

Supplementary Information for

Microcapsule Fabrication by ATRP at the Interface of Non-Aqueous Emulsions

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Author Contributions

Acknowledgements

Experimental

Materials

(3-aminopropyl)triethoxysilane (99%, 919-30-2), triethylamine ($\geq 99\%$, 121-44-8), 2-bromopropionyl bromide (97%, 563-76-8), graphite (7782-42-5), sulfuric acid (95.0–98.0%, 7664-93-9), potassium permanganate (7722-64-7), isopropyl alcohol (67-63-0), zinc nitrate hexahydrate ($\geq 99.0\%$, 10196-18-6), Phenox O-PC™ A0202 ($\geq 97.0\%$, 1987900-95-7), lauryl methacrylate (96%, 142-90-5), potassium bromide (FTIR grade, $\geq 99\%$, 7758-02-3), and acetone (67-64-1) were obtained from MilliporeSigma. Hexylamine (99%, 111-26-2), methanol (99.8%, 67-56-1), hexanes ($\geq 98.5\%$, 110-54-3), hydrogen peroxide (30 v/v% solution in water, 7722-84-1/7732-18-5), magnesium nitrate hexahydrate (> 98.0 , 13446-18-9), divinylbenzene (80%, 1321-74-0), and toluene (108-88-3) were obtained from Fischer Scientific. Non-porous silica particles (20 nm, 99.5%) were obtained from SkySpring Nanomaterials, Inc., 1-ethyl-3-methylimidazolium hexafluorophosphate (99%, 155371-19-0) was acquired from Iolitec, mesitylene (108-67-8) was obtained from Acros Organics, and acetone-d₆ (666-52-4) was received from Cambridge Isotope. Monomers were passed through a basic alumina column to remove any inhibitors prior to use; all other chemicals were used as received without further purification.

Instrumentation

Probe emulsification was completed with a QSonica Q55 Sonicator. Bath sonication was accomplished with a Fisherbrand CPX3800 Ultrasonic Bath 5.7 L. Vortex mixing was done with a Fisherbrand vortex mixer. Centrifugation was completed with a Thermo Scientific Sorvall ST 8 centrifuge. Fourier transform infrared (FTIR) spectroscopy was collected in transmission mode using a Thermo Nicolet 6700 FTIR equipped with a liquid nitrogen-cooled MCT A (HgCdTe) detector with 64 scans at a resolution of 1 cm⁻¹. Approximately 5 mg of sample was added to ~100 mg of KBr in a mortar, ground into a uniform powder with a pestle, then pressed into a pellet using a Specac 15 Ton Hydraulic KBr Press. ¹H NMR nuclear magnetic resonance spectroscopy was carried out using a Bruker Avance NEO 400 MHz NMR spectrometer. Gas chromatography mass spectrometry (GC-MS) was carried out using a Trace GC Ultra paired with a DSQ-II mass spectrometer. Thermogravimetric analysis (TGA) was carried out under N₂ using a TA Instruments TGA 5500. The procedure used for all silica particle experiments was as follows: ramp 20 °C/min to 900 °C. The procedure used for all bulk and microcapsule experiments was as follows: ramp 20 °C/min to 100 °C, isothermal 5 min, ramp 20 °C/min to 600 °C. Thermal analysis was completed using a Setaram Microcalvet differential scanning calorimeter (DSC). Samples of ~15 mg were independently prepared in Hastelloy C276 hermetically sealed vessels, cooled to 10 °C, then heated to 120 °C at a rate of 1 °C/min. The uncertainty for the DSC was obtained by repeated measurement of individually prepared de-ionized water standards. This provided a relative uncertainty of $u_r(T_{fus}) = \pm 0.0009$ and $u_r(\Delta H_{fus}) = \pm 0.036$ at a 95% confidence interval. UV-vis analysis was carried out using an Ocean Insight Flame Spectrometer with a DH-2000-Bal light source. Particle size analysis was completed via field emission scanning electron microscopy (FE-

SEM) or laser diffraction, depending on the sample. For modified silica particles, samples were sputter coated with 7 nm of Pt prior to imaging and analyzed using a FEI Quanta 600 FE-SEM with an accelerating voltage of 20.0 kV. For solid emulsion droplets and microcapsules, a small sample (< 50 mg) was dispersed in toluene and analysis was completed on a Horiba Partica LA-960 particle sizer while the sample was agitated by magnetic stirring. Optical microscopy images/videos were taken using an AmScope 150C-2L microscope equipped with an 18 MP USB 3.0 camera. To prepare emulsions for imaging, one drop of emulsion sample was placed on a glass slide and diluted with one drop of continuous phase. Select microcapsule samples were mounted atop a PE120 heating stage coupled to a water circulation pump from Linkam Scientific and heated to 100 °C (ramp 20 °C/min) for various time intervals. Scanning electron microscopy (SEM) images were taken using a Tescan Vega 3 SEM with an accelerating voltage of 10.0 kV. SEM samples were sputter coated with 10 nm of Au prior to imaging. Elemental analysis was obtained from Atlantic Microlab, Inc. in Norcross, GA.

Visible-Light Photoreactor

All microcapsule preparation experiments were completed using a visible-light photoreactor reported by Miyake *et. al.*³⁴ A 500 cm strip of 24 volt white LEDs purchased from Capetronix (model no. JJ-2835ST-24-60K) was wrapped around the inside of a 1000 mL Pyrex beaker with a diameter of 11.7 cm (**Figure S1**). The outside of the beaker was wrapped in aluminum foil. LEDs were illuminated at 100% intensity for all experiments.

Methods

Synthesis of SiO₂-NH₂. Dry silica (20 nm) was functionalized per a modified method reported by Zhou and colleagues.³⁵ Pristine silica (~3 g) was charged into a 250 mL round-bottom flask with a large stir bar and dried under vacuum at 150 °C on a Schlenk line. After 24 h, the system was cooled to ambient temperature, purged with N₂, and toluene (100 mL) was added via syringe under vigorous stirring. Once the silica was evenly dispersed, excess (3-aminopropyl)triethoxysilane (10 mL) was added dropwise and the mixture was refluxed at 120 °C for 24 h. Modified particles were isolated via centrifugation (4500 rpm, 15 min), washed thrice with acetone (discarding the supernatant each time), and dried under reduced pressure overnight.

Synthesis of SiO₂-Br. SiO₂-NH₂ (~1 g) was charged to a 250 mL round-bottom flask and dried as described previously. The system was purged with N₂, followed by addition of toluene (40 mL) and triethylamine (16 mL) via syringe under vigorous stirring. The flask was immersed in an ice-water bath and a solution of 2-bromopropionyl bromide (8 mL) in toluene (16 mL) was added dropwise via syringe. After 4 h, the solution was diluted with 200 mL of acetone-water solution (1:1 by volume) and sonicated for approximately 30 min. Modified particles were isolated, washed with acetone, and dried as described previously.

Preparation of Graphene Oxide Nanosheets. Graphene oxide (GO) was prepared via modified Hummers' method.³⁶ Graphite flakes (1.0 g) were dispersed in concentrated sulfuric acid (150 mL) at room temperature under constant stirring. Excess potassium permanganate (1.0 g) was added to the graphite/sulfuric acid mixture and stirring continued for 24 h. This addition was repeated three additional times to add a total of 4.0 g potassium permanganate over 96 h. The reaction was quenched via addition to ~750 mL of an ice-water bath and 30 v/v% aqueous hydrogen peroxide was added dropwise until a color change from pink to yellow was observed, indicating successful quenching of excess potassium permanganate. Crude GO was isolated as a yellow-brown solid via centrifugation (4500 rpm, 20 min) and repeatedly washed with isopropyl alcohol to neutral pH (litmus test) via centrifugation (4500 rpm, 20 min). Pristine GO nanosheets were dried under reduced pressure at room temperature and blended into a fine powder.

Preparation of C₆-GO Nanosheets. Dry GO nanosheets (200 mg) were dispersed in dimethylformamide (50 mL) via bath sonication for 30 min. Excess hexylamine (2.6 mL) was added under vigorous stirring and the system was heated at 55 °C for 48 h. Alkylated nanosheets settled in a mixture of methanol and hexanes over the course of approximately two weeks. After this period, the supernatant was decanted and nanosheets were isolated via centrifugation (4500 rpm, 1 h). Nanosheets were washed thrice with toluene (4500 rpm, 15 min), dried under reduced pressure for 24 h, and ground into a fine powder using a mortar/pestle.

Emulsion Preparation. Solid MNH, ZNH, or [EMIM][PF₆] (0.5 g) was heated in a vial at 100 °C until molten. Separately, SiO₂-Br (0.05 g) was dispersed in toluene (5 mL) via sonication/vortex mixing for at least 30 min to ensure particle dispersion. For select microcapsule batches, C₆-GO nanosheets were included as a nucleation additive. Nanosheet concentration was varied by 0.2 mg/mL (given a constant continuous phase volume of 5 mL and SiO₂-Br loading of 0.05) to evaluate the threshold for overcoming undercooling. This particle suspension was added to the molten salt and the mixture was emulsified via probe sonication at 100 °C for three cycles of 20 s on, 5 s off at 50% amplitude. The resulting mixture was rapidly cooled in an ice-water bath, resulting in emulsion droplet solidification.

Microcapsule Synthesis. A small volume (2 mL) of PCM-in-toluene or IL-in-toluene emulsion was diluted in toluene (3 mL), followed by addition of lauryl methacrylate (0.5 mL) and divinylbenzene (0.5 mL) to the continuous phase. Of note, neither monomer is expected to interfere with the core (at room temperature or above the core T_m), but to preclude any possibility of contamination, both monomers are added prior to polymerization (after droplet solidification). Separately, Phenox O-PCTM photocatalyst (~5 mg) was charged to a 10 mL Schlenk flask with a small stir bar. This vessel was evacuated for 20 min, followed by purging with N₂ for 10 min. The entire emulsion/monomer mixture was then added via micropipette through the septum and gently stirred at ambient conditions. After 10 min, the flask was lowered into the white LED photoreactor and irradiated at full intensity for 24 h. Microcapsules of PCM or IL were isolated via

centrifugation (4500 rpm, 60 s), washed thrice with toluene, and dried for 24 h under reduced pressure.

Hollow Shell Preparation. Approximately 100 mg of microcapsules was dispersed in 15 mL of acetone via vortex mixing which dissolved the PCM or IL, leaving behind the hollow shell. The shell was then isolated via centrifugation (4500 rpm, 15 min) and the procedure was repeated two additional times to ensure complete core extraction. The product was dried at room temperature in vacuo overnight.

Determination of PCM Weight Percent of Microcapsules via UV-vis. As previously reported,³³ absorbance profiles of MNH and ZNH concentrations (1 mM to 40 mM) in distilled water were obtained via UV-vis spectroscopy. The measured absorbances at 302 nm were used to produce a calibration curve and the Beer-Lambert law was employed to calculate the concentration of MNH or ZNH extracted from the microcapsule core (**Figure S2**). Approximately 15 mg of microcapsules were dispersed in 3.0 mL of distilled water, the sample was vortex mixed/sonicated to extract all salt hydrate from the core, and the solution was passed through a poly(tetrafluoroethylene) syringe filter (0.45 μ m cutoff) to remove the broken shell material. The weight percent contribution from salt hydrate was determined by measuring the absorbance of the solution at 302 nm and calculating the concentration and mass of extracted salt hydrate. This procedure was replicated thrice and the average determined.

Determination of [EMIM][PF₆] Weight Percent of Microcapsules via ¹H NMR. Per a previously reported procedure,¹⁹ approximately 20 mg of [EMIM][PF₆] microcapsules was added to a vial containing a 0.050 M solution of mesitylene (internal standard) in acetone-d₆. The mixture was then sonicated/vortex mixed to extract all [EMIM][PF₆]. Next, the solution was passed through a poly(tetrafluoroethylene) syringe filter (0.45 μ m cutoff) to remove the solid shell and the eluent was analyzed by ¹H NMR spectroscopy. The weight percent contribution from encapsulated [EMIM][PF₆] was then determined by comparing the relative integration of the methyl peak from mesitylene (2.09 ppm) to the methyl peak of the [EMIM] cation (3.92 ppm) (**Figure S3**). This procedure was replicated thrice and the average determined.

Table S1. Elemental analysis of modified silica particles.

Sample	Elemental Analysis	Result (%)
SiO ₂ -NH ₂	Carbon	4.00
	Nitrogen	1.09
SiO ₂ -Br	Carbon	6.28
	Nitrogen	0.78
	Bromine	5.21

Table 2. Emulsion droplet diameter, microcapsule diameter, and weight percent contribution from the core.

Sample	Average Diameter (μm)	Percent Core (%)
MNH Emulsion Droplet	9.2 ± 3.6	-
MNH Microcapsule	11.5 ± 4.5	94.6 ± 1.5
MNH Emulsion Droplet (C6-GO)	10.8 ± 4.4	-
MNH Microcapsule (C6-GO)	13.0 ± 5.1	95.8 ± 1.3
ZNH Emulsion Droplet	12.2 ± 3.7	-
ZNH Microcapsule	10.4 ± 3.3	95.6 ± 2.4
ZNH Emulsion Droplet (C6-GO)	13.4 ± 5.4	-
ZNH Microcapsule (C6-GO)	11.3 ± 3.7	93.9 ± 4.5
[EMIM][PF ₆] Emulsion Droplet	12.5 ± 3.9	-
[EMIM][PF ₆] Microcapsule	24.2 ± 9.2	95.2 ± 0.01

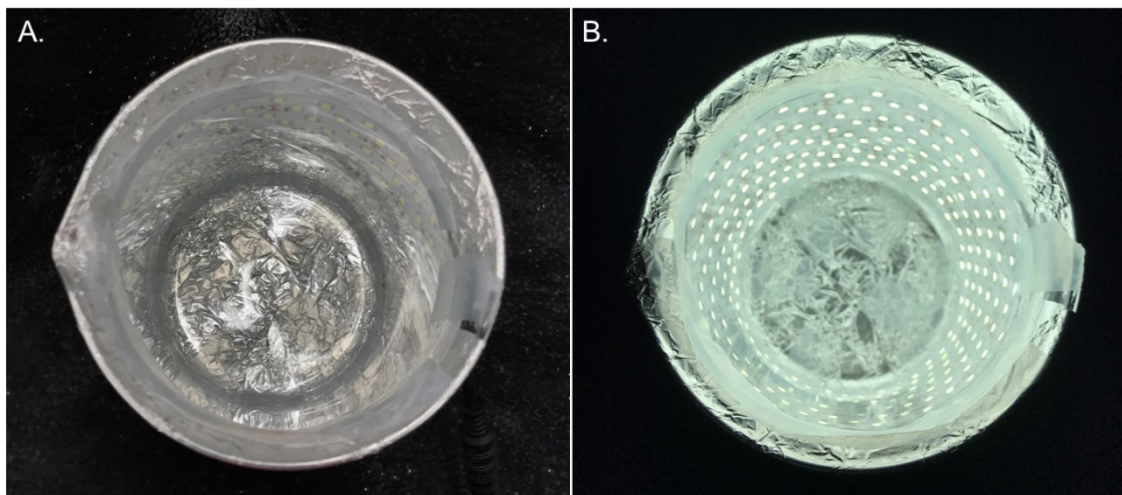


Figure S1. Top view of the visible-light photoreactor with (A) light off and (B) light at 100% intensity.

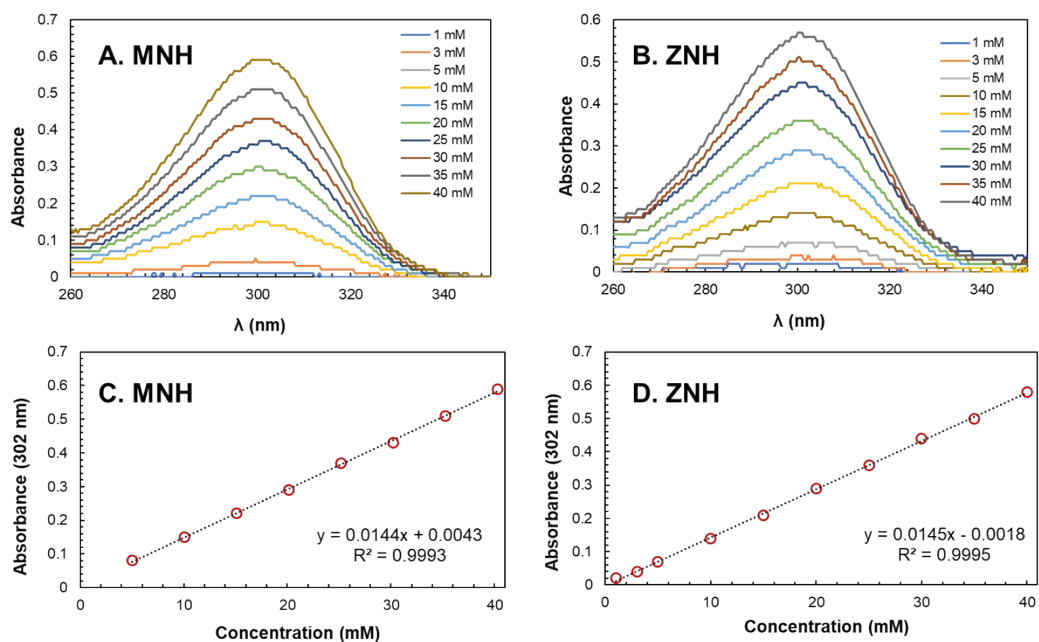


Figure S2. UV-vis absorbance profiles of known concentrations of pure (A) MNH and (B) ZNH in distilled water. Calibration curves developed using absorbances of known (C) MNH and (D) ZNH concentrations at 302 nm.

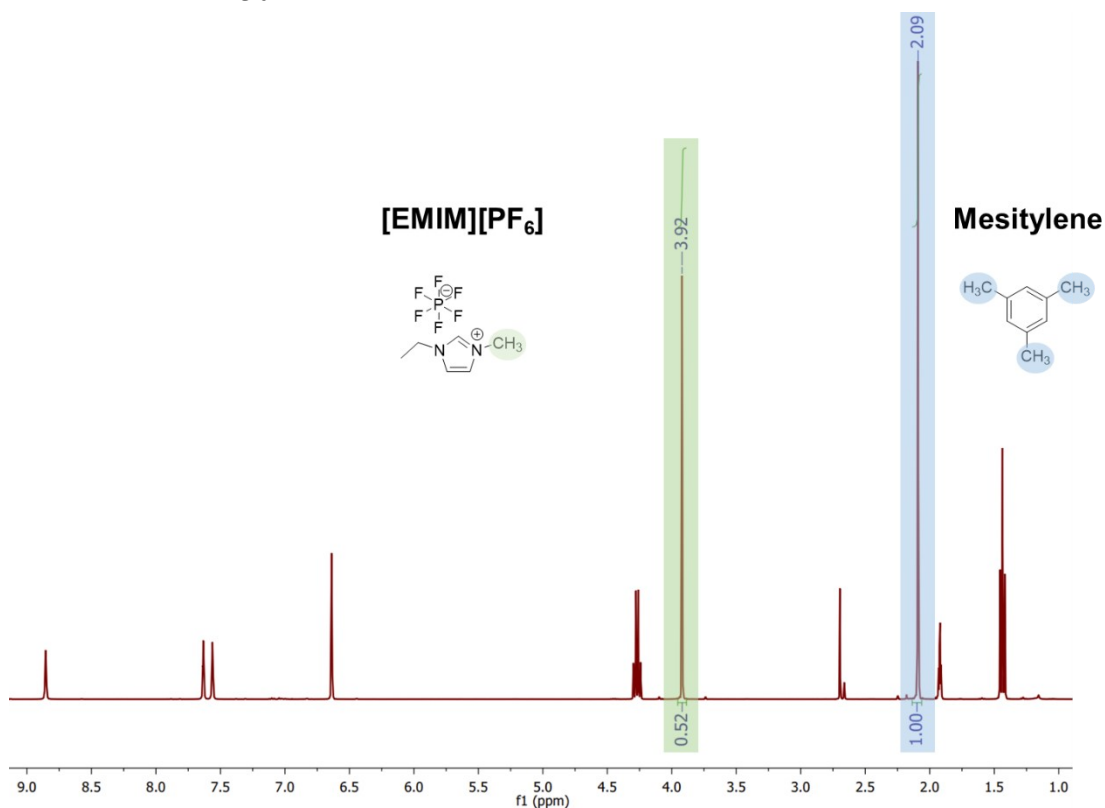


Figure S3. Representative ^1H NMR spectrum of extracted $[\text{EMIM}][\text{PF}_6]$ in deuterated acetone with mesitylene as an internal standard. The relative integration of peaks shaded in green and blue was used to determine weight percent contribution of the core.

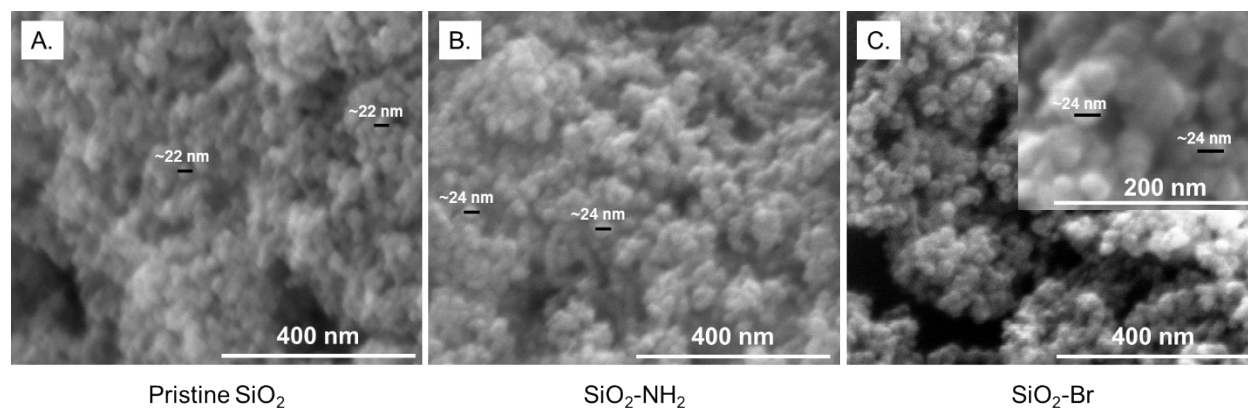


Figure S4. FE-SEM images of (A) pristine SiO₂, (B) SiO₂-NH₂, and (C) SiO₂-Br. Average particle size was determined by adjusting the software-generated scale bar to the apparent particle diameter.

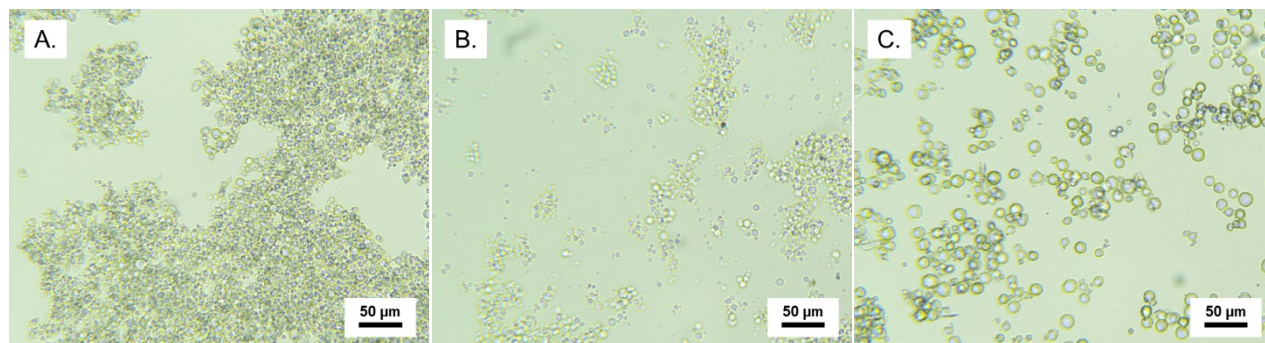


Figure S5. Optical microscopy images of emulsions stabilized by SiO₂-Br. (A) MNH-in-toluene; (B) ZNH-in-toluene; (C) [EMIM][PF₆]-in-toluene.

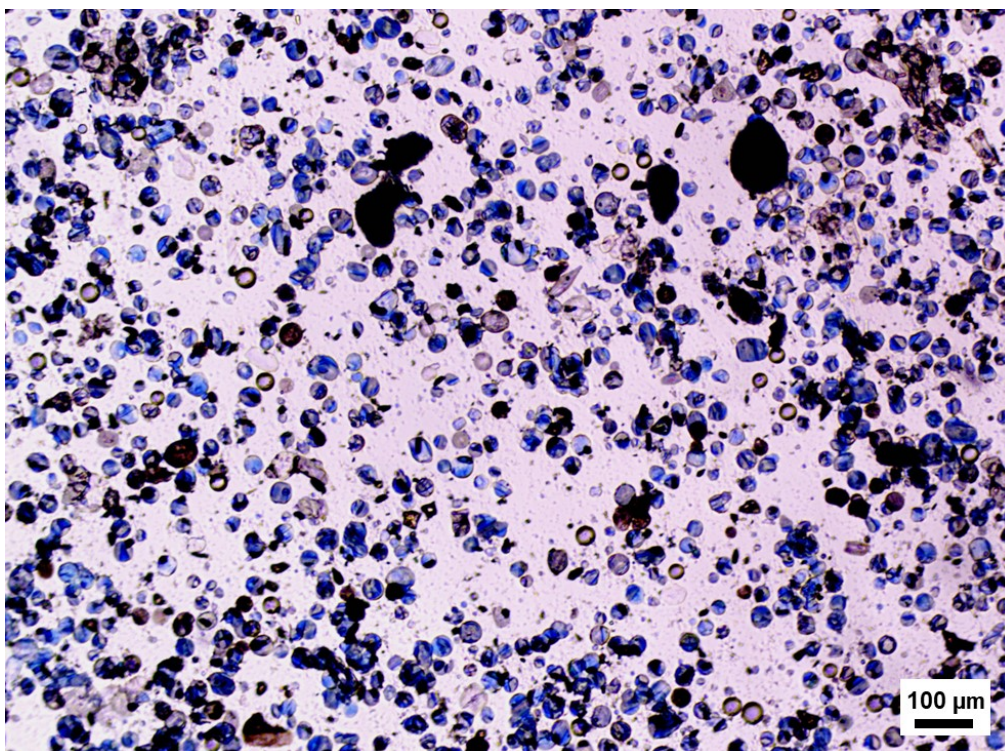


Figure S6. Optical microscopy image of initial microcapsule fabrication attempts pairing MNH-in-toluene emulsion stabilized by $\text{SiO}_2\text{-Br}$ with a $\text{CuCl}/2,2'$ -bipyridine catalyst system and styrene in the continuous phase. The blue color of the emulsion droplets indicates copper salt has entered the core, contaminating the droplets and preventing ATRP.

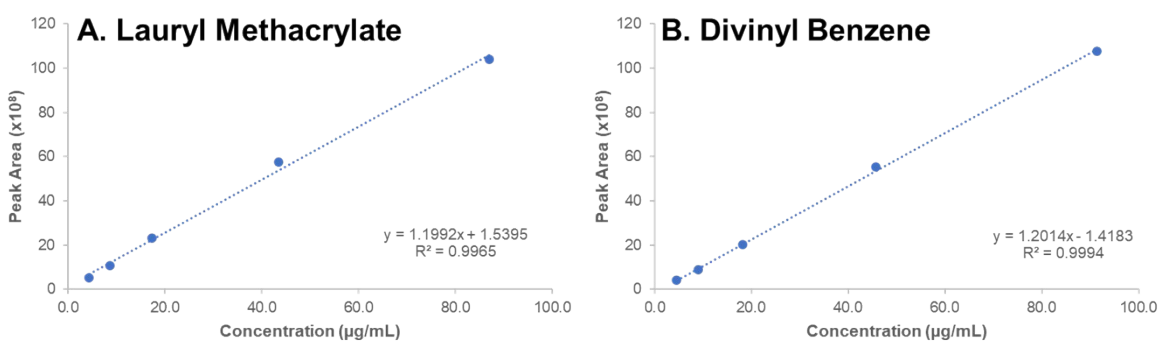


Figure S7. GC-MS calibration data for (A) lauryl methacrylate and (B) divinyl benzene.

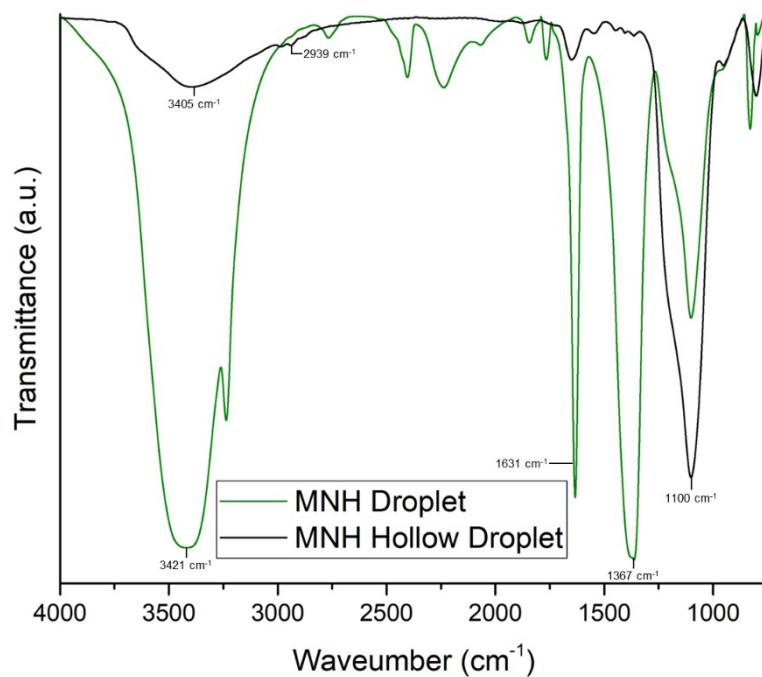


Figure S8. FTIR spectra of pre-polymerization MNH emulsion droplets before (green trace) and after (black trace) core extraction.

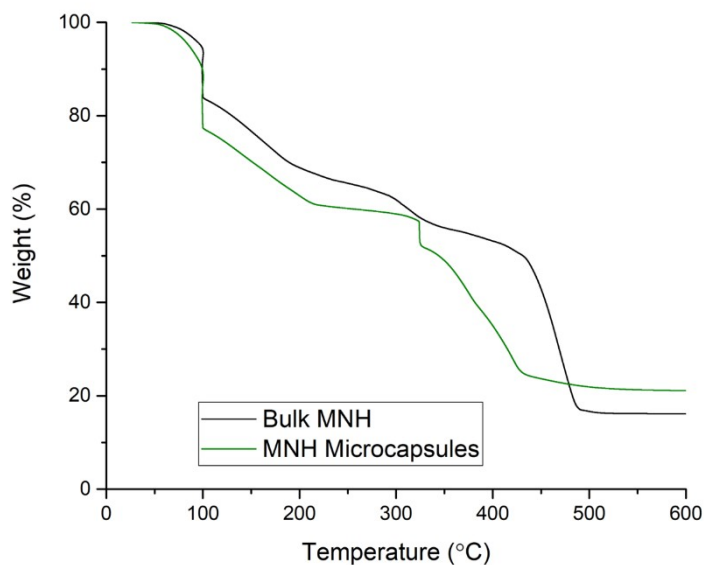


Figure S9. TGA weight loss profiles for bulk MNH (black trace) and MNH microcapsules (green trace).

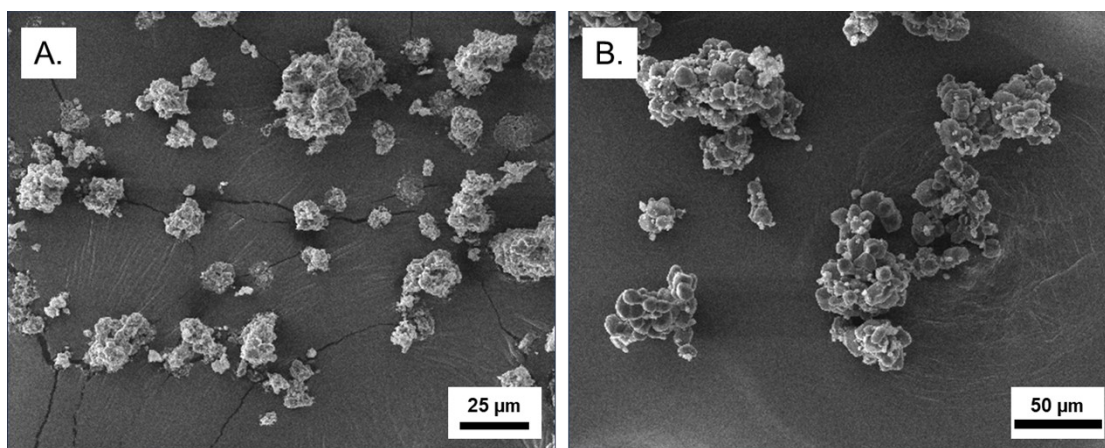


Figure S10. (A) SEM images of (A) ZNH and (B) [EMIM][PF₆] microcapsules.

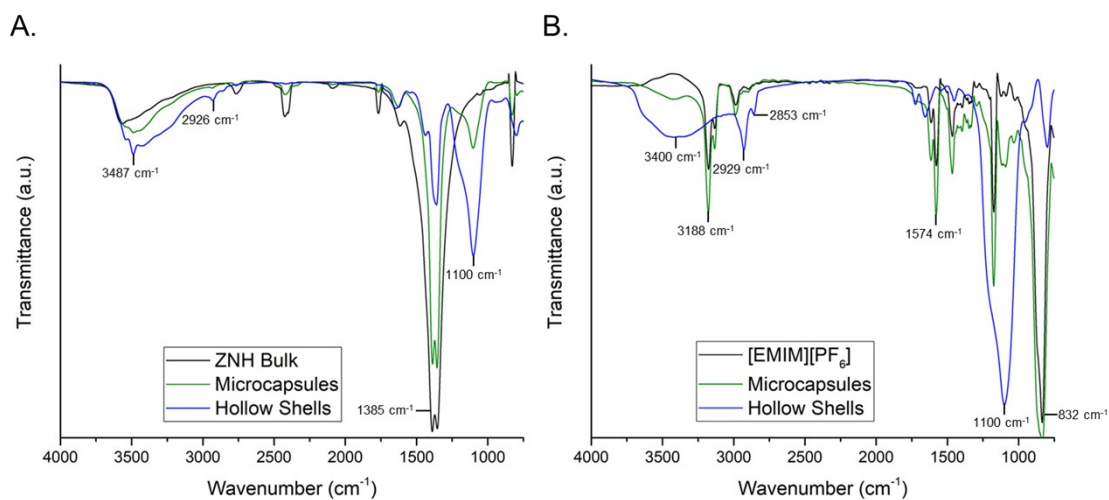


Figure S11. FTIR spectra of (A) bulk ZNH, ZNH microcapsules, and ZNH hollow shells; (B) bulk [EMIM][PF₆], [EMIM][PF₆] microcapsules, and [EMIM][PF₆] hollow shells.

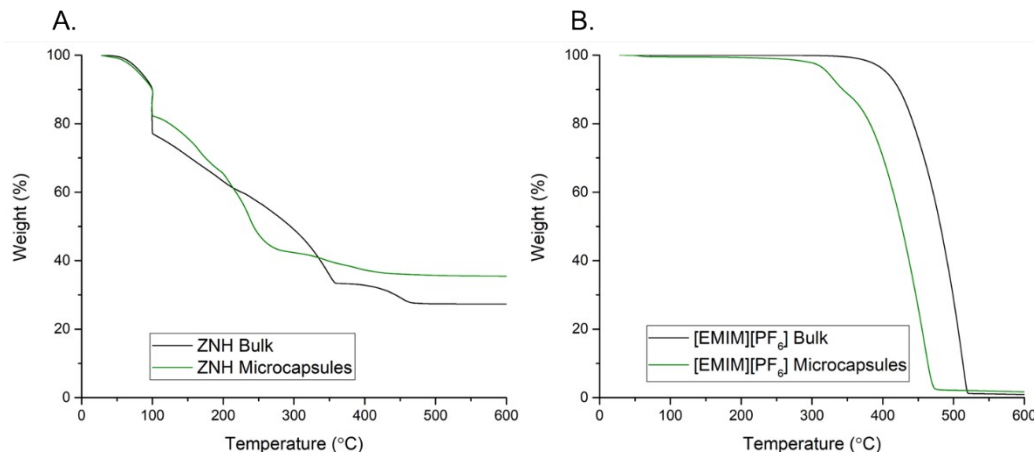


Figure S12. TGA weight loss profiles for (A) bulk ZNH and ZNH microcapsules; (B) bulk [EMIM][PF₆] and [EMIM][PF₆] microcapsules.

Author Contributions

NS and EP conceived the research. NS performed all experiments and prepared the original manuscript draft. CS collected all DSC measurements. ECB completed all UV-vis spectroscopy. All authors reviewed and edited. EP acquired funding for the research.

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