

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Doubly crosslinked microgel-colloidosomes: a versatile method for pH-responsive capsule **assembly using microgels as macro-crosslinkers**

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EXPERIMENTAL DETAILS

MATERIALS:

Ethyl acetate (EA, 99%), methyl methacrylate (MMA, 99%), methacrylic acid (MAA, 99%), glycidyl methacrylate (GMA, 97%), 1-4 butaendiol diacrylate (1,4-BDDA, 90%), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator, 98%) and ethyleneglycol dimethacrylate (EGDMA, 98%) were purchased from Sigma-Aldrich and used as received. All water was of ultrahigh purity and was distilled and de-ionised.

The microgels used in this study were (poly(EA-co-MAA-co-1,4-BDDA)-GMA) and (poly(MMA-co-MAA-co-EGDMA)-GMA) which are abbreviated as MG1 and MG2, respectively. MG1 and MG2 microgels were prepared by reaction of the parent non-GMA containing microgels with GMA using methods previously described^{1, 2}. The characterisation data for MG1 and MG2 are discussed in the text and are also shown in Table S1.

DX MG-colloidosome preparation

Whilst a common approach was used to prepare the DX MG-colloidosomes we investigated variations involving initiator and microgel type as described below **and are summarised in Table S2.**

Preparation of MG1-stabilised emulsions using high photoinitiator concentration

The following preparation method was used for assembling the DX MG-colloidosomes containing MG1 unless otherwise stated. Photoinitiator (10.0 mg, 0.045 mmole) was dissolved in ethyl acetate (1.0 ml). An aqueous phase (4.0 ml) was prepared that contained buffer (pH = 6.8) and MG1 dispersion (0.63 wt.%). The photoinitiator / ethyl acetate solution (10 mg / ml) was added to the aqueous phase and sheared at 10,500 rpm for 120 s to give a microgel-stabilised emulsion using a Silverson L4R high shear mixer equipped with a micromixing head.

Preparation of MG1-stabilised emulsions using low photoinitiator concentration

Photoinitiator (2.0 mg, 0.0089 mmol) was dissolved in ethyl acetate (2.0 ml). An aqueous phase (4.3 ml) without buffer was prepared that contained MG1 dispersion (0.35 wt.%). The photoinitiator / ethyl acetate solution (1 mg / ml) was added to the aqueous phase and sheared at 9,500 rpm for 30 s as described above.

Preparation of MG2-stabilised emulsions

Photoinitiator (6.0 mg, 0.027 mmol) was dissolved in ethyl acetate (2.0 ml). An aqueous phase (4.1 ml) was prepared that contained buffer (pH = 6.8) and MG2 dispersion (0.53 wt.%). The photoinitiator / ethyl acetate solution (3 mg / ml) was added to the aqueous phase and sheared at 10,500 rpm for 120 s as described above.

Preparation of doubly crosslinked microgel colloidosomes

The emulsions were placed in a petri dish (diameter ~ 5.0 cm) which was sealed with parafilm and the sample was UV-irradiated for 10 min at 254 nm using a UV Crosslinker (Ultra-violet Products

LtD). Ethyl acetate was subsequently removed by rotary evaporation at room temperature to give a dispersion of DX MG-colloidosomes.

PHYSICAL MEASUREMENTS:

Potentiometric titration was conducted using a Mettler Toledo DL15 Titrator. Titration was performed in the presence of NaCl (0.1 M) and the titrant was NaOH (1.0 M). Dynamic light scattering (DLS) measurements were conducted using a 50 mW He/Ne laser operated at 633 nm with a standard avalanche photodiode (APD) and 90° detection optics connected to a Malvern Zetasizer Nano ZS90 autocorrelator. Optical microscopy was conducted with an Olympus BX41 microscope using white transmitted light. SEM images were obtained using a Philips FEGSEM XL30 instrument. The microgel dispersions or colloidosomes were diluted in water and dried at room temperature. The SEM samples were coated by carbon prior to examination. Confocal laser scanning microscopy (CLSM) images were obtained using a Leica TCS SP5 broadband confocal instrument. The colloidosomes were labelled using Rhodamine B. TEM measurements were obtained using a Philips CM20 200 kV instrument. The holey carbon grids were dipped into colloidosome dispersions and then allowed to dry at room temperature.

SUPPLEMENTARY FIGURES

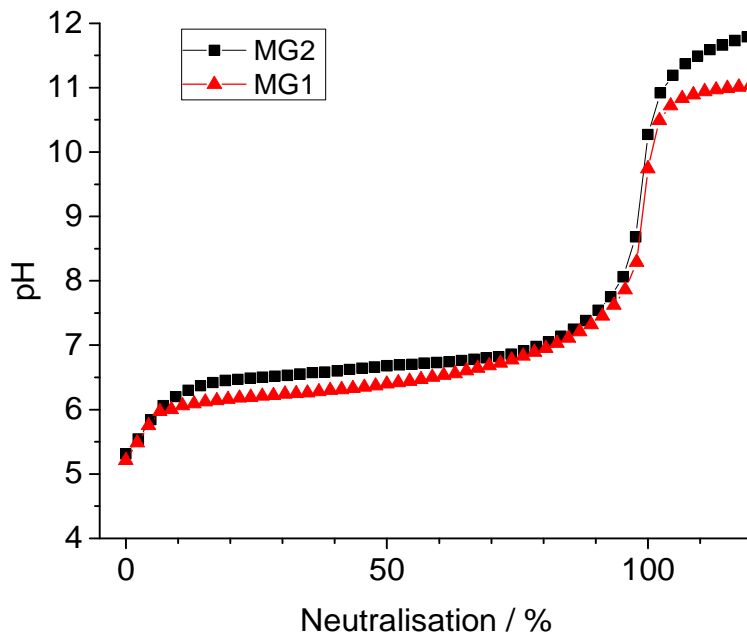


Fig. S1 Potentiometric titration data for MG1 and MG2 particles. MG1 and MG2 represent poly(EA-*co*-MAA-*co*-1,4-BDDA) and poly(MMA-*co*-MAA-*co*-EGDMA)-GMA microgels, respectively.

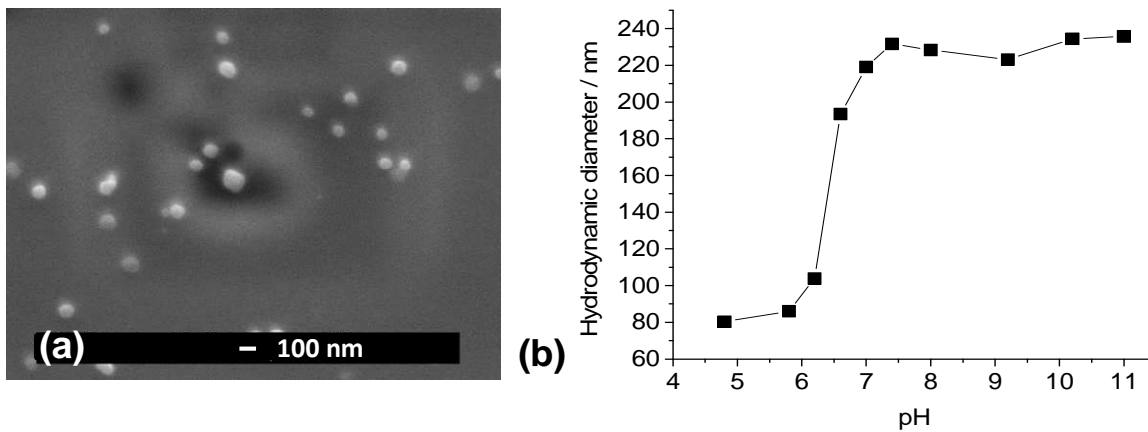


Fig. S2. SEM and DLS data for MG1 particles. (a) shows a representative SEM image and (b) shows the variation of the hydrodynamic diameter with pH.

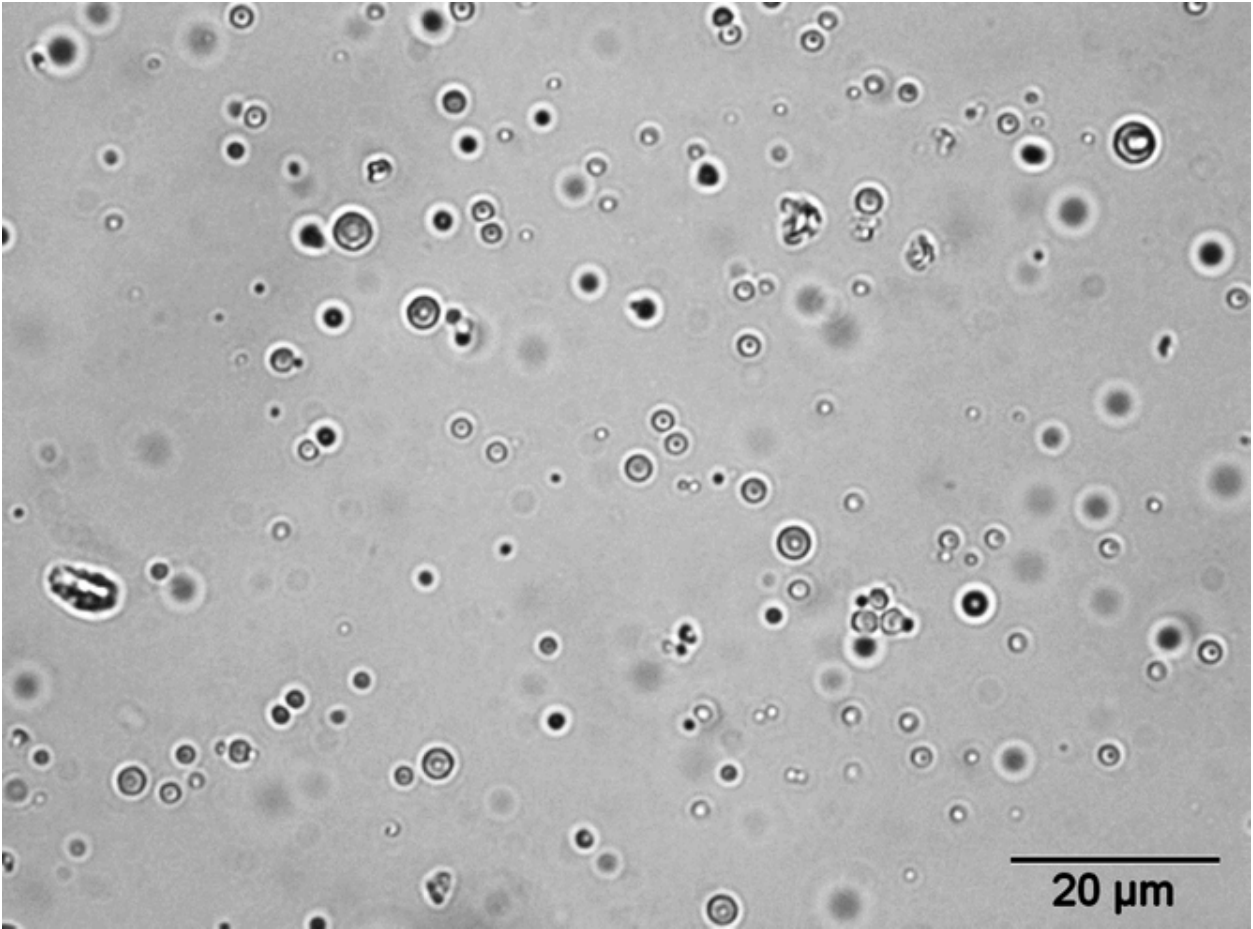


Fig. S3 Optical micrograph of DX MG colloidosomes at pH = 6.4. MG1 particles were used for this experiment.

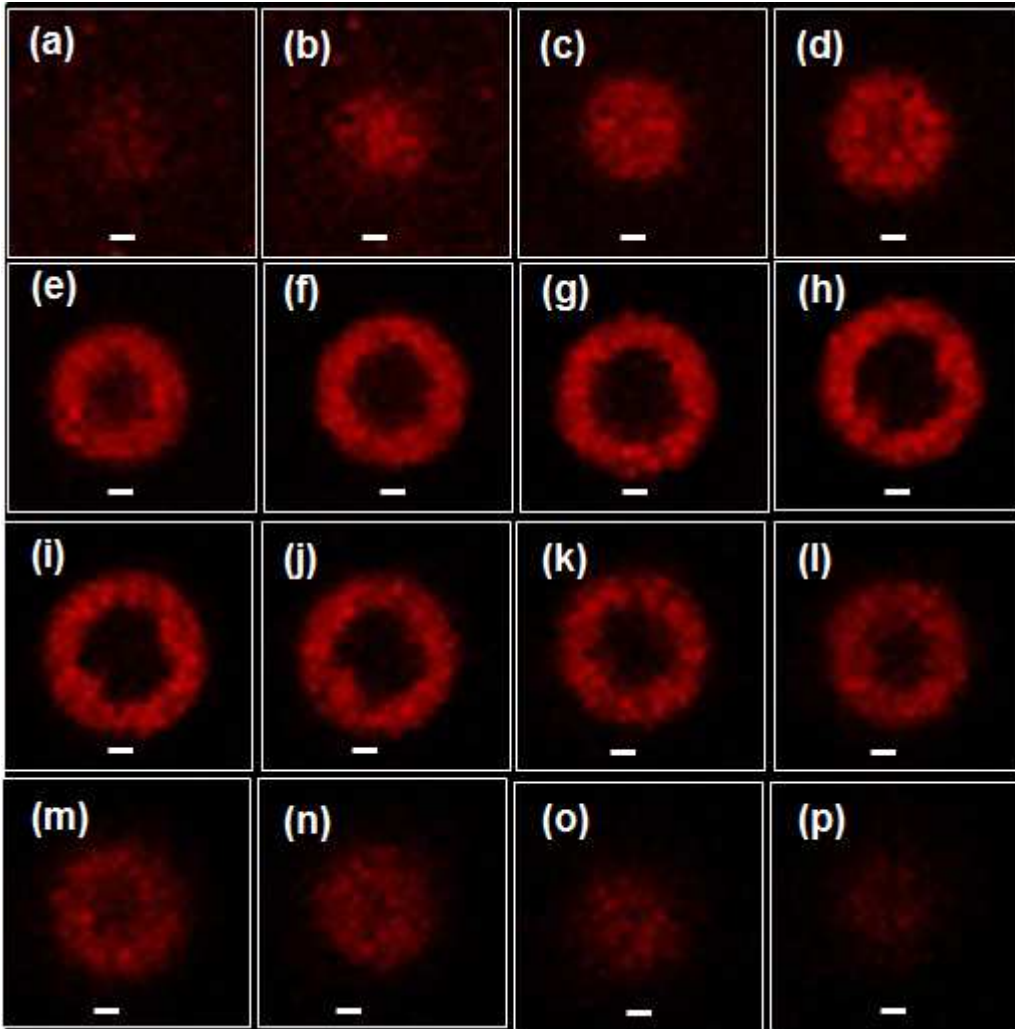


Fig. S4. Sequential z-scanning CLSM images obtained for a DX MG-colloidosome . The top surface is shown in (a) and the image plane moves to the bottom of the colloidosome from (a) to (p). The scale bars are 1 μm . The pH during these experiments was 7.4. MG1 particles were used.

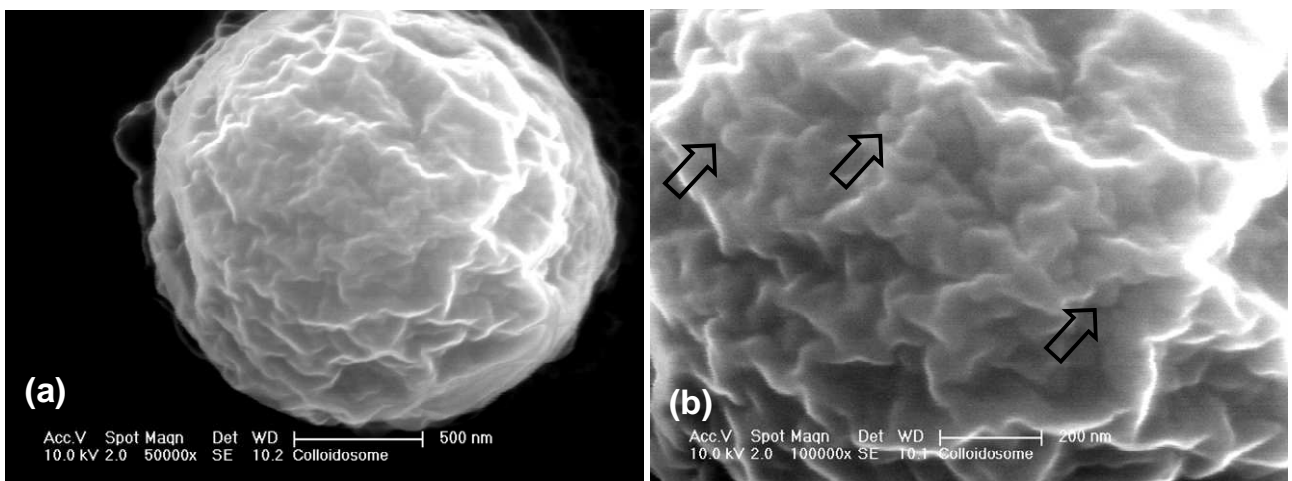


Fig. S5 SEM images of a DX MG-colloidosome particle. (a) Lower magnification image shows a collapsed shell and the higher magnification image (b) shows microgel particles comprised the surface. MG1 particles were used. The arrows identify microgel particles.

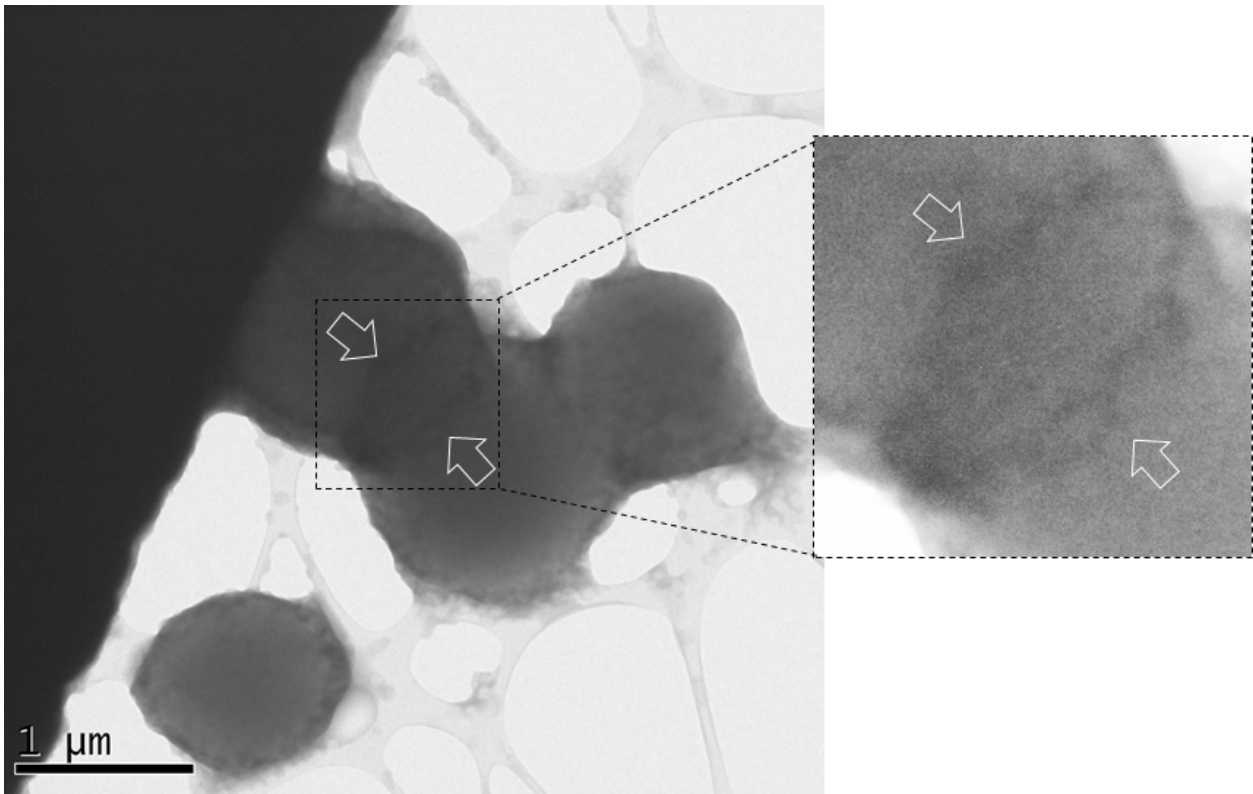


Fig. S6. TEM images of DX MG-colloidosomes. The arrows (and inset) show a window formed by contact between two hollow particles. MG1 particles were used.

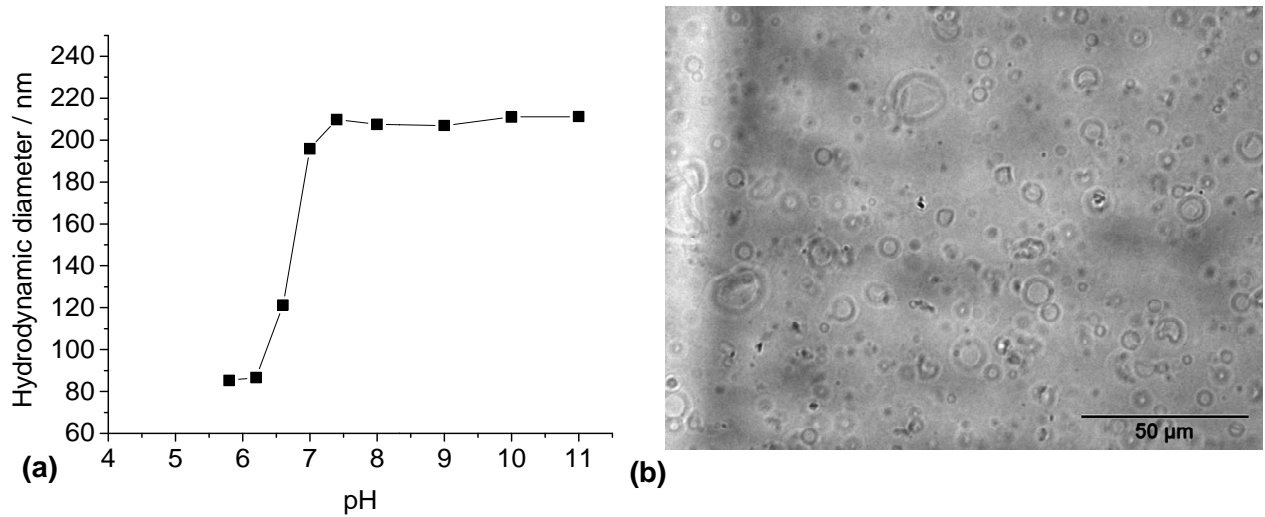


Fig. S7. pH-triggered swelling of MG2 particles. (a) Variation of the hydrodynamic diameter for MG2 particles with pH. (b) Images of DX MG-colloidosomes at pH = 12. These colloidosomes were prepared using MG2.

Table S1. Compositions of the microgels synthesised for this study^a.

Code	Composition	mol.% EA or MMA	mol.% MAA ^a	mol.% GMA	pK_a
MG1	Poly(EA- <i>co</i> -MAA- <i>co</i> -1,4-BDDA)-GMA	59.8	31.0	8.7	6.4
MG2	Poly(MMA- <i>co</i> -MAA- <i>co</i> -EGDMA)-GMA	63.1	27.3	9.1	6.7

^a Determined from potentiometric titration data. Each microgel contained ~ 0.5 mol.% crosslinker.

Table S2. Conditions used to prepare the DX MG colloidosomes^a.

Code	Initiator concentration ^b	m_{init} ^c / mg	V_{Ethyl} ^d / ml	V_{aq} ^e / ml	m_{MG} ^f / mg	ϕ_{Ethyl} ^g	$MR_{Init/MG}$ ^h
MG1	High	10.0	1.0	4.0	25	0.20	0.40
MG1	Low	2.0	2.0	4.3	15	0.32	0.15
MG2	High	6.0	2.0	4.1	22	0.33	0.30

^a Data taken from the experimental details given above. ^b High and low represent DX MGs prepared using high and low photoinitiator concentrations, respectively. ^c Photoinitiator mass. ^d Volume of ethyl acetate. ^e Volume of aqueous phase. ^f Mass of MG used. ^g Volume fraction of ethyl acetate. ^h Mass ratio of MG to photoinitiator used.

References

1. Z. Cui, A. H. Milani, P. J. Greensmith, J. Yan, D. J. Adlam, J. A. Hoyland, I. A. Kinloch, A. J. Freemont, and B. R. Saunders. *Langmuir* 2014, **30**, 13384-13393.
2. R. Liu, A. H. Milani, T. J. Freemont, and B. R. Saunders. *Soft Matter* 2011, **7**, 4696-4704.