

Supporting Information for:

One-Pot, Single-Component Synthesis of Functional Emulsion-Templated Hybrid Inorganic-Organic Polymer Capsules

Rachel L. Harbron, Tom O. McDonald, Steve P. Rannard, Paul. H. Findlay and Jonathan V. M. Weaver*

Materials

Poly(ethyleneglycol) methacrylate ($M_n = 1,100 \text{ g.mol}^{-1}$, PEGMA), 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA), ethyleneglycol dimethacrylate (EGDMA), 1-dodecanethiol (DDT), anhydrous methanol and triethylamine (TEA) were all purchased from Sigma-Aldrich and used as received. Azobis(isobutyronitrile) (AIBN) was purchased from BDH and recrystallized from methanol prior to use. Ethanol was standard laboratory grade.

Methods

Triple-detection GPC Molecular weights, molecular weight distributions and Mark-Houwink α -values were measured using a Viscotek TDA-302 triple-detection gel permeation chromatography (GPC) equipped with two Viscogel HHR-N columns and a guard column with a mobile phase of THF and triethylamine (2.5 %) at 35 °C and a flow rate of 1 mL.min^{-1} .

NMR Polymer compositions were determined by ^1H NMR and were recorded in CDCl_3 using a Bruker DPX-400 spectrometer operating at 400 MHz.

Laser diffraction Emulsion droplet diameters and diameter distributions were measured using a Malvern Mastersizer 2000 equipped with a Hydro 2000 SM dispersion unit. A drop of emulsion was added to the dispersion unit containing approximately 100 mL water with a stirring rate of 1150 rpm. The volume-average droplet diameters ($D_{4/3}$) quoted are obtained from at least 5 repeat runs ($D_{4/3} = \sum D_i^4 N_i / \sum D_i^3 N_i$). The span is a measure of the distribution of the droplet size distribution and is expressed mathematically as $(D(0.9) - D(0.1)) / D(0.5)$, where $D(0.9)$ is the diameter under which 90 % of the particles fall, $D(0.5)$ is the diameter under which 50% of the particles fall and $D(0.1)$ is the diameter under which 10 % of the particles fall. Following measurements the cell was repeatedly rinsed with water.

Light microscopy A drop of emulsion/cross-linked emulsion/capsule was placed on a glass slide and viewed using a calibrated Meiji Techno MX9000 Series microscope equipped with a Luminera Infinity 1 digital camera. Capsule imaging often required drying prior to visualization in order to ensure sufficient contrast was obtained for these hollow structures.

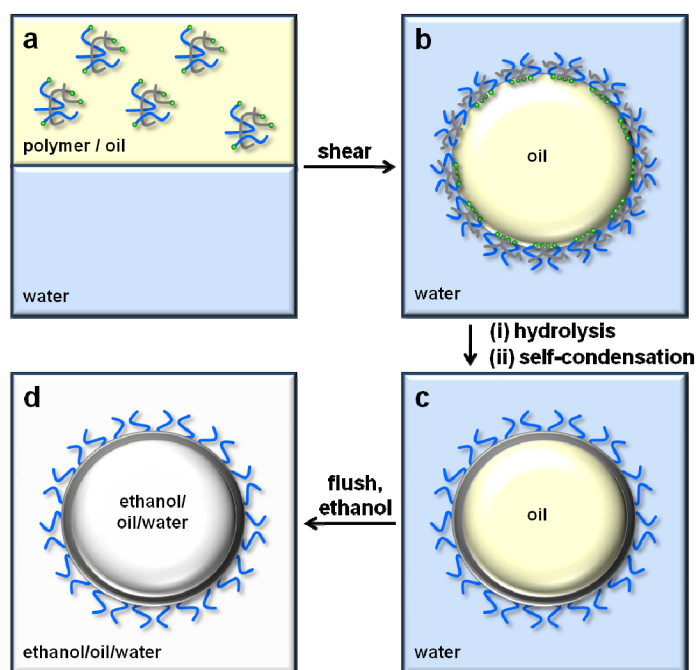
Thermogravimetric Analysis Gravimetric weight loss from capsules and the corresponding branched copolymer (unhydrolyzed) was measured using a TA Instruments TGA Q5000 instrument from 40-1000 °C at a heating ramp of 10 °C per minute.

Scanning electron microscopy The loaded and unloaded capsules were characterised using a Hitachi S-4800 FE-SEM. A 100 µl aliquot of the particle dispersions were pipetted directly onto aluminium SEM stubs and left to dry for 24 hours. The samples were gold coated for 2 minutes at 25 µA using a sputter-coater (EMITECH K550X) prior to imaging.

Confocal microscopy Confocal images of emulsions loaded with DiO (Invitrogen, 0.03 w/v % based on oil) were recorded using Zeiss LSM710 microscope with a Fluar 40x/ 1.30 Oil M27 NA Objective with excitation from the 488 line of an argon ion laser and emission detected between 497 and 540 nm.

TMSPMA₉₅/PEGMA₅-EGDMA₁₀-DDT₁₀ branched copolymer synthesis PEGMA, TMSPMA, branching monomer (EGDMA), dodecane thiol and anhydrous methanol were added to a glass vessel equipped with stirrer bar in pre-determined molar ratios and degassed by nitrogen purge for 30 mins. The solution was heated to 70 °C under an inert atmosphere. Polymerization was started by addition of AIBN and the reaction was left stirring for 48 h. After this time monomer conversions in excess of 97 % were typically achieved and dry methanol was removed by evaporation at reduced pressure. No purification steps were required due to almost complete conversion. The resulting materials were stored under nitrogen and then characterized.

Emulsion, cross-linked emulsion, capsule and loaded capsule fabrication Emulsions were prepared by homogenization of polymer surfactant-in-cineole solutions (0.5 %) with an equal volume of water using an IKA Ultra-Turrax T25 homogenizer at 24,000 rpm for 2 mins. Emulsions were left for at least 20 minutes to equilibrate before characterization. The emulsion was gently cleaned by multiple centrifugation and redispersions. Cross-linked emulsion formation was triggered by the addition of triethylamine to a diluted emulsion solution whilst stirring. Excavated, hollow cross-linked capsules were formed by flushing the cross-linked emulsions with ethanol to remove the internal and continuous phases. Dye-loaded emulsions, cross-linked emulsions and capsules were formed using an identical procedure however a fluorescent dye (DiO) was dissolved in oil (0.03w/v%) before homogenisation. Poly(vinyl stearate) was dissolved in oil (0.5w/v%, 2w/v%, 10w/v%, 30w/v%) before homogenisation and the usual procedure was then followed.



Scheme S1. Schematic representation of the one-pot, single-component fabrication of encapsulated emulsion droplets and hollow capsules. **(a)** biphasic mixture of the branched copolymer dissolved in cineole which was homogenized to give, **(b)** branched copolymer-

stabilized oil-in-water emulsion which hydrolyzed and self-condensed on addition of base to give, (c) encapsulated inorganic-organic hybrid polymeric sheath which can be flushed to give, (d) hollow capsules with PEG surface functionality.

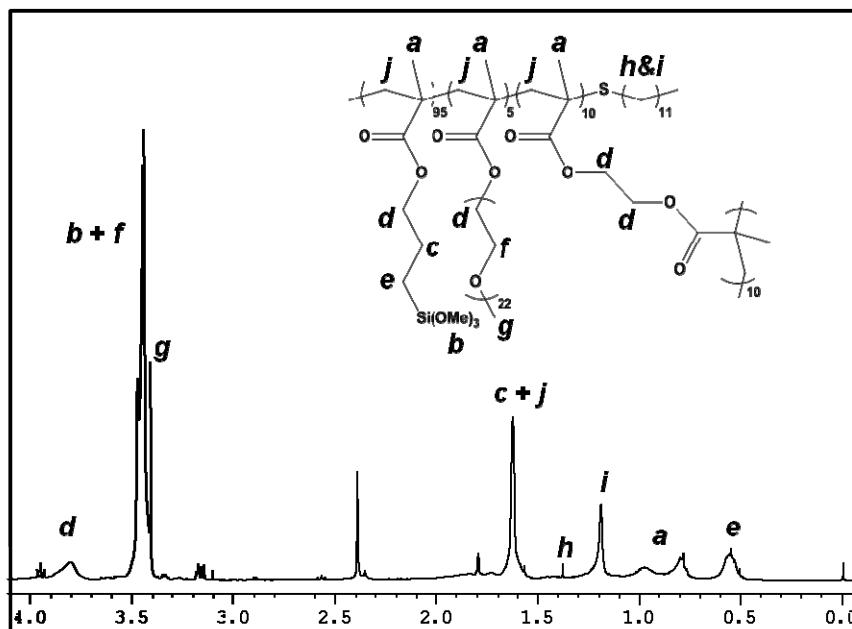


Figure S1. ^1H NMR spectra of TMSPMA₉₄/PEGMA₆-EGDMA₈-DDT₁₂ branched copolymer

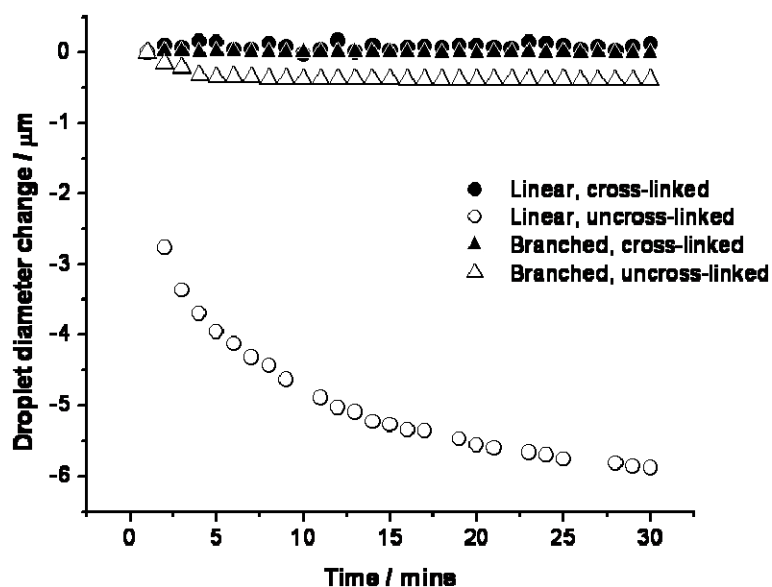


Figure S2. Normalized kinetic experiments monitoring the change in volume-averaged droplet diameters of the branched and linear copolymer stabilized uncross-linked and cross-linked droplets as a function of time.

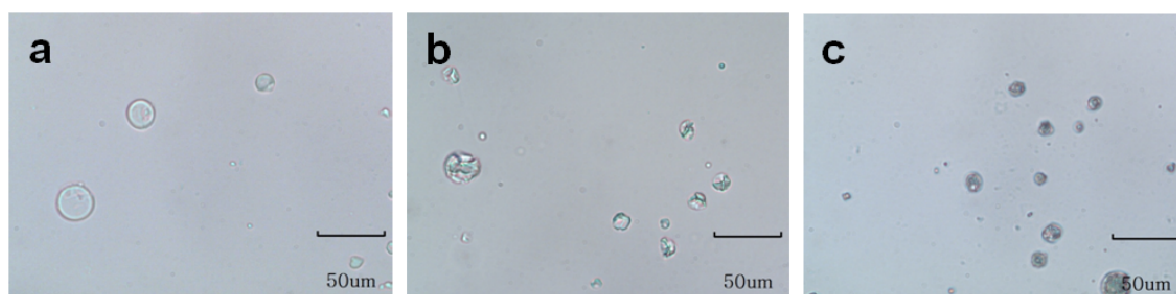


Figure S3. Light micrographs of: **(a)** polymer-loaded (poly(vinyl stearate), 30.0 w/v %) branched copolymer-stabilized emulsion droplets, **(b)** polymer-loaded branched copolymer stabilized cross-linked droplets following base-catalyzed self-condensation of (a) and, **(c)** polymer-loaded branched copolymer-stabilized capsules following flushing of (b) with ethanol.

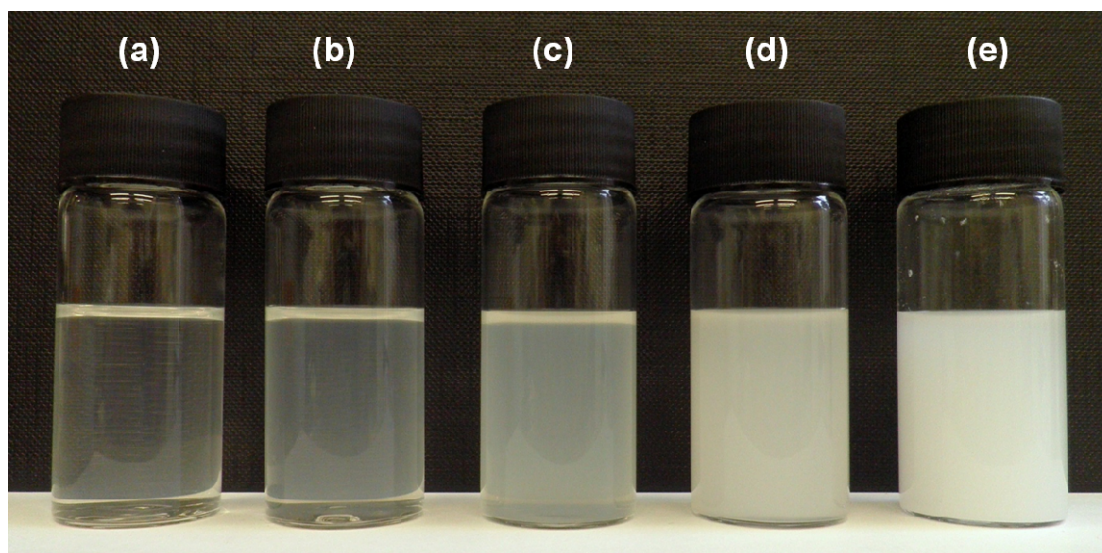


Figure S4. Digital images of the branched copolymer cross-linked capsules following flushing at different poly(vinyl stearate) loadings. (i) 0 w/v % (unloaded), (ii) 0.5 w/v %, (iii) 2.0 w/v %, (iv) 10.0 w/v % and (v) 30.0 w/v %. Loadings based on oil volume and images are recorded at identical concentrations.

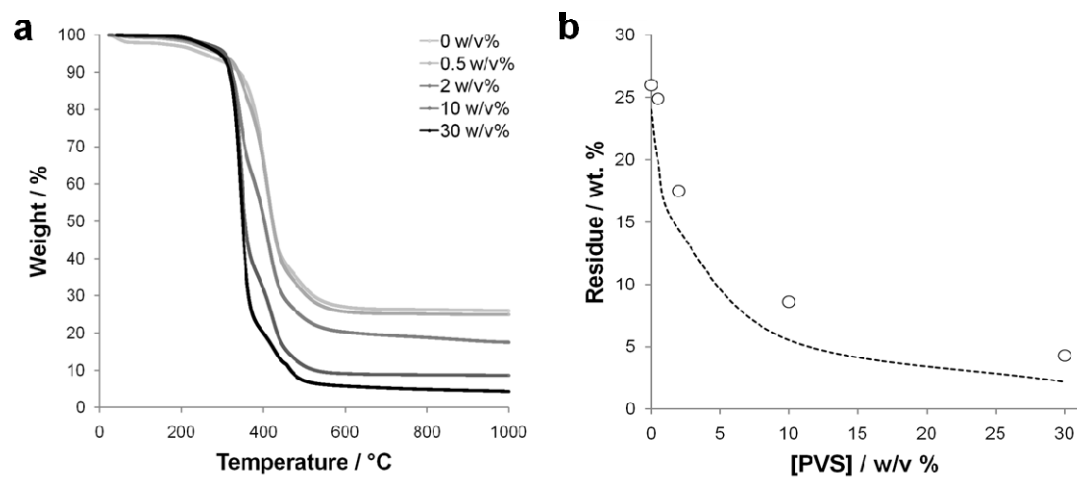


Figure S5. (a) Gravimetric weight loss curves for the capsules and loaded capsules. **(b)** Graph to show the residual inorganic component of the capsules as a function of the degree of poly(vinyl stearate) loading following thermal treatment. Broken line represents theoretical weight loss.