

Electronic Supplementary Information (ESI)

Fabrication of Calcium Phosphate Microcapsules using Emulsion Droplets Stabilized with Branched Copolymers as Templates

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1. Characterization of Branched Copolymer (BCP)

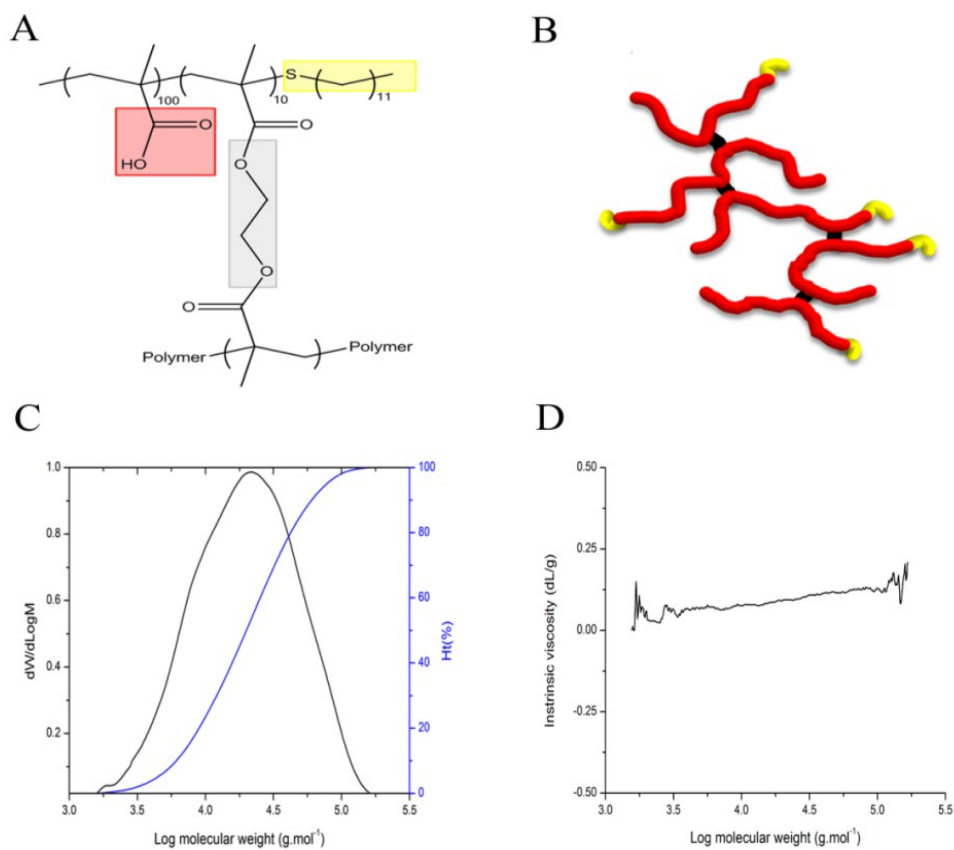


Fig. S1 (A) Chemical structure of the BCP. (B) Schematic illustration of the BCP architecture. The red colour represents the main domain of the BCP, MAA, the black colour represents the branching unit, EGDMA, and the yellow colour represents the hydrophobic chain ends, DDT. The TD-GPC chromatograms of the BCP: (C) molecular weight distribution of the BCP, and (D) Mark-Houwink plot of the BCP.

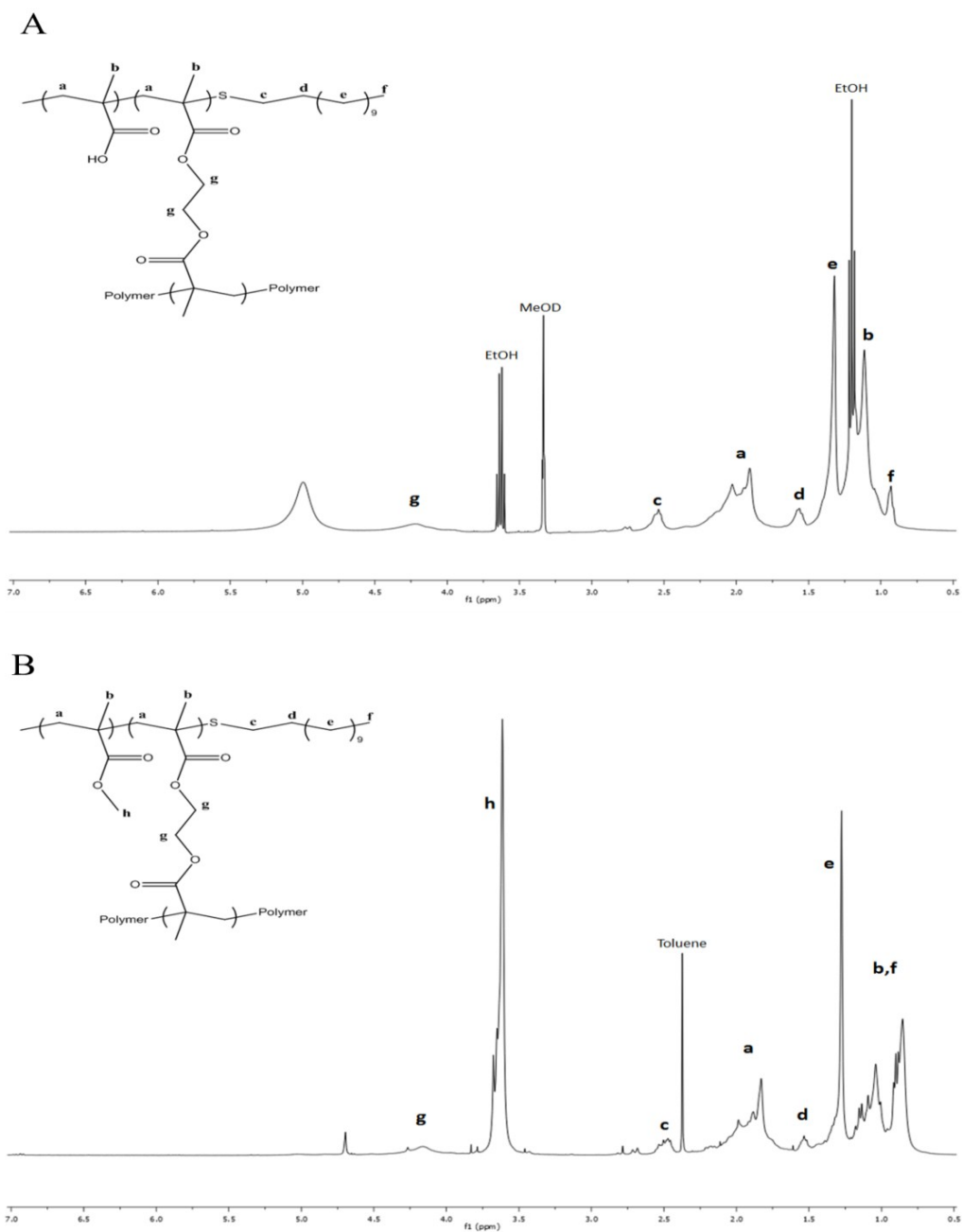


Fig. S2 ^1H NMR spectra of (A) BCP in CD_3OD , and (B) esterified BCP in CDCl_3 .

Table S1 Composition and molecular parameters of the BCP

Target polymer composition ^a	Actual polymer composition ^b	Conversion (%) ^c	M_n ($\text{g}\cdot\text{mol}^{-1}$) ^d	M_w ($\text{g}\cdot\text{mol}^{-1}$) ^d	\bar{D}^d	α^d
MAA ₁₀₀ -EGDMA ₁₀ -DDT ₁₀	MAA ₁₀₀ -EGDMA _{8.7} -DDT _{9.2}	97	13246	27600	2.08	0.23

^a Target molar equivalent based on monofunctional monomer nominally set to 100. ^b Polymer composition was calculated from ^1H NMR spectrum of the esterified BCP. ^c Polymer conversion was calculated by ^1H NMR. ^d Measured by triple-detection GPC in DMF eluent.

2. Potentiometric Titration of BCP

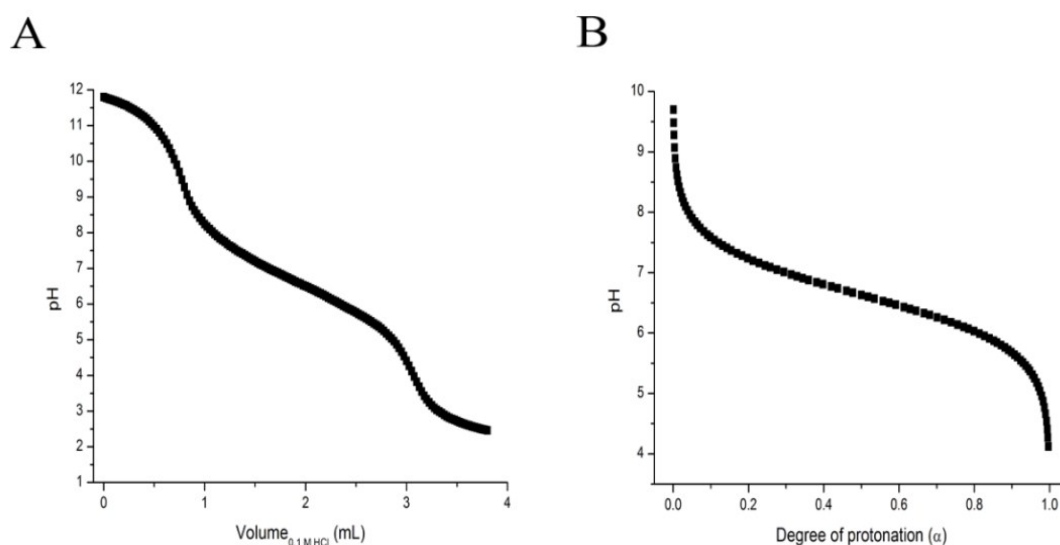


Fig. S3 (A) Acid-base titration curve obtained for BCP, and (B) degree of protonation of BCP with pH.

The degree of protonation (α) of BCP with pH was calculated from the Henderson-Hasselbalch equation. From the acid-based titration curve of the BCP (Fig. S3A), it was found that BCP buffered the solution in the pH range of 10 – 3.5. The titration curve indicated a significant buffering effect of the BCP around pH 6. The overall degree of protonation (α) of the MAA domain in BCP increased from zero to unity as the solution pH decreased from 9.70 to 4.12 (Fig. S3B). It was determined that the pK_a of BCP was 6.63.

3. Emulsion Characterization

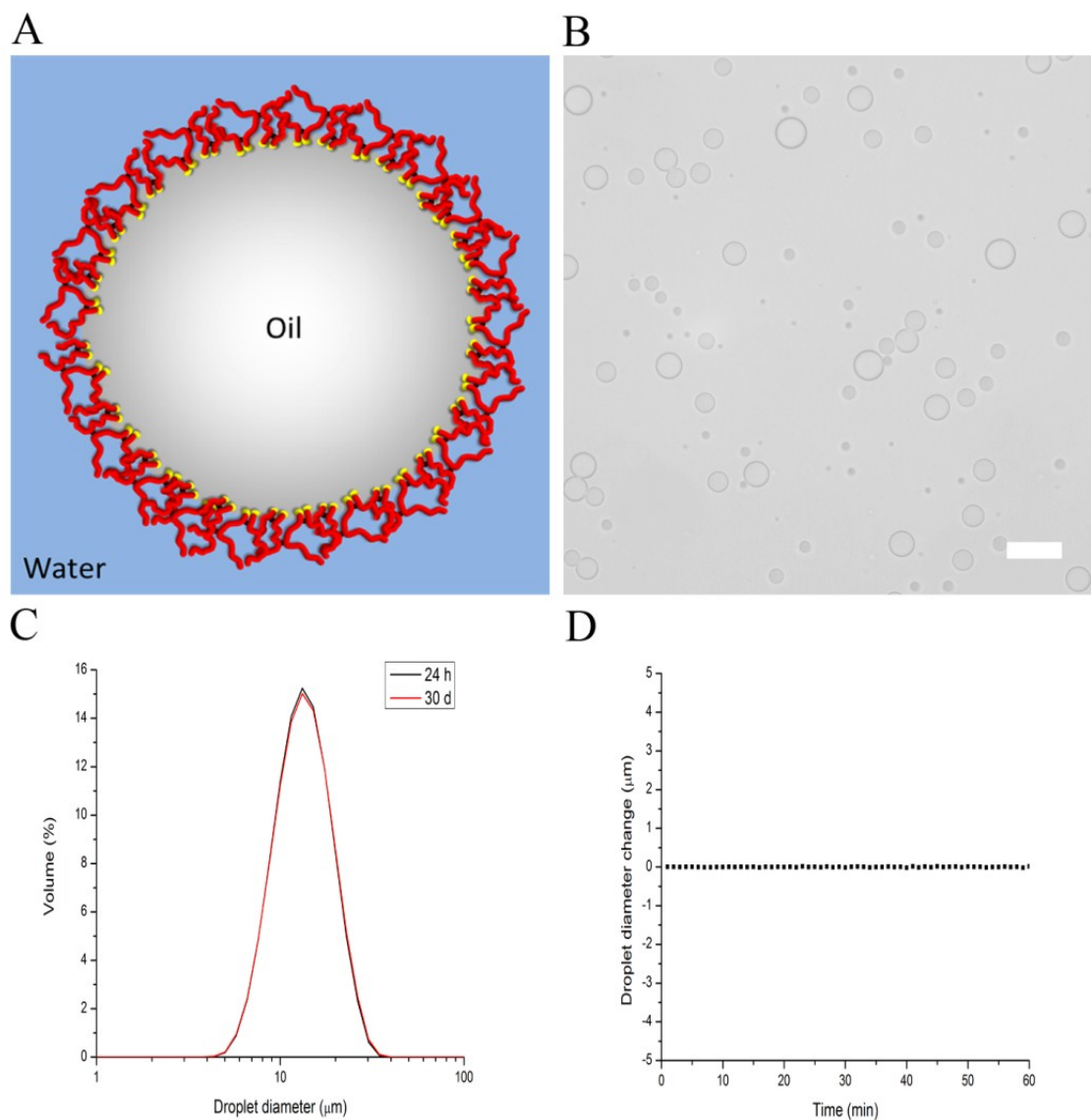


Fig. S4 (A) Schematic representation of an oil/water emulsion droplet stabilised with BCP. The multiple hydrophobic chain ends of BCP, DDT (yellow), anchors at the oil phase, and the MAA domain (red) located at the aqueous phase provides electrostatic stabilisation. (B) Light micrograph of oil in water emulsion droplets stabilized with BCP. Scale bar represents 20 μm . Laser diffraction chromatograms of (C) droplet size distribution at 24 h and 30 days at pH 10, and (D) droplet size diameter change over time at pH 10.

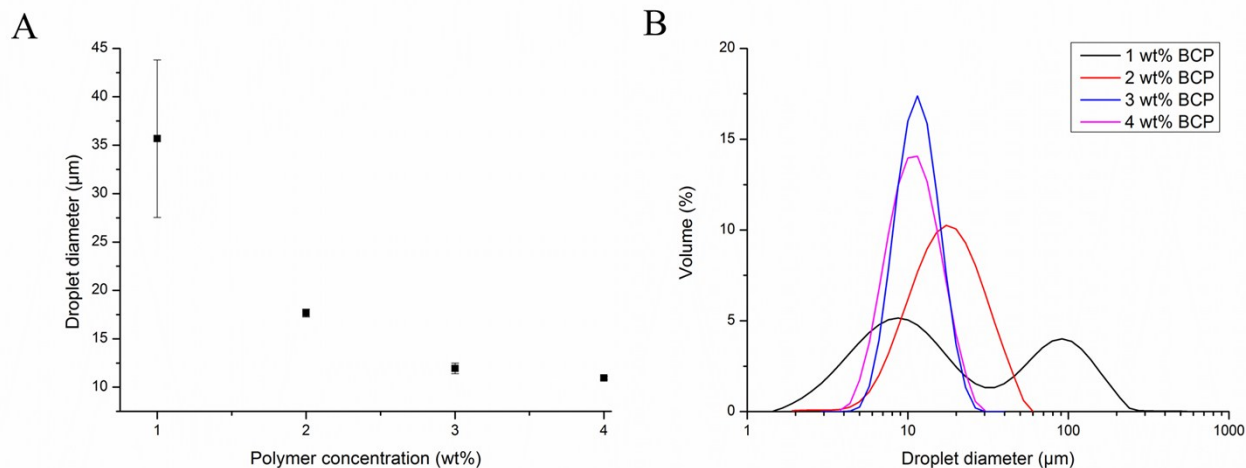


Fig. S5 Laser diffraction chromatograms of emulsion droplets homogenized at 24 000 rpm with varying BCP concentration. (A) Droplet size diameter with varying BCP concentration at pH 10, and (B) droplet size distribution with varying BCP concentration at pH 10.

4. Characterization of Calcium Phosphate (CaP) Capsules

4.1. FTIR

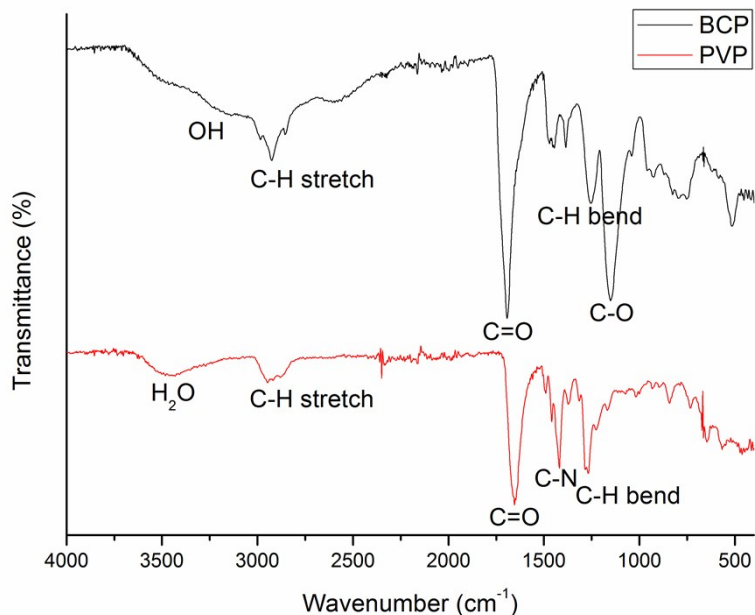


Fig. S6 FTIR spectra of BCP and PVP.

4.2. ICP-OES

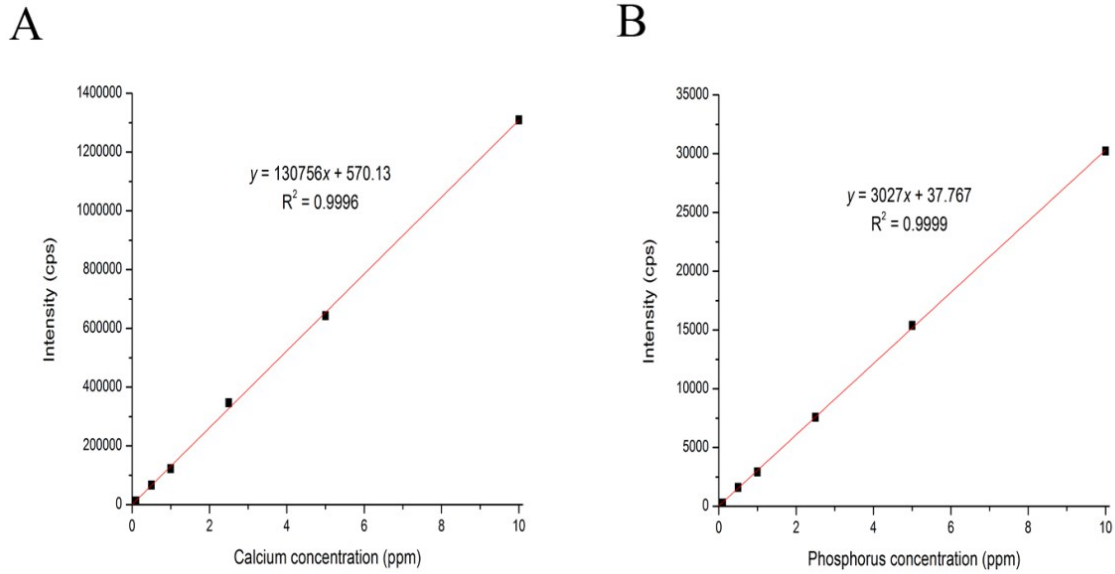


Fig. S7 Calibration standards for (A) calcium and (B) phosphorus.

Table S2 ICP-OES data for CaP capsules and synthetic hydroxyapatite.

Sample	Calcium concentration (ppm)	Phosphorus concentration (ppm)	Ca/P molar ratio
CaP capsules	9.028 (± 0.026)	4.417 (± 0.030)	1.58
Synthetic hydroxyapatite	9.398 (± 0.036)	4.338 (± 0.010)	1.67

4.3. TGA

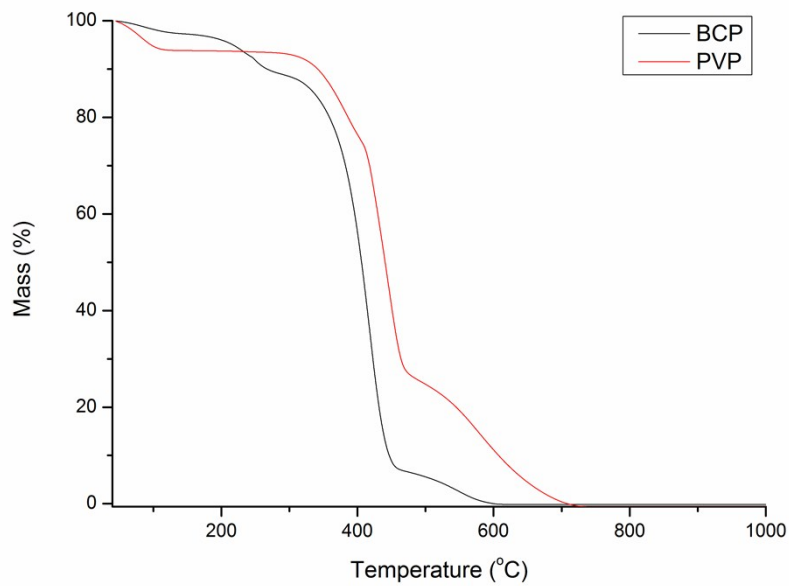


Fig. S8 TG curves of BCP and PVP.

4.4. XRD

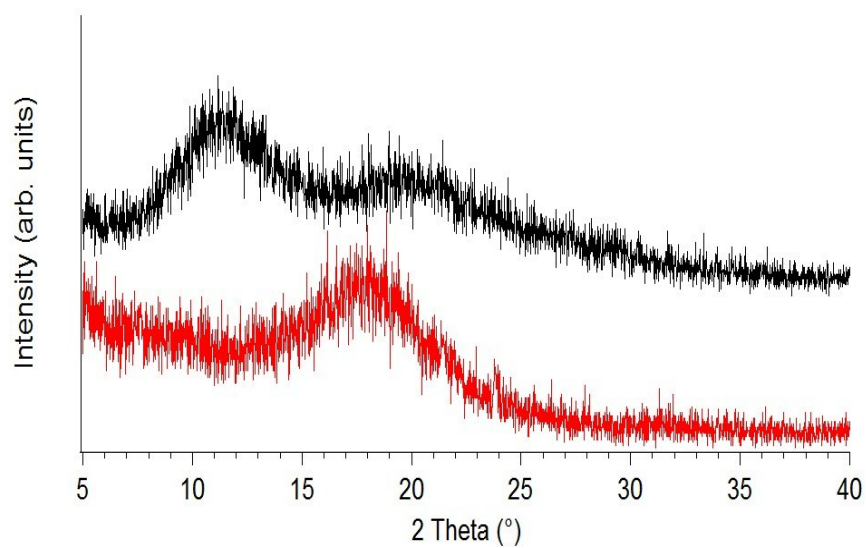


Fig. S9 XRD patterns of PVP (black line), and BCP (red line).

5. Fluorescent Capsules

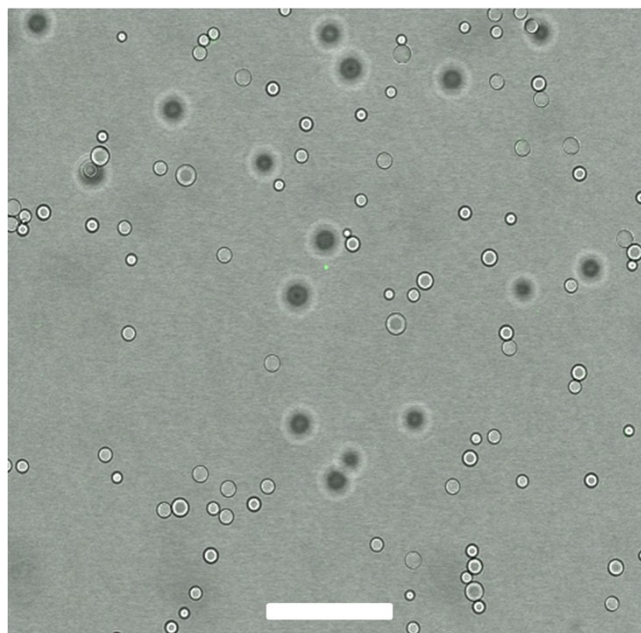


Fig. S10 An overlay confocal micrograph of dodecane droplets stabilized with BCP with Fluo-BP. Scale bar represents 50 μm .