

Supporting information for
Preparation of inverse polymerized high internal phase
emulsions using an amphiphilic macro-RAFT agent as
sole stabilizer

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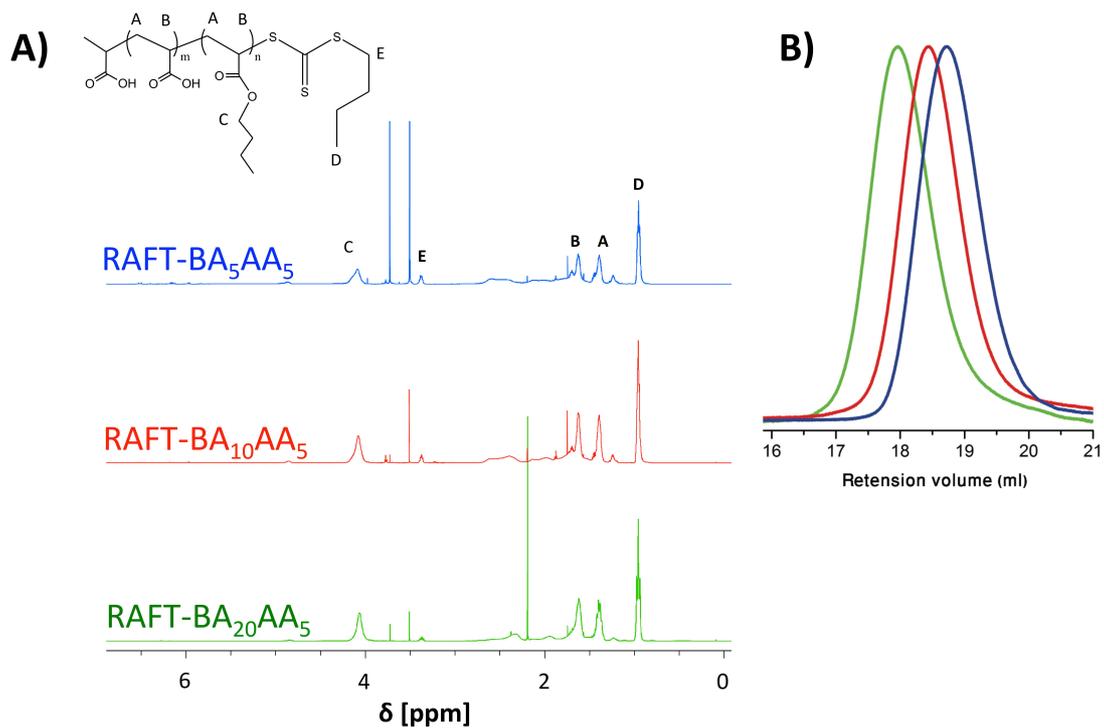


Fig. S1 $^1\text{H-NMR}$ spectra (CDCl_3 , 600 MHz) (A) and SEC (B) of RAFT-BA₂₀-AA₅ (green), RAFT-BA₁₀-AA₅ (red), RAFT-BA₅-AA₅ (blue) quasi-block copolymers.

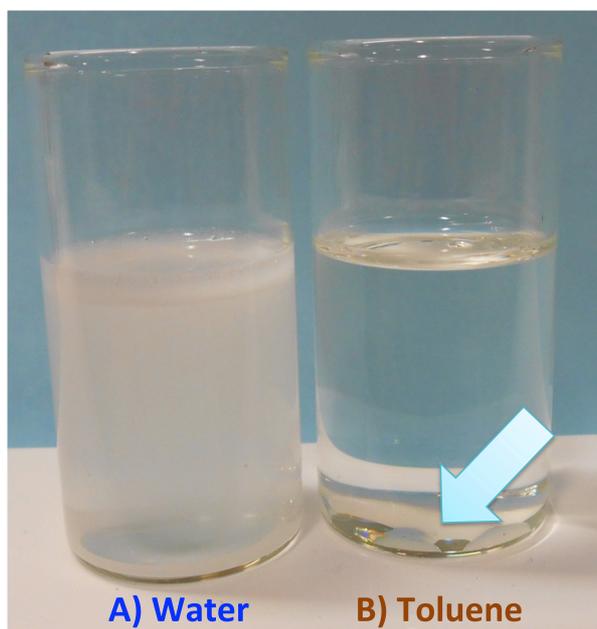


Fig. S2 The emulsion type was determined by the drop test method. One drop of the formed HIPE with macro-RAFT agent-Qb1 was placed into (A) water and (B) toluene. The emulsion droplet was seen to disperse in the water but remained as a droplet in toluene.

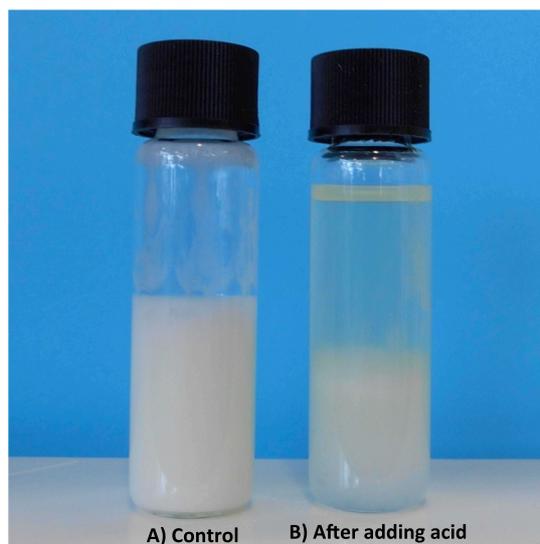


Fig. S3 Triggered demulsification by addition of acid (emulsion formed with macro-RAFT agent-Qb1): A) Control HIPE, B) After addition of acid.

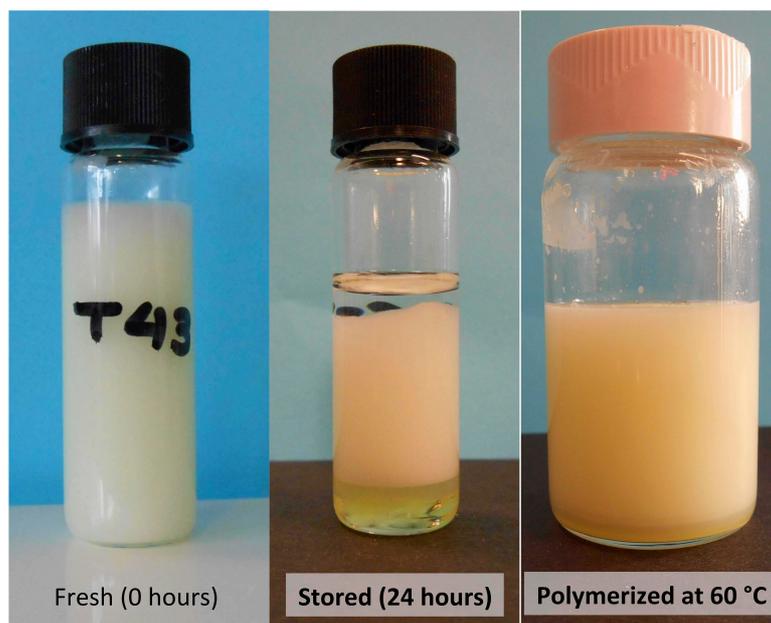


Fig. S4 Effect of basic conditions on the HIPE stability within 24 h, HIPE formulation A2 (emulsion formed with macro-RAFT agent-Qb1). For the polyHIPE obtained by this formulation (KPS, 60 °C, 24 hours) a layer of tough yellow polymer was found at the bottom of the vial.

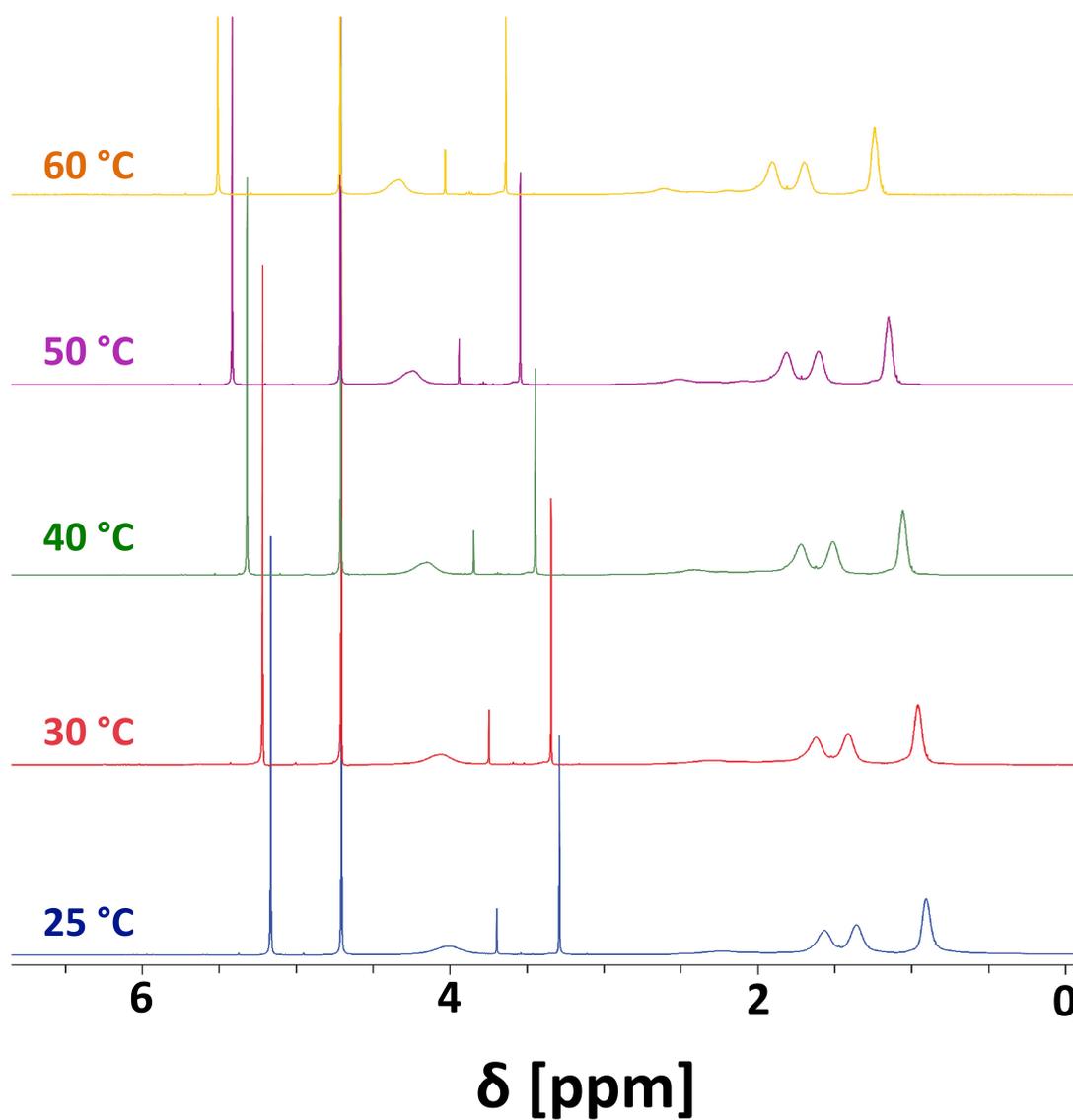


Fig. S5 ¹H-NMR spectra (D₂O, 400 MHz) of RAFT-BA₂₀-AA₅ (0.2 g in 1 ml D₂O in presence of 0.01g of NaOH and 0.01 g Trioxane (as internal standard)) at 25, 30, 40, 50 and 60 °C.

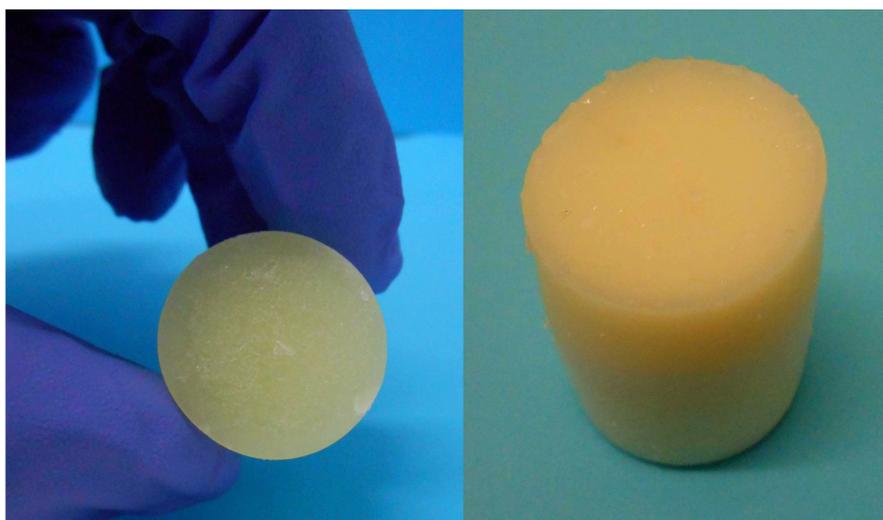


Fig. S6 A yellow solid macroporous polyHIPE obtained by polymerized formulation of HIPE A1 (KPS, 60 °C, 24 hours, after preparation).

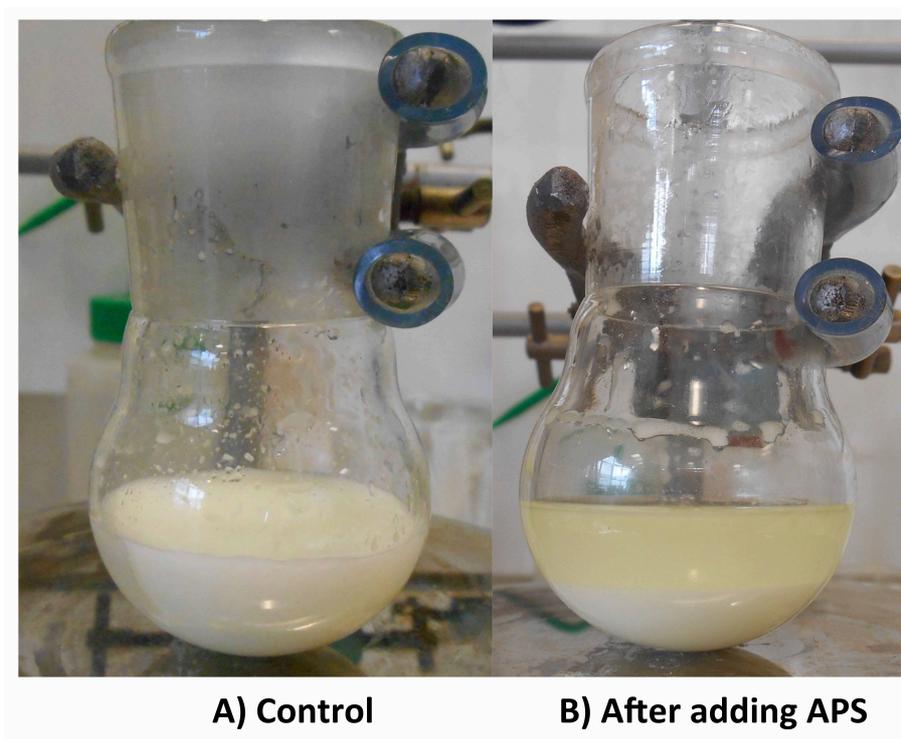


Fig. S7 Phase separation after addition of APS to the HIPE formulation A2 **A)** Control HIPE, **B)** After addition of APS (Image was taken at an interval of 2 min).

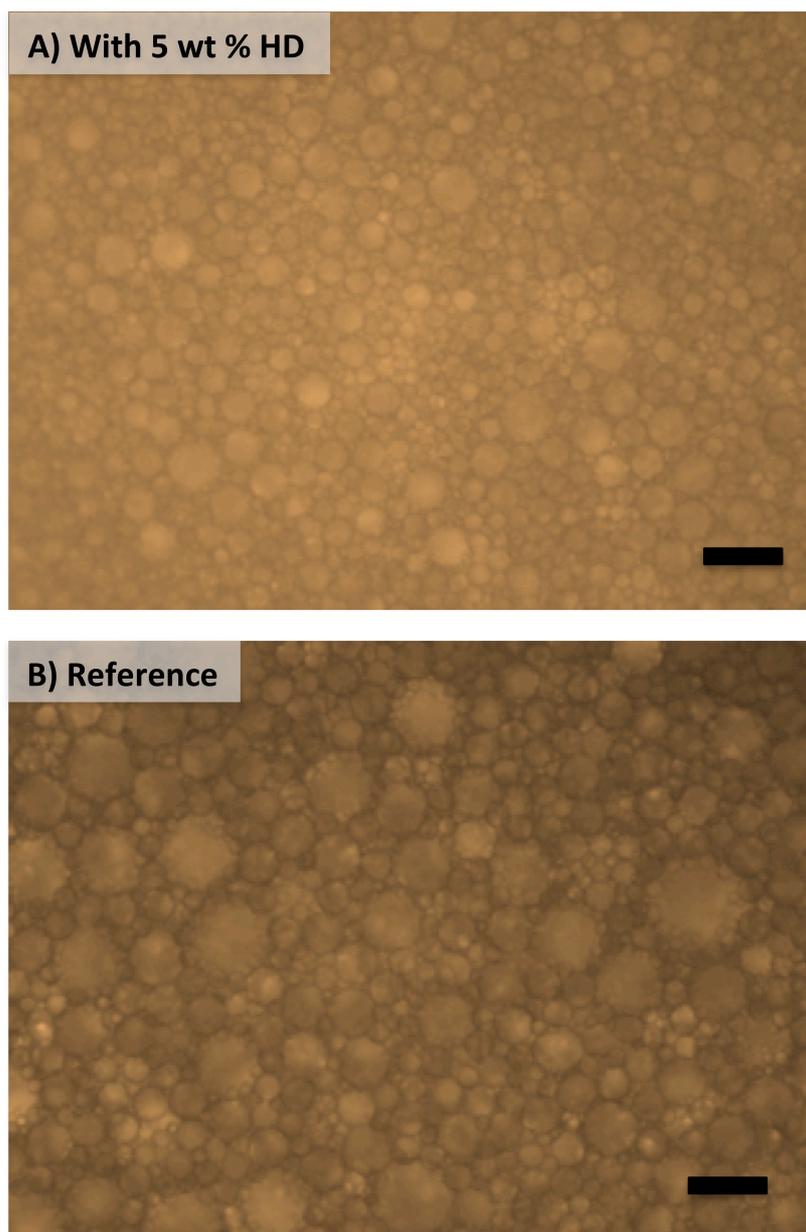


Fig. S8 Optical microscopy of HIPEs stabilized by macro-RAFT agent-Qb1 7 wt%. **A)** in the presence of 5 wt% hexadecane (HD) **B)** With out adding hexadecane (HD). Scale bar is 50 μm .

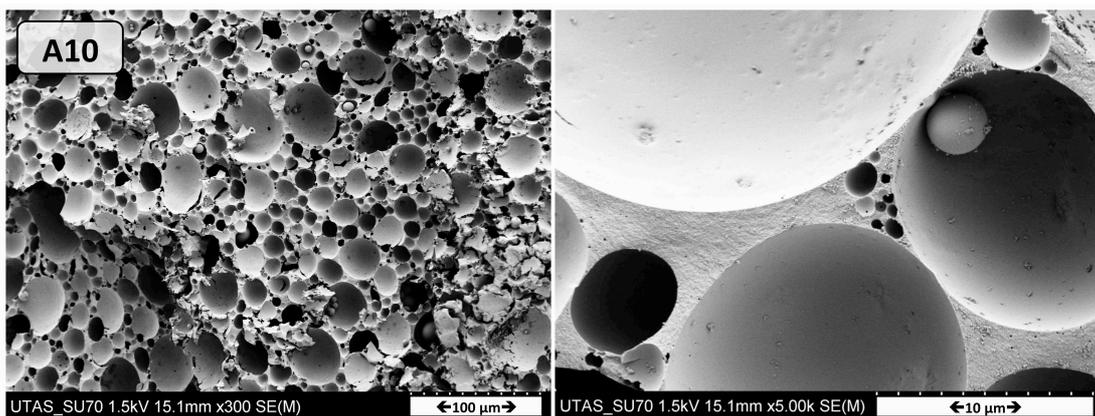


Fig. S9 SEM of polyHIPE stabilized by 7 wt% of macro-RAFT agent-Qb1 in the presence of 20 wt % of hexadecane in the oil phase polymerized at room temperature (TEMED/KPS).

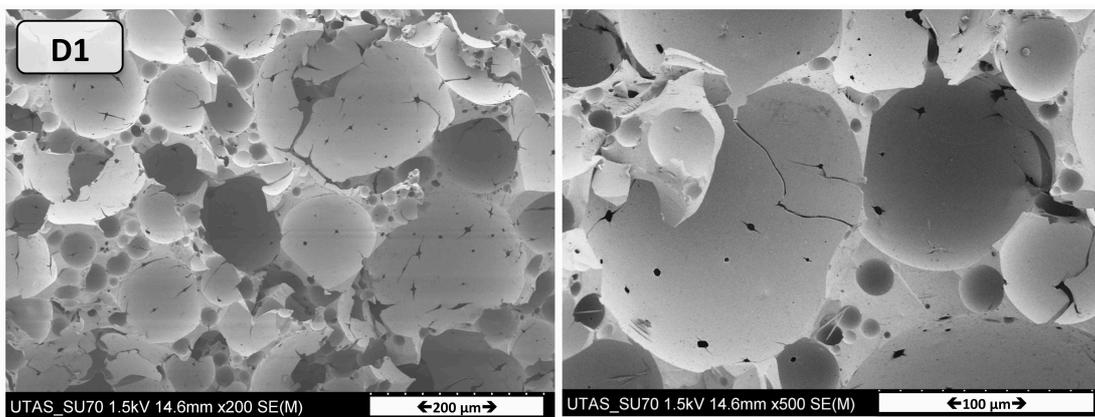


Fig. S10 SEM of PolyHIPE stabilized by macro-RAFT agent-Qb5 7.8% wt, in presence of 5% wt of hexadecane in oil phase and polymerized at room temperature (TEMED/KPS). The amount of macro-RAFT agent for polyHIPEs B1, C1, and D1 are the same based on mole equivalent.

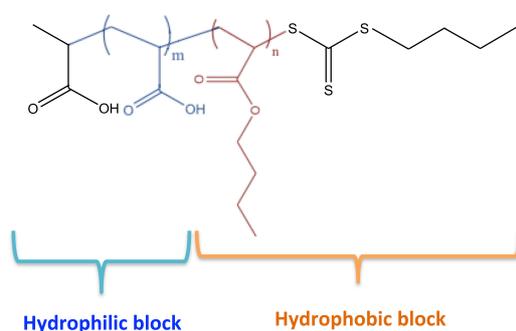
Supplementary Methods:

1) Calculations of HLB values of amphiphilic macro-RAFT agent

The Hydrophile-Lipophile Balance (HLB) is obtained using the Griffin's method (eq 1), from the molecular weight ratio of the hydrophilic block (M_h) and the total molecular weight (M):

$$\text{HLB} = 20 \times M_h/M \quad (1)$$

The hydrophilic and hydrophobic blocks of the amphiphilic macro-RAFT agent are shown in scheme S1.



Scheme S1 Schematic representation of the amphiphilic macro-RAFT

For example for Qb-1 (see table 1),

Hydrophilic block		Hydrophobic block	
Mw of acrylic acid (AA)	72.06	Mw of butyl acrylate (BA)	128.17
Number of units (Feed)	5	Number of units (Feed)	20
Mw of the AA block	360.3	Mw of the BA block	2563.4
RAFT part (Hydrophilic)	73.06	RAFT part (Hydrophobic)	165.32
Hydrophilic group	433.36	Hydrophobic block	2728.72

The calculations for all macro-RAFT agents are summarized in table S1.

Table S1 HLB values of macro-RAFT agents synthesized in this study

$(AA)_x$ - qb -(BA) $_y$	X (feed)	Y (feed)	HLB value ^a
Qb-1	5	20	2.74
Qb-2	20	5	13.05
Qb-3	5	10	4.60
Qb-4	5	5	6.99
Qb-5	10	20	4.50

^aIn the case of inverse HIPE (oil in water), the HLB value is normally in the range of 10-16.

2) Calculations of Sulfur content for polyHIPE A3 (see table 2)

Assuming all of the sulfur from the elemental analysis originates from the macro-RAFT agent:

The sulfur content within polyHIPE A3 was 0.41% (Elemental analysis result). Also, it was determined that the amount of removed macro-RAFT agent- Qb1 from above sample is ~ 29-31% wt (analyzed by using UV-Vis spectroscopy).

The expected amount of the macro-RAFT agent Qb-1 within polyHIPE A3 is around 0.51%, however the elemental analysis data shows less amount (0.41%) inside the polymer (see table S2). Around 20% deviation of elemental analysis result is suggested that this method is not a suitable microanalysis technique for quantification. Hence, for qualification, mapping surface by EDX_SEM analysis (based on Sulfur element) and RAMAN spectroscopy (based on C=S) were done on this sample (see Figures 4 and 6).

Table S2 Calculations of Sulfur content for polyHIPE A3

Macro-RAFT agent Qb-1 (g)	0.42
Wash-out from the sample A3 (maximum)	31%
Amount of macro-RAFT agent Qb-1 with in the polymer (g)	0.2898
Mol of macro-RAFT agent (using Mn,SEC)	9.17669E-05
Mol of sulfur from macro-RAFT agent	0.000275301
Weight of the sulfur (using 32.065 u) (g)	0.008827521
Monomers used in sample A3 (g)	1.729
Expected S% in the polyHIPE if all sulfur comes from macro-RAFT agent (%)	0.51
Amount of sulfur from elemental analysis ¹	0.41

¹Elemental analysis was performed on a sample of AM-MBAM polymerized in bulk (KPS as initiator) subjected to the same washing protocol. The sulfur content within bulk was below than the detection limit.