates; and (d) paraffin oil-filled (PSS/PAH)₄ capsules prepared from MS templates.

quantities of naked monodispersed oil droplets ranging from nanometers to micrometers or oil droplets functionalized with a variety of PEM coatings that can be tailored for specific applications.

We first illustrate the approach for the thermotropic LC 4'-penty-4-cyanobiphenyl (5CB), and we focus on results obtained with 5CB because the birefringent properties of 5CB provide the basis for a simple means (polarized light microscopy) to determine the uptake of the oils into the capsules. Figure 1 shows a bright field optical micrograph of water-filled (PSS/PAH)₄ capsules prepared from mesoporous (MS) silica particles (Figure 1a) and the same capsules after 5CB loading (Figure 1b). The interference colors and optical contrast between the capsules and surrounding aqueous solution indicate that the (PSS/PAH)₄ capsules were filled with 5CB. Moreover, unlike water-filled (PSS/PAH)₄ capsules, the 5CB-loaded (PSS/PAH)₄ capsules did not collapse after drying (see Figure 3), confirming the presence of 5CB in the capsules. Similar results were obtained for capsules prepared from nonporous silica particles (inset in Figure 1b). Optical micrographs of 5CB-filled capsules prepared from the nonporous and MS silica particles were indistinguishable. The same method was used to generate monodisperse silicone oil and paraffin oil droplets (Figure 1c,d), demonstrating the versatility of this technique. Sizing of the oil-filled PEM capsules from microscopy images yielded diameters of $4.7 \pm 0.5 \mu\text{m}$. There is minimal shrinkage in the size of oil-filled PEM capsules compared to that of the silica template used ($5.0 \pm 0.5 \mu\text{m}$). This is consistent with a report by Miller and Bruening, where a 5% reduction in thickness was observed for PSS/PAH PEMs exposed to ethanol.¹⁴

We performed fluorescence microscopy studies to investigate whether or not PEs from the capsule wall infiltrate into the 5CB cores in the oil-filled capsules. Fluorescently labeled PAH (FITC-PAH) was used instead of PAH to form the PEMs. A fluorescence image of 5CB-loaded (PSS/FITC-PAH)₄ capsules in water is shown in Figure 2a. Uniform and ring-only fluorescence was observed for the 5CB-filled capsules, prepared from either the nonporous or the MS spheres. Confocal laser scanning microscopy (CLSM) examination of 5CB-filled (PSS/FITC-PAH)₄ capsules made

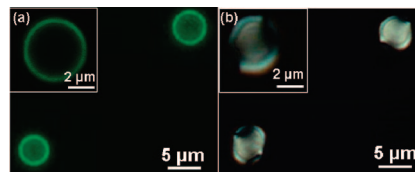


Figure 2. (a) Fluorescence image of 5CB-filled (PSS/PAH-FITC)₄ capsules made from nonporous silica templates (inset is CLSM image of 5CB-filled (PSS/PAH-FITC)₄ capsules made from MS templates). (b) Polarized light micrographs (crossed polars) of 5CB-filled (PSS/PAH)₄ capsules made from nonporous silica templates (inset is polarized light micrograph of 5CB-filled (PSS/PAH)₄ capsules made from MS templates).

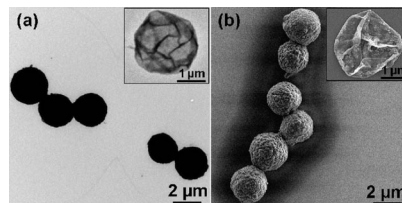


Figure 3. (a) TEM image of 5CB-filled (PSS/PAH)₄ capsules made from MS templates (inset is a TEM image of water-filled (PSS/PAH)₄ capsules). (b) SEM image of 5CB-filled (PSS/PAH)₄ capsules made from MS templates (inset is SEM image of water-filled (PSS/PAH)₄ capsules).

from MS spheres (inset in Figure 2a) also showed a well-defined ring fluorescence of the capsule wall. Further, control experiments with FITC-PSS as the first layer showed similar ring fluorescence (data not shown), demonstrating that both of the PEs present in the capsule wall did not infiltrate into the interior of the 5CB-filled capsules. Polarized light microscopy was used to confirm the infiltration of the LC into the capsules.^{15,16} A polarized light micrograph (crossed polars) of 5CB-loaded (PSS/PAH)₄ capsules made from nonporous silica is shown in Figure 2b, proving that the (PSS/PAH)₄ capsules were filled with 5CB. The micrograph also reveals that the 5CB droplets have a bipolar/boojum configuration, with each droplet containing two point defects at the interface.¹² Similarly, the LCs within 5CB-loaded PSS/PAH capsules made from MS also show the bipolar/boojum configuration (inset in Figure 2b). This further indicates that the properties of the LCs within (PSS/PAH)₄ capsules made from MS and nonporous silica are similar. We used polarized light microscopy to confirm that the 5CB filled 1, 3, 5, 8, and 10 μm (PSS/PAH)₄ capsules. A detailed description of the ordering of LCs within these capsules will be reported in a forthcoming paper.

We postulate that the process of encapsulation of the 5CB within the PEM capsules occurs as follows. Small molecules such as 5CB (miscible with ethanol) readily diffuse through the semipermeable PEM layers. Upon contact with water, the outer surfaces of the capsules are preferentially wet by water (when terminated with PAH), thus dispersing the 5CB-filled capsules in water. We found that removal of 5CB from outside the capsules upon addition of water is less effective when the outermost layer of the capsule wall is PSS, rather than PAH. Bright field micrographs of the 5CB-(PSS/PAH)₃/PSS capsules show LC droplets with smaller LC droplets

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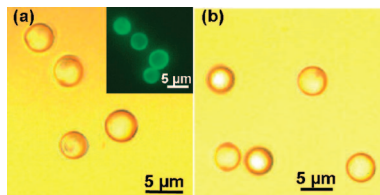


Figure 4. (a) Bright field micrograph of 5CB-(PMA/PVP)₄ capsules made from MS templates (inset is a fluorescence image of 5CB-filled (PMA-FITC/PVP-FL488)₄ capsules made from MS templates). (b) Bright field optical micrograph of naked 5CB droplets obtained after disassembly of PMA/PVP layers. (PMA/PVPON)₄-coated and naked LC droplets possessed similar bipolar configurations (data not shown).

attached to the outer surfaces (data not shown). When the capsule wall is terminated with PSS, 5CB adheres to the capsule wall, likely due to the favorable interaction between PSS and 5CB. This is consistent with our earlier report, where stable 5CB emulsions were formed in the presence of PSS but not with PAH.¹²

The morphology and structural integrity of the 5CB-loaded (PSS/PAH)₄ capsules were characterized with transmission electron microscopy (TEM; Figure 3a) and scanning electron microscopy (SEM; Figure 3b). In contrast to the water-filled (PSS/PAH)₄ capsules (insets in Figure 3a,b), which collapse upon drying, the 5CB-loaded (PSS/PAH)₄ capsules retain a largely spherical shape. Images of 5CB-loaded capsules obtained using TEM show marked increases in electron density (Figure 3a), which is attributed to the presence of 5CB in the capsules. SEM demonstrates that the 5CB-loaded (PSS/PAH)₄ capsules retain a three-dimensional structure (Figure 3b), further confirming 5CB loading.

To determine the amount of 5CB loaded into the (PSS/PAH)₄ capsules, we examined the capsules using flow cytometry and UV-visible spectrophotometry. The number of 5CB-loaded (PSS/PAH)₄ capsules in water (size $4.7 \pm 0.5 \mu\text{m}$), made from MS spheres, was determined by flow cytometry to be $\sim 9.6 \times 10^4 \mu\text{L}^{-1}$. The 5CB-loaded (PSS/PAH)₄ capsule dispersion was then exposed to ethanol to dissolve the LC, and the LC absorbance in the supernatant was measured. By using a UV-visible absorbance calibration curve, we deduced that $88 \pm 2\%$ (vol %) of the capsule interior was filled with 5CB. Analysis of the capsules by optical microscopy showed that the capsules were homogeneously filled, with $>98\%$ of the capsule population loaded with 5CB.

This general method can also be used to prepare naked LCs emulsions by using (PMA/PVPON)₄ capsules. The (PMA/PVPON)₄ capsules were prepared according to our previously reported method, which exploits hydrogen bonding between the PMA and PVPON to facilitate multilayer formation.¹³ Figure 4a shows both bright field and fluorescence micrographs of 5CB-loaded (PMA/PVPON)₄ capsules prepared from MS in acetate buffer of pH 4 (PMA and PVPON were fluorescently labeled with FITC and AlexaFluor 488, respectively). The uniform fluorescence around the capsule demonstrates that the capsule wall is well-defined (inset in Figure 4a). Both of the images are similar to the 5CB-loaded (PSS/PAH)₄ capsules. Naked LC emulsions were prepared by disassembling the PMA/PVPON layers at pH 7.5 (Figure 4b). The absence of fluorescence around the LC droplets suggests that the polymers were completely disassembled and that the LC droplets were free

from PMA-FITC and PVPON-FL488. Moreover, the size of the droplets did not change after disassembly of the PEM layers, which, as for the PSS/PAH capsules, indicates a high LC loading of the capsules. The naked LC emulsions are stable over at least seven days after disassembly of PEM layers, which is probably due to the spontaneous adsorption of hydroxyl ions at the oil-water interface.^{12,17} We are currently studying the long-term stability of the emulsions. Moreover, the LC droplets can also be readily stabilized by surfactants and lipids after disassembly of the PEM layers (data not given). Microelectrophoresis experiments showed similar ζ -potential vs pH curves for these emulsions and uncoated 5CB emulsions in water prepared by sonication, with both emulsions having and isoelectric point (IEP) = 5.1 (see Supporting Information). In contrast, the ζ -potential measurements of 5CB emulsions coated with (PMA/PVPON)₄ have an IEP = 3.2. This further suggests that the 5CB droplets are free from PEM layers after the disassembly. Polarized light micrographs of both the (PMA/PVPON)₄-coated and naked LC droplets showed that they have similar bipolar configurations (data not shown).

In conclusion, a general and facile method to prepare monodisperse, water dispersible PEM-coated and naked emulsions is demonstrated. The formation of PEM-coated 5CB, silicone, and paraffin oil droplets highlights that the technique is robust and easily generalizable. The PAH/PSS capsules were filled to ~ 88 vol % of maximum capacity, and stable emulsions were formed when PAA was the outermost layer. The LCs within the 5CB-loaded (PSS/PAH)₄ capsules assumed a boojum/bipolar configuration. Finally, naked LC emulsions were prepared by using degradable (PMA/PVPON)₄ capsules. This technique has several advantages over microfluidic-based approaches. These include: (i) the ability to readily prepare monodisperse droplets over a wide range of sizes, as capsule templates can be prepared with diameters as small as ~ 10 nm and as large as millimeters; (ii) the preparation of large quantities of emulsion droplets, as the templating method is parallel and scalable (a typical synthesis using 10 mg of silica template particles results in $\sim 10^7$ oil-filled capsules); and (iii) the preparation of emulsion droplets of different composition with well-defined surface functionality. As the presented approach paves the way for the formation of monodisperse emulsions of various materials of controlled size and surface functionality, it is likely to be widely used to form oil droplets with defined properties for a range of applications.

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Supporting Information Available: Details the 5CB-PMA, 5CB after disassembly of PMA/PVPON layers, and pure 5CB emulsions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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