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ARTICLE

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

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Oil-in-water ('inverse') High Internal Phase Emulsions (HIPEs) have been prepared using an amphiphilic macro-RAFT agent with toluene as the internal dispersed phase (~80 vol%) and an aqueous monomer solution as the continuous phase. The water phase consisted of the monomers acrylamide (AM) and *N,N'*-methylenebisacrylamide (MBAM), an initiator as well as the amphiphilic macro-RAFT agent, that is 2-(butylthiocarbonothioylthio)-2-poly(*n*-butyl acrylate)-*b*-poly(acrylic acid), which was used as an anionic polymeric surfactant. The presence of these amphiphilic species allowed the successful preparation of a polyHIPE upon polymerization. The effect of concentration of macro-RAFT agent, pH, initiator, hexadecane as an organic modifier and the polymerization temperature on the morphology of the resulting porous materials was investigated. Varying the lengths of the hydrophilic and hydrophobic blocks of the macro-RAFT agent resulted in polyHIPEs with different porous structures. The presence of RAFT functionality in the polyHIPE was confirmed by elemental analysis, EDX-SEM, Raman and FT-IR spectroscopies. Raman mapping revealed full coverage of the void walls with dithiocarbamate groups.

Introduction

High internal phase emulsions (HIPEs) are concentrated mixtures of droplets dispersed in another liquid, where the minimum droplet volume fraction is 74 vol%. HIPEs are commonly stabilized by commercially available, non-ionic small molecular surfactants, where these amphiphiles decrease the interfacial tension between the two phases (typically an oil phase and aqueous phase), allowing for emulsification.^{1,2} To prepare a stable HIPE, the surfactant must rapidly adsorb at the interface and lower the interfacial tension between the phases to form a rigid interfacial film.³ Commercially available emulsifiers which can stabilize particular HIPEs⁴ include Triton X-405,⁵ Span 80 (Sorbitan monooleate)⁶ or a mixture of nonionic, anionic, and cationic surfactants: Span 20 (Sorbitan monolaureate), DDBSS (Dodecyl benzenesulfonic acid sodium salt), and CTAB (Cetyltrimethylammonium bromide).^{7,8} Amongst these, Span 80 is the

most commonly used emulsifier for water-in-oil (w/o) HIPE stabilization.⁴ As alternative to surfactants of low molar mass HIPEs can also be stabilized by amphiphilic block copolymers with a hydrophilic and hydrophobic segment, otherwise known as polymeric surfactants,⁹ as well as solid particles the latter referred to as Pickering emulsifiers.¹⁰⁻¹³

Polymeric surfactants are an attractive alternative to traditional surfactants as they offer a wide variety in chemical composition and molecular architecture.¹⁴ However, commercially available polymeric surfactants that have been used in HIPE stabilization are limited to polyethylene oxide (PEO)-based copolymers, including Hypermers[®], Pluronic[®] and Synperonic[®].^{15,16} Although widely used to stabilize HIPEs, the stabilization of a particular system requires careful selection of surfactant or mixtures of emulsifiers in order to obtain the required hydrophobic-hydrophilic balance (HLB) to warrant HIPE stability.

When the continuous phase is solidified through polymerization, a cellular monolithic structure commonly with interconnected pores and hence open cellular network, is produced, which is referred to as poly(HIPE).^{6,17-21} The cell walls of the porous poly(HIPE) are functionalized by the surfactants used, either through physis- or chemisorption. The ability to tailor the functionalization of the relatively large inner total surface area of interconnected pores by use of specific emulsifiers allows for poly(HIPE) design of interest for a range of applications, one being separation science. Availability of block copolymers with a specific HLB value and

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chemical functionality has become straightforward with the development of reversible-deactivation radical polymerization techniques. Among them, the reversible addition–fragmentation chain transfer (RAFT) process is particularly attractive due to its compatibility with a vast array of monomers and mild reaction conditions.^{22, 23} Through the use of RAFT it is now possible to synthesize a wide variety of macromolecules using non-specialized equipment, allowing for the synthesis of well-defined (co)polymers with narrow molecular weight distributions and controlled architecture.^{24, 25}

The RAFT process allows the synthesis of amphiphilic block polymers required for the fabrication of HIPEs, with the most common method being sequential polymerization of two monomers of opposing lyophilicity (e.g. a hydrophilic monomer and then a hydrophobic monomer).^{26, 27}

Currently, the most explored methods to functionalize polyHIPEs include the incorporation of a co-monomer with the desired functionality, or via a post-polymerization functionalization approach.²⁸ Although functionalization via post-polymerization allows for greater control over the morphology and void diameter of the polyHIPE, this process includes an additional step. Battaglia et al.²⁹ have recently introduced a slightly different method in which commercially available amphiphilic block copolymers (polystyrene-*b*-poly(ethylene oxide) (PS-PEO), poly(1,4-butadiene)-*b*-poly(ethylene oxide) (PBD-PEO), poly(1,4-butadiene)-*b*-poly(acrylic acid) (PBD-PAA), and polystyrene-*b*-poly(acrylic acid) (PS-PAA)) were employed as the macromolecular surfactants for water-in-oil emulsions to produce polystyrene/divinylbenzene foams. The presence of the hydrophilic block of the block copolymer on the pore surfaces of styrene-divinylbenzene polyHIPEs was demonstrated. Following on from this work, Gao et al.³⁰ introduced a well-defined amphiphilic macro-RAFT agent (denoted poly(Styrene_m-*b*-AA_n)) that was able to stabilize a w/o HIPE and prepare Sty-*co*-DVB polyHIPEs possessing closed voids. In that work the morphology of the obtained polyHIPEs were tailored by means of controlling emulsion parameters such as the initiator and aqueous phase volume fraction, however varying the composition of the diblock copolymer was not used to explore possible polyHIPE morphologies. This concept was explored by Debuigne et al.³¹ by using a series of well-defined amphiphilic poly(ethylene oxide)-*b*-poly(styrene) (PEO-*b*-PST) as polymeric surfactants to stabilize water-in-oil (w/o) HIPEs. They identified important parameters such as the length of hydrophilic block for the preparation of Sty-*co*-DVB polyHIPEs where the surface is coated by a polymeric surfactant.

To the best of our knowledge, there are no reports where an amphiphilic macro-RAFT agent is used as the polymeric surfactant for the stabilization of an inverse, oil-in-water (o/w) HIPE. In this work, we report the preparation of an inverse HIPE, (comprising 80 vol% dispersed phase) which is stabilized by an amphiphilic macro-RAFT agent (as a quasi (block-like) copolymer poly(butyl acrylate)-*qb*-poly(acrylic acid)). The effect of amphiphilic macro-RAFT agent concentration, pH, initiators (both water soluble and oil soluble, in addition to redox initiation), hexadecane (as a hydrophobic organic

modifier to prevent Ostwald ripening) and the polymerization temperature on the morphology of the resulting materials was investigated. Furthermore, the composition of the polymeric stabilizer (the ratio of hydrophilic to hydrophobic units) was varied with an aim to prepare highly interconnected, hydrophilic polyHIPEs. Ultimately, these materials have potential applications for use as a stationary phase in flow through applications e.g. for extraction or as the stationary phase in separation science.

Experimental Section

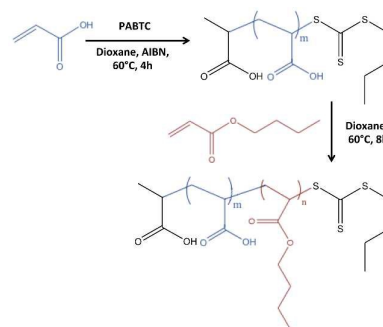
Materials

Acrylic acid (AA, Merck, ≥99%) was purified by distillation under reduced pressure. *n*-Butyl acrylate (BA, Sigma-Aldrich, 99%) was passed through a column of Al₂O₃ to remove the inhibitor. The RAFT agent, 2-[[[(butylsulfanyl)carbonothioyl]sulfanyl] propanoic acid (PABTC), was synthesized as described in Ref. 32.

Acrylamide (AM, Sigma-Aldrich, ≥98%), *N,N'*-methylenebisacrylamide (MBAM, Sigma-Aldrich, ≥99.5%), methanol (Fluka), basic alumina (Al₂O₃, Brockman activity I, 60-325 mesh), hexadecane (Sigma-Aldrich), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Sigma-Aldrich, 99%), sodium hydroxide (Sigma-Aldrich, ≥98.0%) and ammonium persulfate (APS, Ajax Chemicals, ≥98.0%), were all used as received. Toluene was obtained from Chem-Supply (Gillman, SA, AUS). 2, 2'-azobis(isobutyronitrile) (AIBN, MP Biomedicals, Eschwege, Germany) and potassium persulfate (KPS, M&B, 98%) were recrystallized from methanol and water, respectively.

Synthesis of amphiphilic polymeric surfactant by RAFT polymerization

A series of amphiphilic macro-RAFT agents consisting of AA and BA were synthesised as reported in the literature.³³ The Z group of the RAFT agent (PABTC) is an *n*-butyl group and the R group is 2-propionic acid, as shown in Scheme 1. AA was chosen for its high solubility in basic water, aiding dissolution of the macro-RAFT agent in the aqueous continuous phase.



Scheme 1 Schematic representation of the RAFT polymerization approach towards (quasi)-copolymerization of Acrylic acid (AA) and Butyl acrylate (BA) using PABTC at 60 °C.

A typical polymerization protocol (one-pot, two-step polymerization) used in this work is summarized: In a first step,

1 g (4.2×10^{-3} mol) of PABTC and 0.068 g (4.0×10^{-4} mol) of AIBN were introduced into a round-bottom flask which was then sealed with a rubber septum, and purged with argon for 10 min. Then in a second step 1.51 g (2.1×10^{-2} mol) of AA was dissolved in 30 mL of dioxane and the solution was added to the round-bottom flask. This was purged with argon for 10 min. The reaction was allowed to proceed at 60 °C for 4 h under constant stirring. At this time, the reaction was stopped by removing the flask from the oil bath and a small aliquot of the solution was taken for electrospray ionization mass spectroscopy (ESI-MS) studies to determine the molecular weight of the AA single block.

For the polymerization of the hydrophobic block, BA was added to the round bottom flask at a molar ratio (relative to the initial chain transfer agent concentration) equal to the desired number of monomer units per macro-RAFT agent. The mixture was purged with argon for 10 min and further polymerization for 8 h at 60 °C was performed. At this time, a small aliquot of the solution was removed for size exclusion chromatography (SEC) and ^1H NMR analysis, the results of which are summarized in Table 1. Dioxane was removed through rotary evaporation under reduced pressure. The polymer was then stored at 4 °C until use.

Table 1 Macro-RAFT agents synthesized in this study

(AA) _x -qb-(BA) _y	X (feed)	Y (feed)	BA/RAFT ^a (NMR)	M _{n,SEC} ^b (g mol ⁻¹)	Đ
Qb-1	5	20	19.5	3158	1.05
Qb-2	20	5	-	2244	1.14
Qb-3	5	10	12.8	1963	1.06
Qb-4	5	5	5.2	750	1.19
Qb-5	10	20	20.5	3722	1.04

^aNumber of units of BA were determined by ^1H NMR using the signal of RAFT end group around 3.4 ppm respect to signal of methylene group of BA around 4.1 ppm. ^bMolecular weight and polydispersity determined by SEC analysis (THF used as eluent). Calculated according to PS standards.

Synthesis of hydrophilic 'inverse' polyHIPEs

The prepared amphiphilic macro-RAFT agents were used as stabilizer for the preparation of acrylamide-based polyHIPEs. In a typical procedure, the macro-RAFT agent was dissolved in 4 ml of water containing NaOH, acrylamide (AM, 1.420 g, 1.99×10^{-2} mol), the crosslinker N,N'-methylenebisacrylamide (MBAM, 0.309g, 2.00×10^{-3} mol) and the radical initiator KPS (0.04 g, 1.47×10^{-4} mol). In order to provide a suitable pH environment to ensure the solubility of the macro-RAFT agent, differing amount of NaOH were required depending on the intended concentration of the macro-RAFT agent used. Using a syringe pump, the dispersed phase (toluene, 16 mL) was then added drop-wise at a rate of 0.8 ml per min with constant stirring at 1000 rpm. The temperature of the emulsion has already been found to influence droplet coalescence and the size of primary pores.³⁴ Because of this, the flask containing the continuous phase was kept at 30 °C by using a water bath for all emulsions during their preparation.

The emulsion was stirred for an additional 20 min after complete addition of the internal toluene phase. The emulsion was transferred to a glass vial and then cured at 60 °C in a water bath for 24 h. A small aliquot of all emulsions were kept in closed vials in the dark at room temperature, in order to determine emulsion stability. In order to study the droplet size of the emulsion, small samples of the HIPEs were withdrawn with a Pasteur pipette, then deposited directly on a clean microscope glass slide and analyzed. The resultant polyHIPE was purified via Soxhlet extraction with acetone for 72 hours as well as 72 hours with water. The experimental conditions used for the preparation of the different polyHIPEs can be found in Table 2.

Characterization

NMR analyses were performed on either a 400 MHz or 600 MHz Bruker Ultra Shield Avance Spectrometer. For all NMR analyses deuterated solvents were used as stated. Size exclusion chromatography (SEC) was performed with a Wisco-tech instrument using a refractive index detector (RID) and two chromatography columns (two PSS S linear 3μm, Polymer Standard Services GmbH, PSS), THF (HPLC grade) was used as an eluent at a flow rate of 0.5 mL/min. The column oven was kept at 40 °C. The calculated molecular weights were based on calibration with respect to polystyrene (PS) standards of narrow dispersity with a molecular weight range of 160–154000 g mol⁻¹ (PSS-Polymer Laboratories). The injection volume was 0.1 mL. Electrospray Mass Spectrometer Analysis was carried out using a ThermoFinnegan LTQ Orbitrap detector with Finnigan LCQ Data Processing and Instrument Control Software.

Emulsion droplets were observed using an optical microscope Nikon (model Eclipse E200), equipped with a camera (Tucsen, model IS500). Images of the emulsions were analyzed by ImageJ (NIH image) and the mean droplet size (n=100) and droplet size distribution were evaluated by triplicate. PolyHIPEs were characterized by field emission gun scanning electron microscopy (FE-SEM) studies using a Hitachi SU-70 FESEM in the Central Science Laboratory, University of Tasmania. All samples were platinum coated for 15 s in an argon atmosphere (Emitech 550, Emitech Ltd., UK), except where samples scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) analysis were prepared and the materials were sputter-coated with carbon (Ladd 40000 carbon evaporator).

The calculation of the average pore and window diameter (if windows were present) was performed on sets of at least 100 pores and 100 windows, respectively, using the image analysis software ImageJ (NIH image). A statistical correction was employed to obtain more accurate value, as each value was multiplied by $2/(3^{1/2})$ as described by Carnachan et al.³⁴

The sulfur content of the polyHIPEs was determined with a Thermo Finnigan EA 1112 Series Flash Elemental Analyser. FTIR spectra were recorded by a Bruker Vertex 70 infrared spectrometer equipped with an ATR probe. Raman spectra of samples were recorded in the frequency range of 350 to 5000

cm⁻¹ using a Renishaw inVia Raman microscope with Streamline. Solid samples were pressed gently using a spatula before being placed on the sample holder. A CCD line detector in the exit focal plane of the monochromator was used for recording the spectra. The laser source was a Nd:YAG laser. The Brunauer–Emmett–Teller (BET) surface area and microporosity were assessed using a Tristar II analyzer for the

nitrogen adsorption/desorption isotherm at 77 K (Particle and Surface Science, Gosford, AUS). A Metertech SP-8001 UV/Vis spectrophotometer was used to evaluate the concentration of macro-RAFT agent removed from the polyHIPEs after the soxhlet extraction with acetone.

Table 2 Conditions used for the preparation of hydrophilic inverse polyHIPEs

Sample code	macro-RAFT agent	%wt ⁽¹⁾	Initiator (temperature)	pH ⁽²⁾	Oil modifier (Hexadecane (HD))	HIPE stability (hours)	<D> (μm) Optical microscopy		(SEM) (μm)	
							Fresh	After 24h	<D> ⁽³⁾	<d> ⁽³⁾
A1	Qb-1	3.5	KPS (60 °C)	8.3	-	>12	63.2	68.0	12.9	(-)
A2	Qb-1	7	KPS (60 °C)	7.4	-	>12	78.1	71.8	22.2	2.2
A3	Qb-1	10.5	KPS (60 °C)	8.2	-	>12	86.9	49.7	42.9	(-)
A4	Qb-1	14	KPS (60 °C)	8.6	-	>12	68.4	45.7	11.0	(-)
A5	Qb-1	17.5	KPS (60 °C)	7.7	-	>12	59.7	40.2	10.1	(-)
A6	Qb-1	7	AIBN (60 °C)	7.4	-	>12	57.5	49.9	33.8	(-)
A7	Qb-1	7	KPS/ TEMED (RT)	7.4	-	>12	75.0 ⁽⁴⁾	71.3	16.2	1.0
A8	Qb-1	7	KPS (60 °C)	7.4	5% wt ⁽¹⁾	>24	49.2	54.4	18.2	(-)
A9	Qb-1	7	KPS/ TEMED (RT)	7.4	5% wt ⁽¹⁾	>24	58.3 ⁽⁴⁾	51.3	12.3	0.8
A10	Qb-1	7	KPS/ TEMED (RT)	7.4	20% wt ⁽¹⁾	>24	49.8 ⁽⁴⁾	51.5	12.6	3
B1	Qb-3	4.1 ⁽⁵⁾	KPS/ TEMED (RT)	7.7	5% wt ⁽¹⁾	>48	32.3 ⁽⁴⁾	26.8	5.3	0.8
B2	Qb-3	7	KPS/ TEMED (RT)	7.3	5% wt ⁽¹⁾	>48	28.6 ⁽⁴⁾	31.5	8.2	1.3
C1	Qb-4	1.5 ⁽⁵⁾	KPS/ TEMED (RT)	7.1	5% wt ⁽¹⁾	>48	16.8 ⁽⁴⁾	20.5	4.3	0.4
D1	Qb-5	7.8 ⁽⁵⁾	KPS/ TEMED (RT)	6.5	5% wt ⁽¹⁾	< 10 min	-	-	-	-

⁽¹⁾ All amounts are based on the weight percentage (w.r.t. the continuous phase). ⁽²⁾ Differing amounts of NaOH were added depending on the intended concentration of the macro-RAFT agent (At a basic pH, carboxyl groups are deprotonated and poly(acrylic acid) is soluble in water). ⁽³⁾ A void describes the pores of the PolyHIPE and <D> is average size of voids. Window refers to the interconnecting pores between two adjacent droplets and <d> is average size of windows. ⁽⁴⁾ Sample stability test was performed before adding TEMED. ⁽⁵⁾ These amounts are equivalent to the same molar ratio used for sample A3, converted by using Mn of the macro-RAFT agent obtained by size exclusion chromatography.

Results and Discussion

Synthesis of amphiphilic quasiblock macro-RAFT agent

RAFT is a simple and effective polymerization technique,^{35, 36} which yields well-controlled polymers exhibiting an almost infinite range of functionalities. The macro-RAFT agent can be modified through alterations to the length of both blocks. The AA block is pH-sensitive; the BA block is hydrophobic and hence the polymer is amphiphilic in nature. Alterations in the length of each block provide additional control over the behaviour of the macro-RAFT agent. The high propagation rate coefficient of both BA and AA together with their high efficiency in one-pot RAFT polymerization means that specific amphiphilic block co-polymers to be used as stabilizers can be prepared in a simple fashion.

This one-pot polymerization technique has been utilized to achieve the synthesis of quasi (block-like) copolymers using sequential monomer addition.^{37, 38} This approach yields quasi-block copolymers (Qb) when the conversion of monomer in the first step (e.g. acrylic acid) is lower than 100% prior to a

second monomer being incorporated.³⁹ The NMR spectrum of the macro-RAFT-AA₅ revealed the presence of unreacted AA after the first polymerization step, suggesting the formation of quasi-copolymers after the polymerization reaction of the second block of BA, during which time residual AA monomer can be consumed (See table 1).

The molecular weight of the macro-RAFT-AA₅ was estimated by electrospray ionization mass spectrometry (ESI-MS). Figure 1 shows a typical mass spectrum for the PABTC-mediated polymerization of acrylic acid targeting a degree of polymerization of 5 (RAFT-AA₅). The spectrum indicates a distribution of AA oligomers containing a different number of repeat units of AA (from 2 up to 8), which were chain extended in the second step polymerization of BA. For every macro-RAFT-AA₅ polymer analyzed the raw ESI-MS spectrum was qualitatively similar to that in Fig. 1.

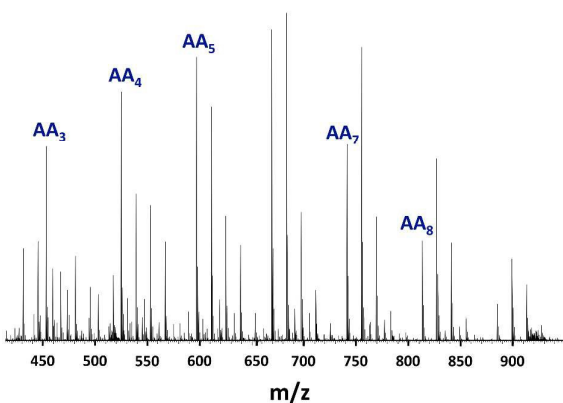


Fig. 1 Mass spectrum of RAFT-AA₅ obtained by ESI-MS.

The number of BA units in each quasi-copolymer was estimated by comparing the ¹H NMR integral of the S-CH₂-group of PABTC at 3.4 ppm and the -O-CH₂- groups of the n-butyl group of each BA repeat unit at ~4.1 ppm (see Supporting Information Fig. S1-A). As reported in Table 1, there was a good agreement between the targeted units of the BA and the actual number of units of BA in the prepared quasi-copolymers. This indicates the controlled character of the polymerization process when using PABTC as RAFT agent for the polymerization of BA. SEC analyses of the three different macro-RAFT agents showed copolymers were prepared under RAFT control (*D* < 1.2) as well as the elution at longer retention times of copolymers containing a lower amount of BA units (see Supporting Information Fig. S1-B).

Stability of oil-in-water HIPEs using quasi-block copolymers as surfactants

At basic pH, the poly(AA-*qb*-BA) quasiblock copolymers prepared here are anionic polyelectrolytes and can exhibit properties similar to an anionic surfactant, while still bearing the reactive trithiocarbonate terminal group. In order to establish the possibility of stabilizing HIPEs with these polymers, macro-RAFT agent-Qb1 (see Table 2) was chosen as a starting point to examine its potential for the stabilization of toluene-in-water emulsions, with AM, MBAM and NaOH present in the water phase. 3.5% wt of the macro-RAFT agent with respect to the aqueous phase resulted in the successful stabilization of HIPEs with oil volume fractions between 60 and 90%. The emulsion droplets were spherical but polydisperse (See figure 2). The drop test method was used to determine that the prepared HIPE was an inverse (o/w type) system^{40, 41} (see Supporting Information Fig. S2). Additionally, the macro-RAFT agent-Qb2 was designed for use based on its HLB value, which is suitable for the stabilization of o/w emulsions⁴² (see Supporting Information). However, no amount of this polymer and/or varying the internal phase volume resulted in sufficiently stable emulsions for curing. Similarly an (AA)₅ macro-RAFT agent (no BA units) was unable to stabilize any emulsion under these conditions.

Optical microscopy was used to examine the synthesized HIPEs immediately after preparation as well as 24 hours post-

synthesis, in order to examine emulsion stability. Optical micrographs and photos of the resultant emulsions under various conditions of macro-RAFT loading (in this instance Qb1) are shown in Fig 2. The mean emulsion droplet diameter slightly increased with increasing amounts of macro-RAFT agent, reaching a maximum of ~87 μm when the macro-RAFT agent concentration was ~ 10.5% wt (w.r.t. the continuous phase). At higher levels (> 14% wt) the mean droplet diameter decreased to ~60 μm. Further increases to the amount of macro-RAFT did not result in any further reduction in the droplet size.

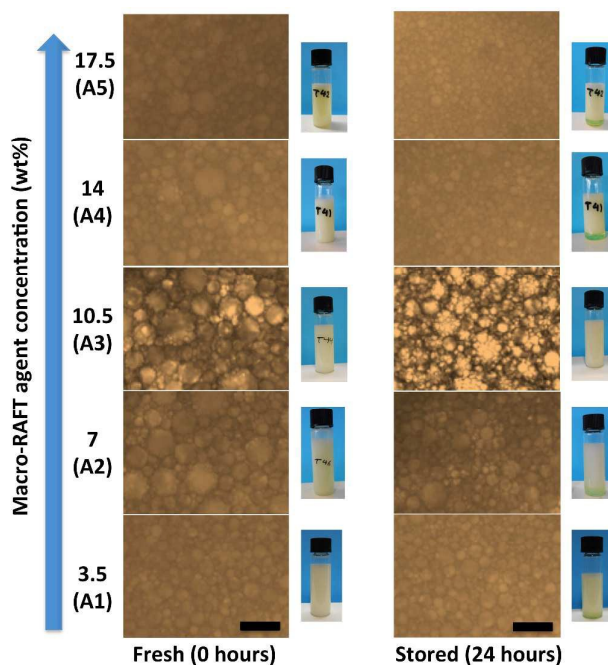


Fig. 2 Optical microscopy and photographs of HIPEs stabilized by different amount of macro-RAFT agent-Qb1; after preparation (0 hours, left column) and after 24 hours (right column). The scale bar in all cases is 40 μm.

Given the solubility of pAA in water is reduced at low pH, it was expected that the HIPE would be relatively unstable under acidic conditions. This was demonstrated by the addition of a few drops of concentrated HCl to a prepared emulsion (HIPE formulation A2), whereby phase separation immediately occurred (see Supporting Information Fig. S3). Additionally HIPE stability was investigated under basic conditions (pH > 9) using HIPE formulation A2. In order to do this, we added further NaOH to the aqueous phase of HIPE A2 formulation (the pH of this solution was 12.5) prior to mixing and emulsification with toluene. After 1 hour, the emulsion had separated into three phases; a clear liquid as top layer, a middle layer similar to the freshly prepared emulsion, and a yellow oil at the bottom of the vial (see Fig S4). The oily yellow layer was transformed into a tough polymeric mass after polymerization of the HIPE (60 °C for 24 hours), suggesting that the macro-RAFT agent is not an efficient emulsifier at high pH (See Supporting Information Fig. S4). This result may be

attributed to the increased ionic strength of the system at a more basic pH, reducing the stability of the inverse HIPE.

For further study, the macro-RAFT agent-Qb1 was investigated by NMR under basic conditions and at different temperatures, by measuring the NMR spectra of the copolymer as a function of time potential changes in NMR spectra were recorded. As shown in Fig. S5 no major changes in NMR spectra occurred upon increasing temperature up to 60 °C. Hence, sodium hydroxide was added to the aqueous phase for all samples in order to ensure the pH was between 7 and 8.

Synthesis of hydrophilic polyHIPEs

The o/w emulsions discussed in the previous section were polymerized in order to obtain porous polyHIPEs. A homogeneous and stable yellow polyHIPE A1 was obtained that retained the shape and volume of the mold (no apparent shrinkage was observed). The polymerized samples could be handled without breakage (see Supporting Information Fig. S6). Increasing the macro-RAFT agent-Qb1 concentration from 3.5% wt to 17% wt had a significant effect on the morphology of the resulting polyHIPEs (e.g. on the void size) as can be seen from the SEM images (Fig. 3).

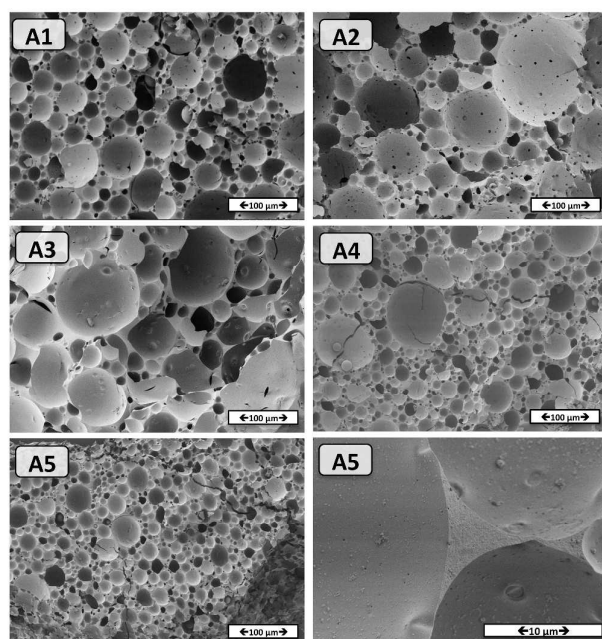


Fig. 3 Scanning electron micrographs of emulsion templated macroporous polymer made by polymerization of HIPEs stabilized solely by different amount of macro-RAFT agent-Qb1 (w.r.t. the continuous phase) at 60 °C in presence of KPS as initiator.

The prepared polyHIPEs retained their yellow colour after washing the samples with acetone using a soxhlet apparatus and subsequent washing with water (see Supporting Information Fig. S6), providing a visual cue regarding the incorporation of the macro-RAFT agent. Elemental analysis confirmed the presence of sulfur amount within the polyHIPEs (e.g. the sulfur content within polyHIPE A3 was 0.41%). Further

evidence for the presence of the macro-RAFT agent on the surface of the polyHIPE was obtained from Energy Dispersive X-ray analysis (EDX), clearly indicating that sulfur was present at the surface of the polyHIPE A3 (Fig. 4).

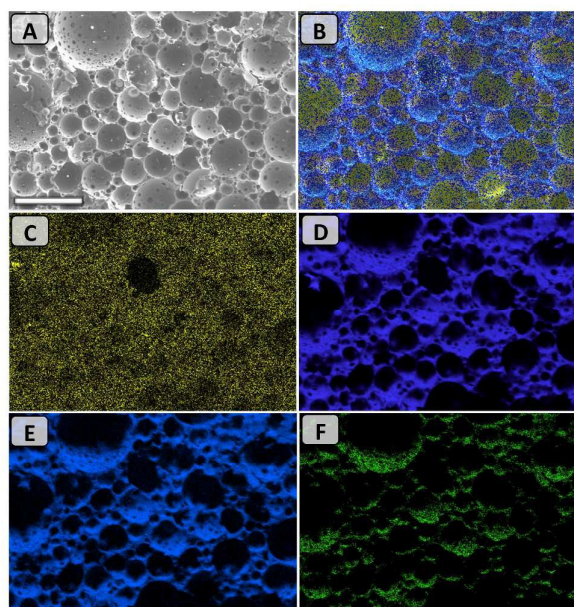


Fig. 4 EDX mapping analysis on polyHIPE A3; (A) SEM image and (B) Overall mapping elements on the same spot: corresponding to sulfur (C), carbon (D), oxygen (E), and nitrogen (F) mapping. Scale bar is 50 μm.

As KPS was used as initiator, the sulfur content is likely due in part to the presence of initiator-derived endgroups. To determine the amount of the RAFT-agent “trapped” inside the polyHIPE, the washes from the polyHIPE during purification were analyzed. The solvent washings (acetone) were yellow, suggesting the removal of some of diblock-copolymer from the material, and these washings were analyzed by using UV-Vis spectroscopy.⁴³ It was determined that, in the case of polyHIPE A3, the amount of removed macro-RAFT agent-Qb1 is ~ 29-31% wt (see Supporting Information).

To further investigate the inclusion of the macro-RAFT agent within the polyHIPE structure, FTIR analyses were performed on the resultant material, in comparison to a sample of AM-MBAM polymerized in bulk (KPS as initiator) subjected to the same washing protocol. The FTIR spectrum of PolyHIPE A3 shows the presence of an extra band at 1710 cm^{-1} respect to bulk polymer, which is present in the FTIR spectrum of the macro-RAFT agent (Fig. 5). This signal corresponds to the carbonyl stretch of the carboxylic acid group of the AA block, and is a good evidence of the incorporation of the macro-RAFT agent in to the polymer structure.

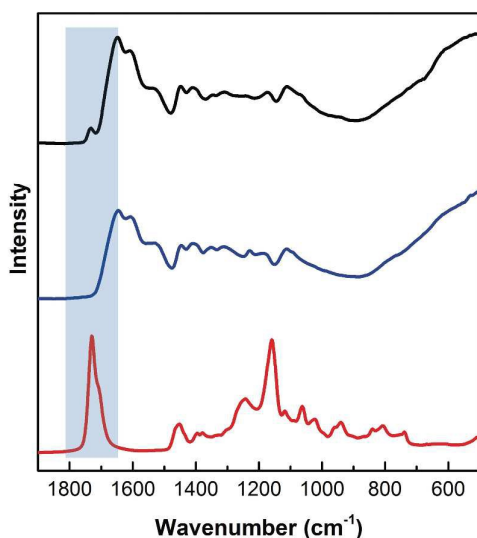


Fig. 5 ATR-IR of macro-RAFT agent-Qb1 (red line), bulk polymer (blue line) and polyHIPE A3 (black line). The peak around 1650-1800 cm^{-1} is highlighted.

Further spectroscopic analysis of prepared polyHIPEs was performed via Raman spectroscopy at randomly selected regions across the polyHIPE surface. Peaks in the Raman spectrum of the macro-RAFT agent used to prepare polyHIPE A3 correlate with peaks observed in the spectrum obtained from subtracting the bulk poly(AM-co-MBAM) polymer from A3 (see Figure 6A). In addition, the polyHIPE surface was mapped for the presence of the C=S peak at 1107 cm^{-1} (Fig. 6-B). The map confirmed the presence of the C=S groups in the same physical location as the walls of the polyHIPE voids, which are solely due to the trithiocarbonate end group of the RAFT agent.

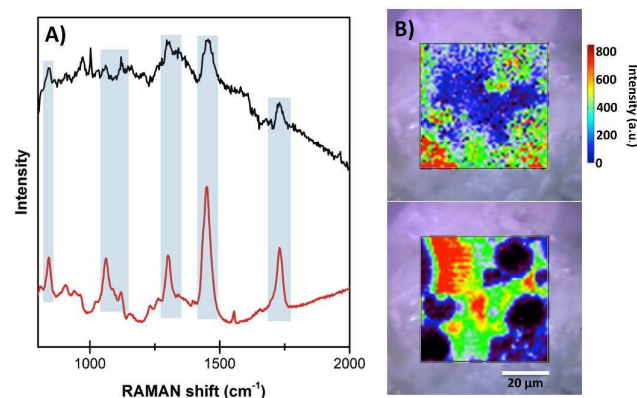


Fig. 6 (A) Raman spectra of macro-RAFT agent-Qb1 (Red line), difference between polyHIPE A3 and bulk polymer (Black line). (B) Raman mapping (upper) is based on the C=S peak at 1107 cm^{-1} of macro-RAFT agent-Qb1 on the surface of polyHIPE A3 by normalizing the peak intensity. Raman mapping (bottom) based on signal to baseline from 1383 to 1493 cm^{-1} at the same area (Dark blue regions in the lower image are void locations within the polyHIPE.)

Effect of initiator

Oil-soluble (AIBN) and water-soluble (APS) thermal initiators, as well as a redox initiation system (TEMED/ KPS) were also investigated for the preparation of polyHIPEs and their influence on the resultant morphology of the material. In all cases the macro-RAFT agent-Qb1 concentration was kept constant at 7% wt (w.r.t. the continuous phase). Stable emulsions were not obtained when APS was employed as the water-soluble initiator. Upon further investigation it was found that when APS was added to a pre-formed emulsion, phase separation immediately occurred (see Supporting Information Fig. S7). This may have been due to changes of the pH of the HIPE.

When AIBN (dissolved in the toluene phase) was used, a predominately closed-structure polyHIPE was obtained (Fig. 7 (sample A6)). It has been shown previously that the locus of initiation has a significant effect on porosity of the resultant polyHIPE.⁴⁴ In this case, more extensive droplet coalescence can occur as the polymerization is not “localized” at the oil-water interface when the initiator is in the organic phase. Variation in the structure of a polymerized emulsion by changing initiators was also reported by Bismarck et. al for the preparation of poly(sty-co-DVB) by polymerization of medium internal phase emulsion templates.⁴⁵ They observed that changing the initiator from water-soluble (KPS) to oil soluble (AIBN) resulted in materials with a more open structure; here we demonstrate the opposite trend in an inverse (o/w) system.

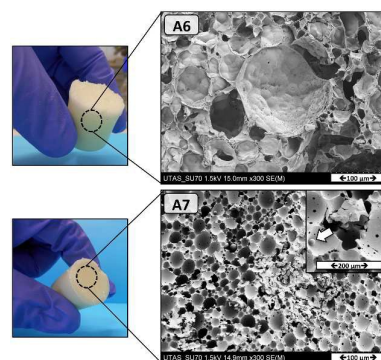


Fig. 7 SEM of polyHIPEs stabilized by 7% wt of macro-RAFT agent-Qb1, polymerized at 60 °C (A6- in presence of AIBN as initiator) and (A7- in presence of TEMED (a reducing agent) with KPS) at room temperature.

In order to reduce droplet coalescence and Ostwald ripening, room-temperature polymerization using a KPS/TEMED redox couple as initiator was performed. SEM analysis of the resulting polymer (sample A7) is shown in Fig. 7, showing heterogeneity in the structure as well as the formation of micron-sized particles within some voids. This could be explained considering the partition of monomer toward the oil phase and the formation of water in oil droplets within the HIPE.⁴⁶ It is believed that, as the polymerization begins at room temperature, the effect of destabilizing mechanisms such as

coagulation and Ostwald ripening decreases, causing the more homogeneous structure within obtained polyHIPE.⁴⁷

Effect of hexadecane as an organic modifier

The preparation of a hydrophilic polyHIPE from an inverse HIPE typically requires careful emulsion stabilization and polymerization due to the possibility of Ostwald ripening.⁴⁸ Ostwald ripening in emulsions is a process of gradual growth of the larger droplets at the expense of smaller ones due to mass transport of soluble dispersed phase (oil) through the continuous phase (water) leading to emulsions containing droplets with different sizes.⁴⁹ In the case of o/w emulsions, the addition of a particularly hydrophobic oil such as hexadecane (HD) is known to help arrest ripening, due to reduced transport through the continuous phase.⁵⁰ In this work, HD was added the oil phase of our emulsions (5% wt w.r.t. continuous phase) followed by polymerization either with KPS (at 60 °C, sample A8) or KPS/TEMED (at room temperature, sample A9). When KPS was used as initiator, SEM analysis (Fig. 8) and optical microscopy (Fig. S8) demonstrated that the addition of HD resulted in emulsions with smaller droplet sizes that were stable over a longer period of time, resulting in a more regular porous structure (in comparison to Figure 3). When KPS/TEMED was used (A9), smaller voids were formed compared to A8, in addition to evidence of interconnectivity (windows) on the voids, which was not observed in polyHIPE A8. These two differences may result from the polymerization temperature and the effect of that on the interfacial tension between oil droplet and aqueous phase. Increasing the HD loading to 20 wt % (polyHIPE A10, Fig S9) resulted in a polyHIPE with significant heterogeneity.

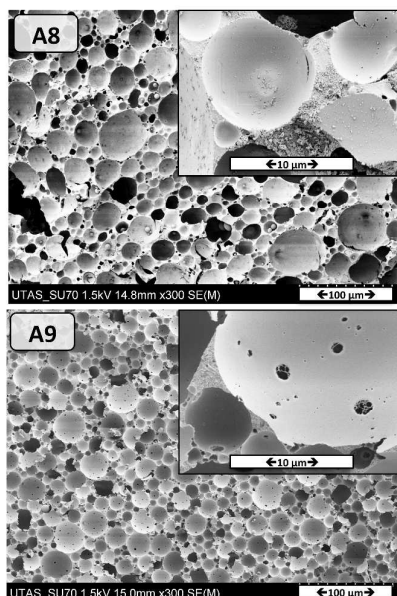


Fig. 8 SEM of PolyHIPEs stabilized by 7% wt of macro-RAFT agent-Qb1, polymerized in presence of 5% wt hexadecane as oil modifier (A8) polymerized at 60 °C with KPS (A9) polymerized at room temperature (TEMED/ KPS).

Tuning the polyHIPE structure by means of the macro-RAFT agent composition

Finally, we consider the effect of the diblock copolymer composition on the stability and nature of the resultant emulsion. To establish the role of the hydrophobic BA block, macro-RAFT agents Qb3 and Qb4 were used (both consisting of 5 AA repeat units with differing BA lengths). The procedure for the preparation of HIPE A9 was chosen and all other variables kept constant (the same mole equivalent of the diblocks were used in each case). HIPEs were successfully prepared (denoted HIPE B1 (using macro-RAFT agent-Qb3) and HIPE C1 (using macro-RAFT agent-Qb4)), with both showing increased stability in comparison to HIPE A9 of 48 hours storage without phase separation (See Table 2). SEM images of the obtained polyHIPEs after polymerization are shown in Fig. 9. In comparison to polyHIPE A9, both polyHIPEs B1 and B2 possess open porous networks with an increased number of windows. This increased level of interconnectivity was demonstrated with a near two-fold increase in BET specific surface area ($2.17 \text{ m}^2 \text{ g}^{-1}$ for B1, as opposed to $1.17 \text{ m}^2 \text{ g}^{-1}$ for A9). These results suggest that macro-RAFT agents with a shorter hydrophobic block favour the formation of open network, interconnected inverse polyHIPEs in comparison to macro-RAFT agents with a longer hydrophobic block. It is believed that macro-RAFT agents with a longer of hydrophobic block are less labile during the HIPE preparation and stabilization, providing greater stabilization of the obtained polyHIPE, as reported previously.²⁹

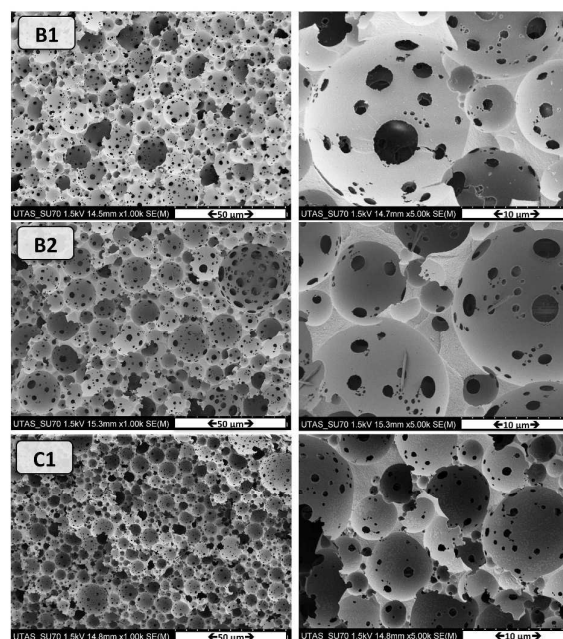


Fig. 9 SEM of PolyHIPE stabilized by B1) macro-RAFT agent-Qb3 4.1% wt, B2) macro-RAFT agent-Qb3 7% wt C1) macro-RAFT agent-Qb4 1.5% wt, in presence of 5% wt of hexadecane in oil phase and polymerized at room temperature (TEMED/KPS).

The macro-RAFT agent-Qb5 was synthesized to investigate the influence of increasing the number of hydrophilic units (from 5 to 10 in comparison to Qb1) on the stability of the resultant HIPE, while keeping the hydrophobic block length constant. In this instance phase separation of the HIPE occurred in less than 10 minutes. Rapid room temperature polymerization of this system (using the TEMED/KPS redox couple) resulted in a heterogeneous polyHIPE (D1, Fig. S10) with extremely large voids. In conjunction with the influence of changing the BA block length, the resultant structure and connectivity of the formed polyHIPE is strongly dependent on the nature and composition of the diblock copolymer used as stabilizer.

Conclusions

We have established a strategy to produce functional polyHIPEs by introducing macro-RAFT agent as a surfactant and a tool to transfer the RAFT moiety to the surface of the polyHIPEs. The results indicate that poly((AA)_x-qb-(BA)_y) can stabilize high internal phase o/w emulsions. By the polymerization of the continuous phase of these systems, highly porous emulsion templated materials were prepared. EDX with SEM revealed the presence of sulfur on the surface. FT-IR spectra for the polyHIPEs showed new carboxyl groups within the polyHIPE which come from the macro-RAFT agent. Raman mapping showed a significant proportion of the C=S functionality on the void structure of the polyHIPE. This is consistent with the presence of the RAFT moiety on the surface. The successful preparation highlights the ability to stabilize the oil-in-water system with a well-chosen amphiphilic macro-RAFT agent.

We believe that the RAFT functionality on the surface of the polyHIPE materials could provide a powerful substrate for subsequent surface chemistry reactions. The long-term aim is to decorate these materials with different functional groups. Future work will focus on the extension of this approach to a wider range of materials, and on achieving fine control over porous structure by tuning the hydrophilic and hydrophobic units.

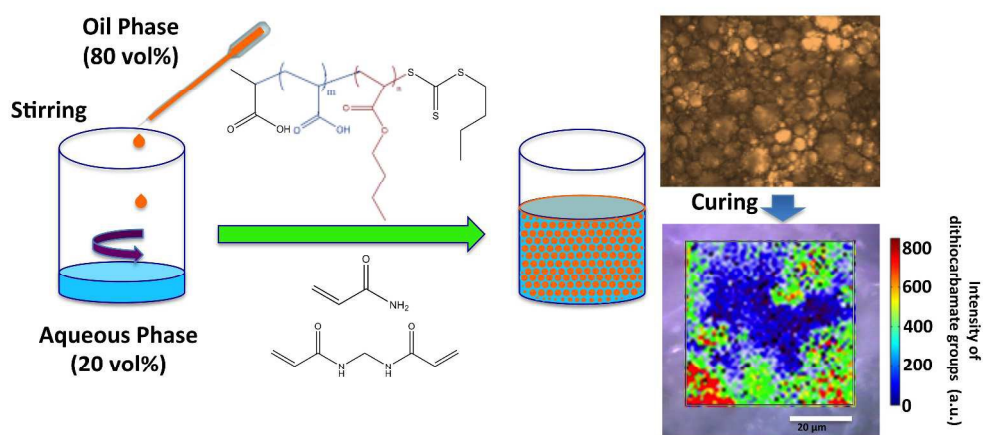
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