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Reversible surface functionalisation of emulsion-templated porous polymers using dithiophenol maleimide functional macromolecules

A. M. Eissa,[a,b,c*] P. Wilson,[d] C. Chen,[a] J. Collins,[d] M. Walker,[e] D. M. Haddleton[d] and N. R. Cameron[a,b]

Instruments and analysis

^{1}H and ^{13}C NMR spectra were recorded on Bruker HD-300 and HD-400 spectrometers and referenced relative to deuterated solvent shifts using deuterated solvents obtained from Aldrich.

Size exclusion chromatography (SEC) measurements were conducted using an Agilent 390-LC MDS fitted with differential refractive index (DRI), light scattering (LS) and viscometry (VS) detectors equipped with 2 x PLgel 5 mm mixed-D columns (300 x 7.5 mm), 1 x PLgel 5 mm guard column (50 x 7.5 mm) and autosampler. All samples were passed through 0.2 μmnylon filter before analysis. The mobile phase was DMF containing 5 mM NH_4BF_4 with a flow rate of 1 ml min^{-1} at 50 °C. SEC data was analysed using Agilent Technologies SEC Software. Calibration curves were produced using Agilent Easi-Vials linear poly(methyl methacrylate) standards (200 – 4.7 x 10^{5}g mol^{-1}). Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell.

PolyHIPE morphology was investigated using a Philips/FEI XL30 ESEM operating at 25 kV. Fractured polyHIPE pieces were sputter-coated with gold using a Bio-Rad E5400 sputter coating system and mounted on carbon fibre pads adhered to aluminium stubs. Average void diameters were then calculated using Image J Version 1.50i. One hundred voids were randomly chosen from an SEM image of the sample and the diameters measured. Void diameters measured in this way underestimate the true value as the voids are unlikely to be exactly bisected. Therefore a statistical correction factor was used to account for this underestimate[1].

The x-ray photoelectron spectroscopy (XPS) data were collected at the Warwick Photoemission Facility, University of Warwick, more details of which are available at (http://go.warwick.ac.uk/XPS). The samples investigated in this study were attached to electrically-conductive carbon tape, mounted on to stainless steel sample plates and loaded in to an Omicron multiprobe spectrometer which possesses a base pressure of ~ 2 x 10^{-11} mbar.

XPS measurements were performed in the main analysis chamber, with the sample being illuminated using a XM1000 monochromated Al k_α x-ray source (hv = 1486.7 eV). Due to the insulating nature of the samples, a CN10 charge neutraliser was used to flood the surface with a beam of low energy electrons which prevented the surface from becoming positively charged during the experiment. The data were subsequently charge corrected using the C-C/C-H peak at 284.6 eV as a reference. The measurements were conducted at room temperature and at a take-off angle of 90° with respect to the surface parallel. The core level spectra were recorded using a SPHERA analyser at a pass energy of 10 eV (resolution approx. 0.47 eV), from an analysis area 1.1 mm in diameter. The spectrometer work function and binding energy scale were calibrated using the Fermi edge and $3d_{5/2}$ peak recorded from a polycrystalline Ag sample prior to the commencement of the experiments. The data were analysed in the CasaXPS package, using Shirley backgrounds and mixed Gaussian-Lorentzian (Voigt) lineshape. For compositional analysis, the analyser transmission function has been determined using clean metallic foils to determine the detection efficiency across the full binding energy range. This approach yields experimental errors of ± 0.1 eV and ± 2.0 atomic % in the binding energies and compositions respectively.

Both survey and core level XPS spectra were recorded from a surface area of 300 x 700 µm, with such a large area deemed to be representative of the whole sample surface

Materials

Poly(ethylene glycol) methyl ether and *N*-isopropylacrylamide were purchased from Sigma-Aldrich. Water used as reaction solvent was HPLC grade. α-Methoxy ω-aminopoly(ethylene glycol) was purchased from Rapp Polymere and stored at – 18 °C. Dithiophenolmaleimide was prepared according to literature precedence.[2] Dithiophenolmaleimide functional poly(poly[ethylene glycol] methyl ether acrylate) (DTM-pPEGA$_{100}$) was prepared during a previous investigation.[3] Copper (I) bromide (CuBr, 98%, Sigma-Aldrich) was purified according to the method of Keller.[4] Tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN)[5] was synthesized according to literature procedure and stored at -10 °C prior to use. Membrane dialysis tubing (1K MWCO) was obtained from Spectrum Laboratories and allowed to rest in water for 20 minutes before use.

All other reagents and solvents used in the polyHIPE synthesis were obtained at the highest purity available from Sigma-Aldrich and used without further purification apart from the surfactant Hypermer B246 (a block copolymer of polyhydroxystearic acid and polyethylene glycol), which was obtained from Croda International.

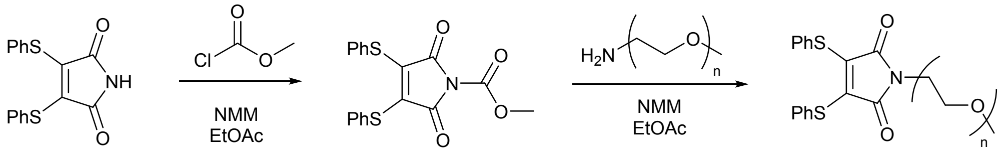
PolyHIPE preparation

In a 250 mL two-necked round-bottomed flask, an oil phase consisting of monomers (trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) (4.84 g) and dipentaerythritol penta/hexa-acrylate (DPEHA) (3.47 g), 1,2-dicholorethane (DCE) (7 mL), surfactant Hypermer B246 (0.45 g) and photoinitiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide/2-hydroxy-2-methyl-propiophenone blend (0.78 g) was stirred continuously at ambient temperature using a D-shaped polytetrafluoroethylene (PTFE) paddle attached to an overhead stirrer at 350 rpm. An aqueous phase of deionised water (70 mL) was added drop-wise to the oil phase, with stirring, to form a HIPE with an internal (aqueous) phase volume fraction of 80%. Once all the aqueous phase was added, the HIPE was transferred immediately into a cylindrical PTFE mould (diameter 15 mm, depth 30 mm). The mould was secured between two glass plates and passed under a UV irradiator (Fusion UV Systems Inc. Light Hammer® 6 variable power UV curing system with LC6E benchtop conveyor) ten to fifteen times on each side, at a belt speed of 5.0 m/min., to ensure complete curing. The cured polyHIPE material was washed by immersion in acetone and then soxhlet extraction with dichloromethane for 24 h. The polyHIPE was then dried under reduced pressure at ambient temperature for 24 h.

Determination of residual thiol content using Ellman's reagent

Following a previously described method, the thiol loading of thiol–acrylate polyHIPEs was determined using a colourimetric assay[6]. Briefly: 5–10 mg polyHIPE was frozen in liquid nitrogen and then ground to a powder with a mortar and pestle. The polyHIPE powder was then transferred to a 5 mL volumetric flask containing 1 mL of THF. The polyHIPE was left to swell for 15 minutes. A solution of Ellman's reagent (1 mL, 5 µmol) in ethanol was prepared which was then added to the polyHIPE along with 5 µL of diisopropylethylamine. The flask was then shaken for 1 minute and then diluted to 5 mL with ethanol. The solution was then filtered and the absorbance of the filtrate was measured at 412 nm.

Synthesis of DTM-PEG$_{100}$



Scheme SI-1. Synthesis of DTM-PEG$_{100}$

Adapted from Baker *et al.*[2] Briefly, to a solution of 3,4-dithiophenolmaleimide (2 g, 6.38 mmol) was dissolved in EtOAc (70 ml) and *N*-methylmorpholine (0.70 ml, 6.38 mmol) was added. Methylchloroformate (0.54 ml, 7.02 mmol) was added dropwise and solution stirred for 1 hour. The solution was washed with H_2O (2 x 100 ml) and dried with $MgSO_4$ before the solvent was removed in vacuo yielding a bright orange-yellow powder.

^{1}H NMR ($CDCl_3$, 400.03 MHz) δ (ppm): 7.25-7.35 (10 H, m, SPh), 3.91 (3 H, s, $COCH_3$); ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ (ppm): 161.7 (C=O), 147.7 (C=O), 137.1 (C=C), 132.5 (SPh), 129.1(SPh), 128.9 (SPh), 128.0 (SPh), 54.3 ($COCH_3$).

Without further purification, to the *N*-methoxycarbonyl-3,4-dithiophenolmaleimide (75 mg, 0.2 mmol) in DCM (5 ml) was added amino-PEG$_{100}$ (1.01 g, 0.2 mmol) in DCM (10 ml). After stirring at ambient temperature for 30 minutes silica gel was added and the reaction mixture stirred overnight. The solution was filtered and DTM-PEG$_{100}$ precipitated into hexane: diethyl ether (1:1), resulting in a bright yellow powder.

^{1}H NMR ($CDCl_3$, 300.13 MHz) δ (ppm): 7.10-7.55 (10 H, m, SPh), 3.86 (2 H, t, 5.09 Hz, $CONCH_3$), 3.62 (480 H, s, OCH_2CH_2), 3.36 (3 H, s, OCH_3)

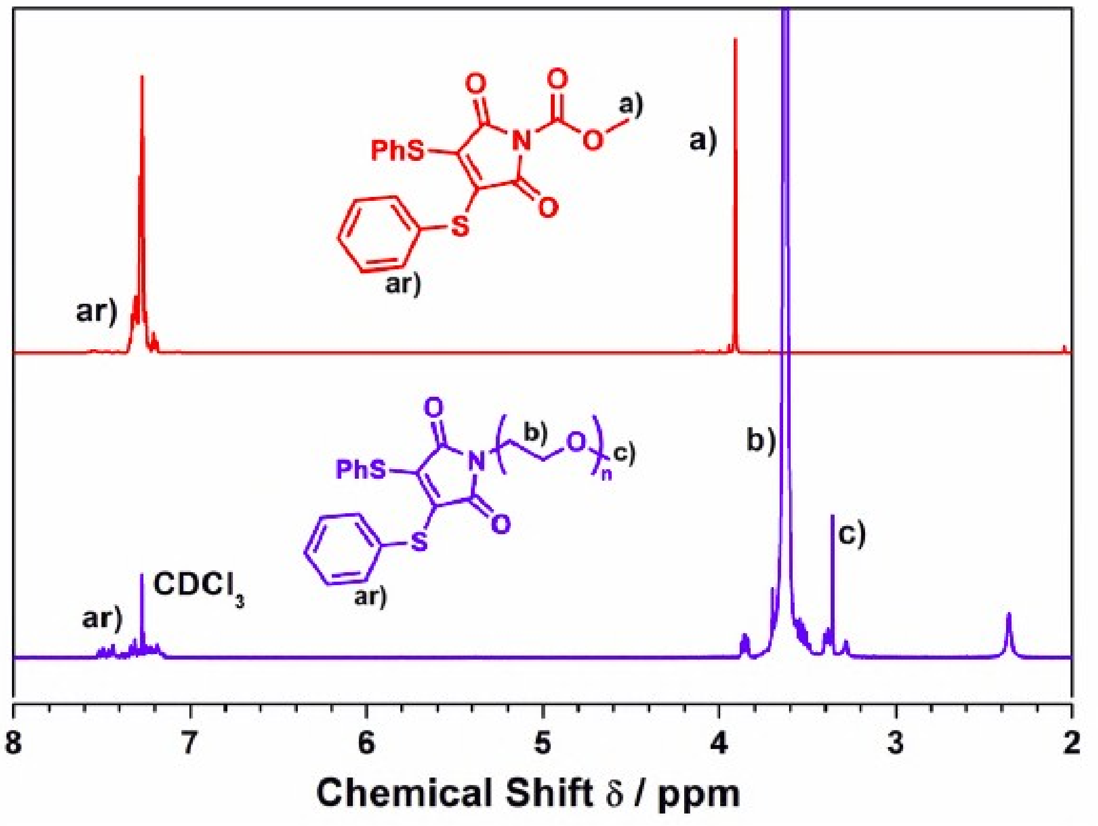
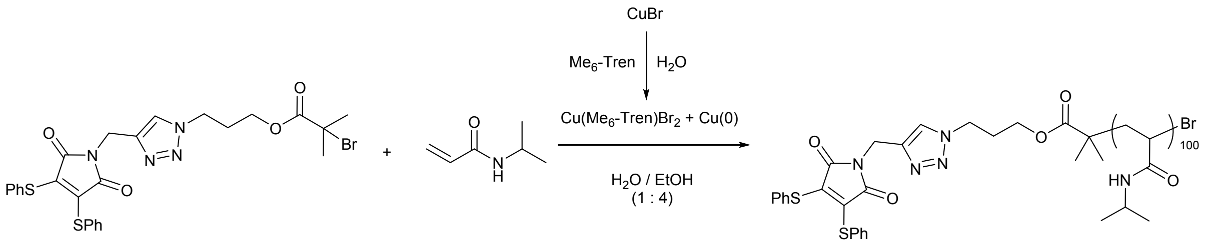


Figure SI-1. 1H NMR spectra of *N*-methoxycarbonyl-3,4-dithiophenolmaleimide (top) and DTM-PEG$_{100}$ (bottom) in $CDCl_3$

Synthesis DTM-pNIPAM$_{100}$



Scheme SI-2. Synthesis of DTM-pNIPAM$_{100}$

Cu(I)Br (3.6 mg, 25 µmol) and Me$_6$TREN (6.6 µl, 25 µmol) were added to H_2O (1 ml) and degassed under nitrogen flow. Separately, to NIPAm (0.704 g, 6.2 mmol) and dithiophenol initiator (37.4 mg, 62 µmol) were added ethanol (6 ml) with H_2O (0.5 ml) and the solution degassed under nitrogen flow. After 20 minutes the two solutions were added together and allowed to polymerise at ambient temperature. After 24 hours samples were removed for ^1H NMR revealed that the reaction had reached 98 % conversion. The crude polymer was purified by dialysis against water (3 days, 1 kDa MWCO) ($M_{n,th}$ = 11300 gmol^{-1}, $M_{n,SEC}$ = 9200, $Đ$ = 1.12).

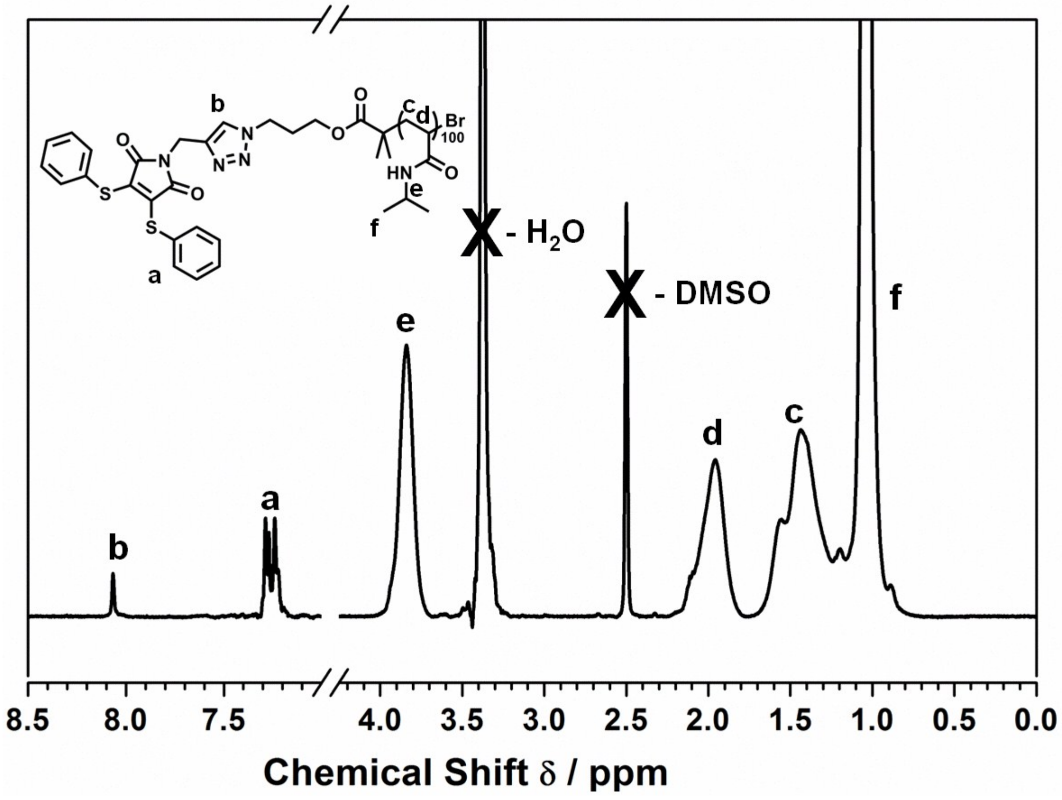


Figure SI-2. ^{1}H NMR spectrum of DTM-pNIPAM$_{100}$ in DMSO-d$_6$

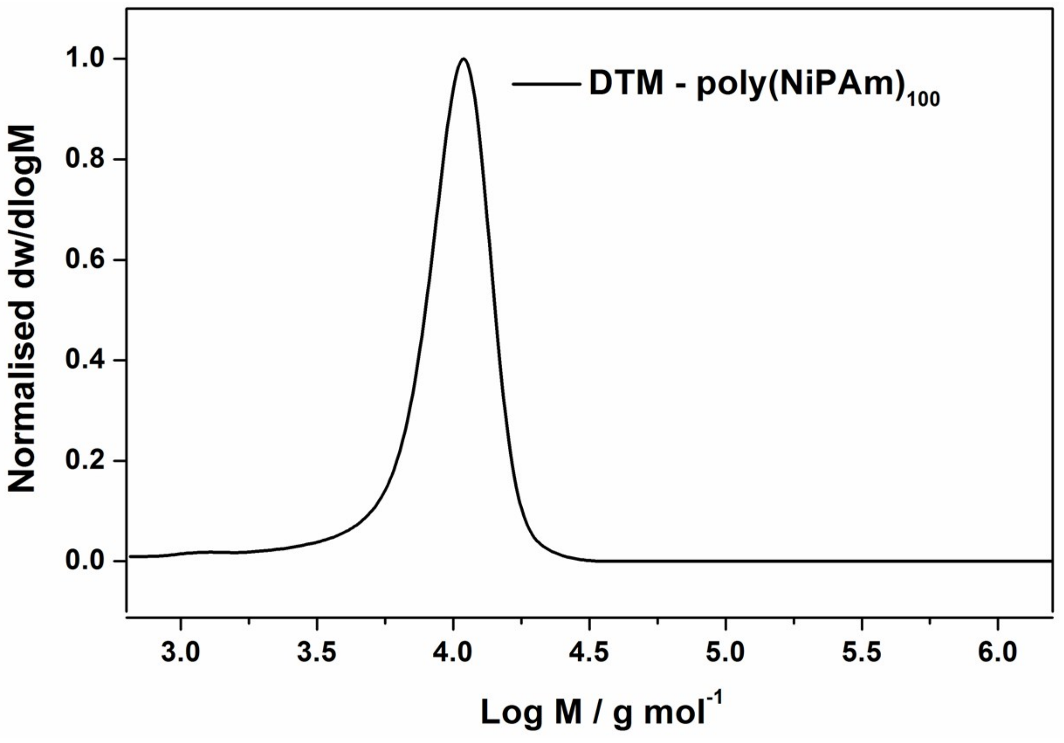


Figure SI-3. DMF GPC of DTM-pNIPAM$_{100}$ (M_n = 9200 g.mol^{-1}, *Đ* = 1.12)

Table SI-1. Residual thiol content on polyHIPE materials obtained by colorimetric assay using Ellman's reagent

PolyHIPE	Residual thiol concentration (mmol g^{-1})
Before functionalisation	0.125
Functionalised with DTM	0.010
Functionalised with DTM-PEG_{100}	0.042
Functionalised with DTM- $pPEGA_{100}$	0.041
Functionalised with DTM-$pNIPAM_{100}$	0.050

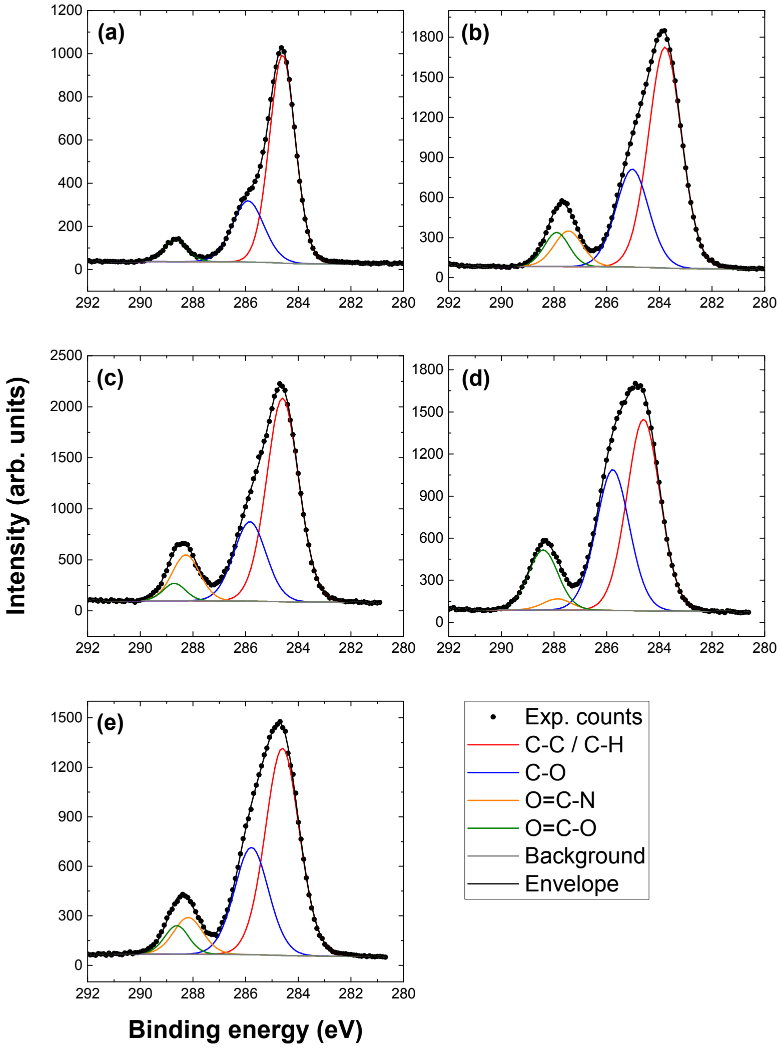


Figure SI-4. High-resolution peak-fitted C 1s spectra for unfunctionalised and functionalised polyHIPE surfaces

Table SI-2. Composition profiles showing peak assignment and percentage of each C 1s component for unfunctionalised and functionalised polyHIPE materials

	Unfunctionalised		DTM-functionalised		pNIPAM$_{100}$-functionalised		pPEGA$_{100}$-functionalised		PEG$_{100}$-functionalised	
Bonding environment	Binding energy	% of C 1s	Binding energy	% of C 1s	Binding energy	% of C 1s	Binding energy	% of C 1s	Binding energy	% of C 1s
C-C/C-H	284.6	68.52	284.6	58.85	284.6	60.81	284.6	48.37	284.6	56.56
C-O	285.9	24.87	285.84	26.12	285.84	23.74	285.77	35.54	285.78	29.27
O=C-N			288.27	8.18	288.27	11.82	287.87	2.44	288.18	8.64
O=C-O	288.63	6.61	288.71	6.84	288.71	3.63	288.41	13.65	288.61	5.53
O=C-N : O=C-O ratio		n/a		1.20		3.26		0.18		1.56

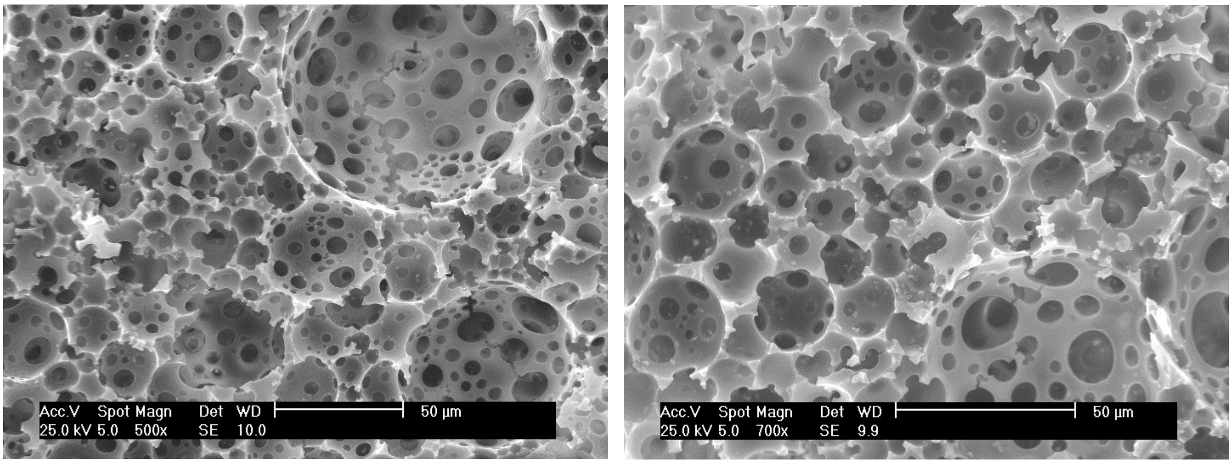


Figure SI-5. SEM images of thiol-acrylate polyHIPE material from different batches, showing reproducibility of morphology

References

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