

1 **Supporting information for**
2 **Morphology control in polymerised high internal phase**
3 **emulsion templated via macro-RAFT agent**
4 **composition: Visualizing surface chemistry**

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37 Typical end-group removal process

38 To investigate this, the RAFT part of the macro-RAFT agents (See Table 1) were
 39 cleaved using a typical protocol with minor modifications. Briefly, a mixture of macro-
 40 RAFT agent Qb-1 (0.2 g, 0.13 mmol), benzoyl peroxide (BPO) (0.5 g, 2.06 mmol), and
 41 toluene (6 g) was placed in a round-bottom flask, sealed, and degassed with argon gas
 42 for 20 minutes. 2-Propanol was degassed with argon gas in a separate sealed round
 43 bottom flask. The 2-propanol (6 g) was removed through a syringe equipped with a long
 44 needle and injected to the mixture. The round-bottom flask containing the mixture was
 45 then heated to 100 °C for 6 h. Completion of butyl-trithiocarbonate RAFT-end group
 46 removal was determined by ¹H-NMR after evaporating the volatile solvents from the
 47 product in a vacuum oven at 40 °C overnight. The ¹H-NMR spectrum of the product
 48 demonstrated the absence of signals associated with the butyl trithiocarbonate end group
 49 at 3.3 ppm (CH₃-(CH₂)₂-CH₂-S-C(S)-S-) and 4.8 ppm (the first chain length of CH
 50 oligomer backbone adjacent to the sulfur). Toluene and 2-propanol were then removed
 51 through rotary evaporation under reduced pressure and all polymers were purified by
 52 precipitation in a cold methanol/water mixture (80/20 v/v %) to remove the unreacted
 53 BPO.

54 **Table S1.** Elemental analysis data

Sample ID	N%	C%	H%	S%
Bulk polymer	0.17	90.76	8.23	0.00
PolyHIPE A1	0.18	80.56	7.79	0.69
PolyHIPE A3	0.09	85.72	8.41	0.00

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56 **Table S2.** RAFT synthesis of P(AA)-qb-P(Sty)

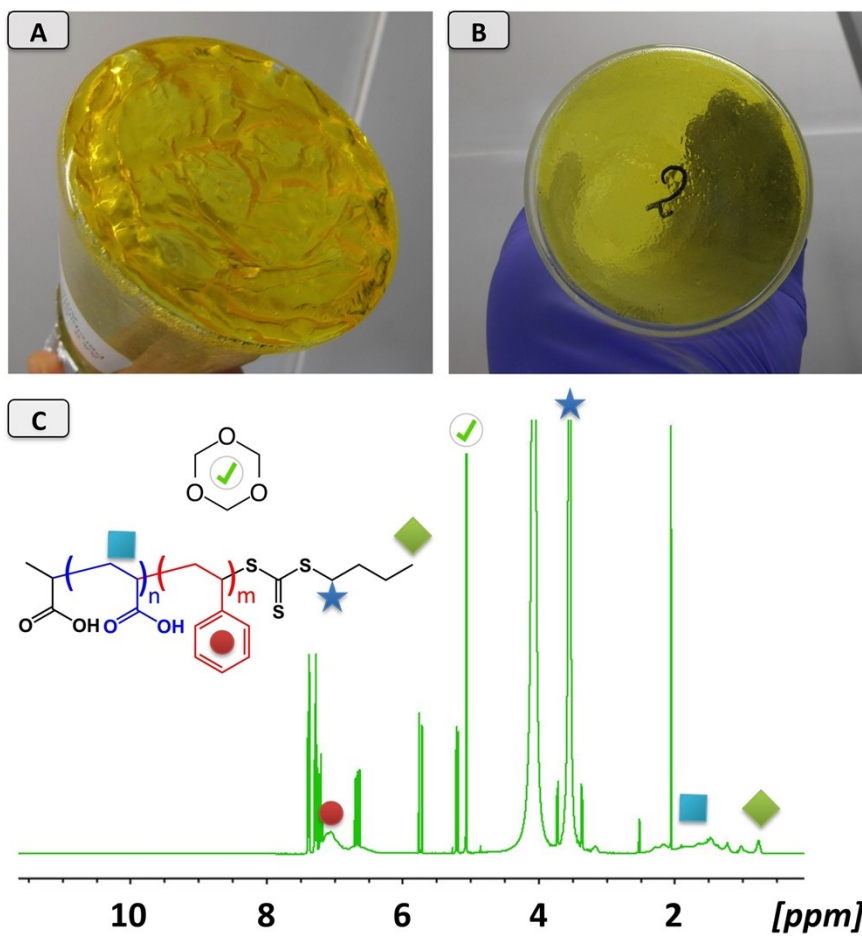
(AA) _x -qb-(Sty) _y	AA/ RAFT (NMR) ^a	[Sty]/ [(AA) _x - CTA	Sty/ RAFT (NMR) ^a	Conversion		M _{n, th} (g mol ⁻¹) ^{b,c}		M _{n, SEC} (g mol ⁻¹) ^e	Đ ^e
				First Step	Second Step	First Step	Second Step		
Qb-1	6	5.9	6.8	98.3	57.3	663.2 ^b	1379.2 ^c	1291	1.19
Qb-2	3	5.8	1.5	98.1	50.0	450.0 ^b	762.9 ^c	1015	1.12
End group removed-Qb-1	6	-	-	98.3	57.3	663.2 ^b	1214.9 ^d	1245	1.19
End group removed-Qb-2	3	-	-	98.1	50.0	450.0 ^b	598.6 ^d	902	1.12

57 ^aDetermined by ¹H NMR in DMSO-d₆ (internal reference, 1,3,5-trioxane). ^{b,c}The M_{n(theory)} was estimated using the
 58 formula: ^bM_{n(theory)} = $\left(\frac{[M]_0}{[RAFT]_0} \times M_{\text{monomer}} \times \text{conversion} (\%) \right) + M_{\text{RAFT}}$ and ^cM_{n(theory)} = $\left(\frac{[M]_0}{[RAFT]_0} \times M_{\text{monomer}} \times \text{conversion} (\%) \right) + M_{n, \text{macro-RAFT}}$; where M_{monomer} and M_{RAFT} are the molar masses of the corresponding monomer
 59 and RAFT agent, respectively, and [M]₀ and [RAFT]₀ are the initial concentrations of the corresponding monomer
 60 and RAFT agent, respectively. ^dM_{n(theory)} = $\left(\frac{[M]_0}{[RAFT]_0} \times M_{\text{monomer}} \times \text{conversion} (\%) \right) + M_{n, \text{macro-RAFT}} - M_{\text{th, RAFT-Z}}$
 61 group + 1 ^eMolecular weight and polydispersity determined by SEC analysis (THF used as eluent). (More details of
 62 procedure are available in the experimental part). Calculated according to PSty standards.

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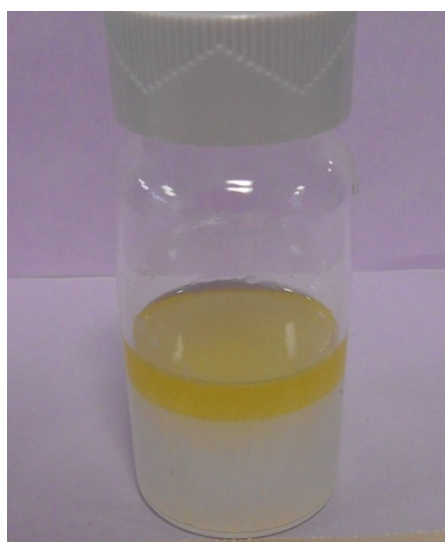
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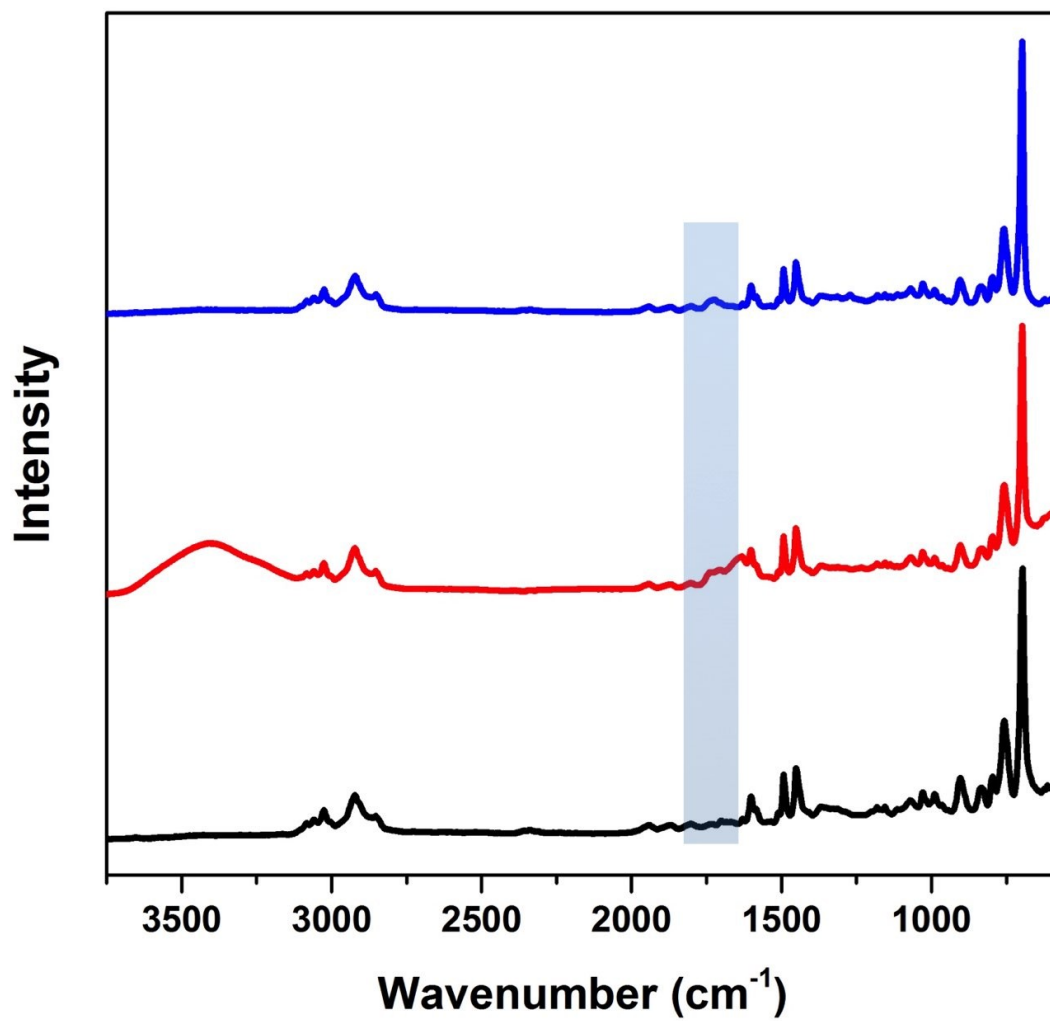


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 68 **Fig. S1** A) Macro-RAFT agent Qb-1 B) Macro-RAFT agent Qb-2. C) ¹H NMR spectra of
 69 macro-RAFT agent Qb-1 (DMSO-d₆).

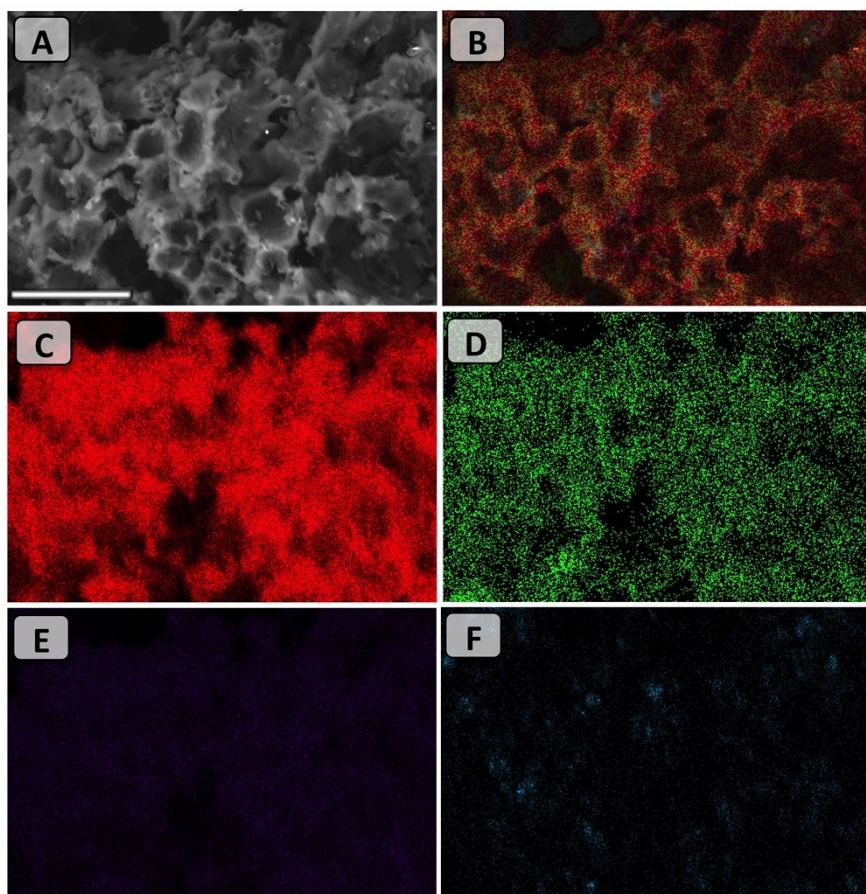
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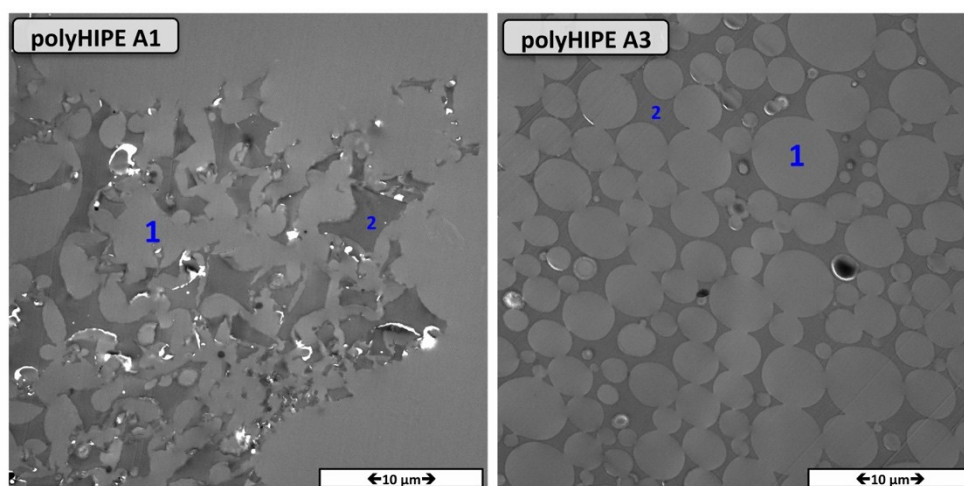
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 74 **Fig. S2** Phase separation after preparation of HIPE A4 formulation.



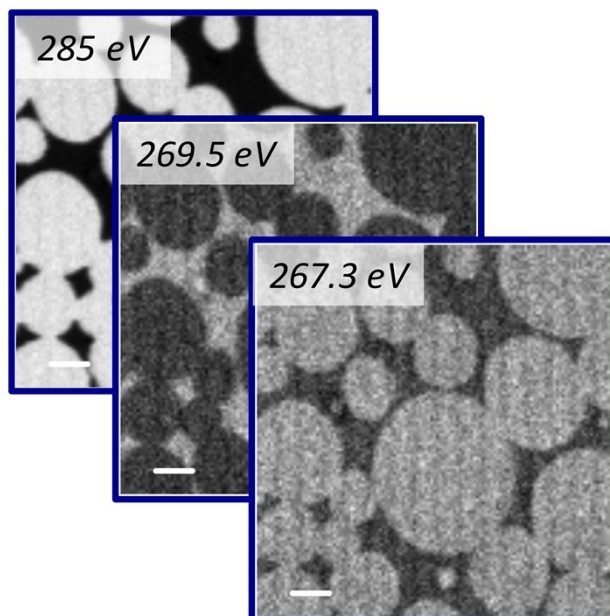
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76 **Fig. S3** ATR-IR of bulk polymer (black line), polyHIPE A1 (red line), and polyHIPE A3 (blue line) (from bottom
77 to top). The peak around 1650- 1850 cm⁻¹ is highlighted.
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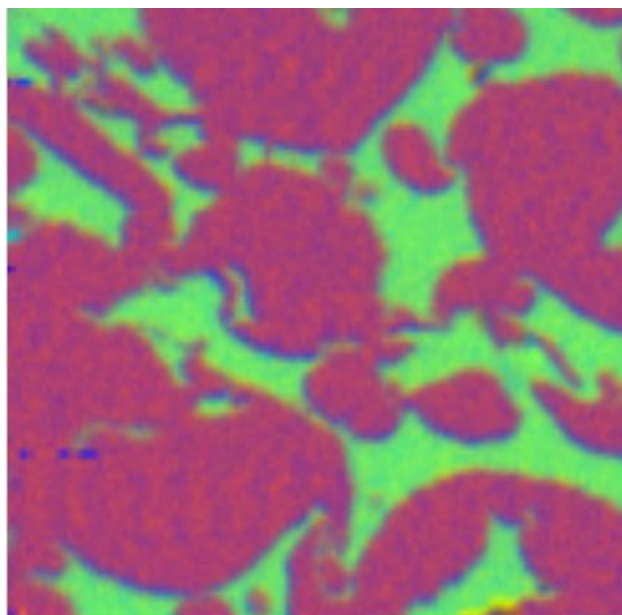
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 81 **Fig. S4** EDX mapping analysis on polyHIPE A1; (A) SEM image and (B) Overall mapping elements on the
 82 same spot: corresponding to carbon (C), oxygen (D), calcium (E), and chloride (F) mapping. Scale bar is 10
 83 μm .
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 86 **Fig. S5** TEM images of polyHIPEs: (a) polyHIPE A1 and (b) polyHIPE A3 embedded in epoxy. The zones are:
 87 the epoxy embedding materials (1), the cross-linked polystyrene-DVB (2). The scale bar is 10 μm .
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92 **Fig. S6** STXM optical density (OD) images at different energies 280-320 eV (More than 80 images have
93 been collected. Three images with strong chemical contrasts were selected. The scale bar is 1 μm .
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96 **Fig. S7** STXM color coded composite map of polyHIPE A1 (red=epoxy, green=PSty, blue=macro-RAFT agent)
97 (10 μm \times 10 μm).
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