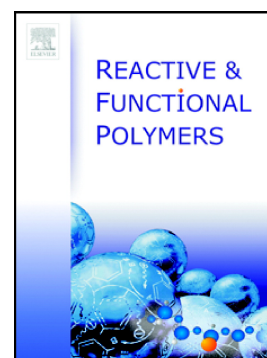


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Efficient Preparation of Macroporous Poly(Methyl Methacrylate) Materials from High Internal Phase Emulsion Templates

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Abstract

Thermo- and photo-initiated polymerization of emulsion templates for making macroporous poly(methyl methacrylate) materials both suffer from low energy efficiency and require tedious sample preparation (removal of inhibitors, inert atmosphere) or specialized equipment to be used. Here, an easy and efficient method for the preparation of such open pore materials with up to 93 % porosity is demonstrated by using redox-initiated polymerization in the oil phase of high internal phase emulsion templates. The method eliminates the need of heating/irradiation and monomer purification, thus reducing the preparation costs without sacrificing the mechanical properties of the porous materials. It also allows of two component HIPE curing systems to be made, stored and used in the field for a rapid preparation of open pore monoliths in spaces with complex geometry. This is demonstrated by the *in situ* preparation of a filter and a static mixer for foam generation. The proposed method has a considerable potential for further practical exploitation in filtration, separation, microfluidics, chromatography and other fields where porous materials are used.

Keywords: (water-in-oil emulsion templates, redox-initiated polymerization, benzoyl peroxide, open pore polyHIPEs, polymer filters)

1. Introduction

The emulsion templating has been established as a versatile and reliable method for making macroporous polymeric materials with tunable porosity, pore sizes, connectivity [1, 2, 3] and

diverse applications in tissue engineering [1, 2, 4], gas storage [5], catalysis [6], chromatography [7], filtration and separation technology [8]. High internal phase emulsions (HIPEs) containing over 74 vol% of the internal water phase dispersed as micrometer size droplets in the continuous oil phase of monomers have been commonly used for the preparation of polymeric materials with high porosity. The polymerization of the continuous phase of water-in-oil (w/o) emulsion templates gives polymerized HIPEs (polyHIPEs) which upon evaporation of the water droplets produce macroporous polymers. This approach has been successfully applied for the fabrication of polyHIPEs via thermo-initiated or photo-initiated polymerization of emulsions prepared from a variety of monomers and crosslinkers [1, 2, 9]. However, the polyHIPE preparation using methyl methacrylate (MMA) has been found challenging because the emulsion templates phase separated quickly upon heating [1]. Indeed, reports on the successful preparation of MMA-based polyHIPEs via thermo-initiated polymerization are rare [10, 11]. There, purified monomers and inert atmosphere have been used to enhance the polymerization of w/o HIPE templates stabilized either by solid particles [10] or by 35 % surfactant and up to 20 % co-stabilizer in the oil phase [11]. Photo-initiated polymerization has been used with better success in the preparation of methacrylate-based polyHIPEs because it does not require heating [12]. However, its application is limited to thin transparent samples and requires powerful light sources. Both thermo- and photo-initiated polymerization approaches suffer from low energy efficiency and often require tedious sample preparation (removal of inhibitors, inert atmosphere, etc.) or specialized equipment to be used.

The use of redox-initiated polymerization as an alternative method has the advantage that it does not require an external energy source (heat or light) and the polymerization can occur at room temperature. Water-soluble redox couples, such as ammonium persulphate - N, N, N',N'-tetramethylethylenediamine (APS - TEMED), have been used for the preparation of polyHIPEs from hydrophilic or hydrophobic monomers [13, 14, 15]. The use of oil-soluble

benzoyl peroxide (BPO) - tertiary amine redox couples for the bulk polymerization of MMA dates back to 1950s and has been widely utilized for rapid polymerization of acrylic-based materials in dentistry and medical restoration applications [16]. Recently, this approach was used for making injectable polyHIPE scaffolds by rapid polymerization of w/o HIPE templates prepared in inert atmosphere from purified dimethacrylates at elevated temperature (37 °C) [17]. In contrast, we focus our investigation on the preparation of porous PMMA materials, because the MMA is an inexpensive widely used monomer and the PMMA is a polymer with excellent mechanical properties, thus suitable for a variety of engineering applications [18, 19].

This work demonstrates for the first time that surfactant stabilized w/o HIPEs with a continuous oil phase of methyl methacrylate (MMA) and 10-30 vol% ethylene glycol dimethacrylate (EGDMA) crosslinker can be easily polymerized via free radical initiation in the oil phase using a BPO - amine redox couple. The polymerization occurs at ambient conditions (room temperature, air) without the need of any monomer purification, heating or UV irradiation. The morphology and mechanical properties of the macroporous poly(methyl methacrylate) (PMMA) materials obtained by this method are compared to those produced by the traditional thermo-initiated polymerization using azobisisobutyronitrile (AIBN) initiator.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, 99 %), benzyl methacrylate (BeMA, 96 %), isobutyl methacrylate (97 %), ethylene glycol dimethacrylate (EGDMA, 98 %), benzoyl peroxide (BPO, 50 % blend with dicyclohexyl phthalate as stabilizer), *N,N*-Dimethyl-*p*-toluidine (DMPT, 98.5 %), azobisisobutyronitrile (AIBN, 98 %), Pluronic[®] L-121 surfactant (average $M_n \sim 4,400$) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 99 %) were purchased from Sigma-Aldrich.

2.2. Sample preparation

All chemicals in redox-initiated polymerization experiments were used as received. Emulsion templates were prepared in volumes of 50 mL by adding deionized water dropwise (syringe pump, 4 mL min⁻¹) to the oil phase (a mixture of MMA and 10-30 vol% EGDMA) containing 1 w/v% BPO initiator (as received) and 5 w/v% Pluronic[®] L-121 surfactant in a 500 mL three-neck flask under continuous stirring with an overhead stirrer at 200 rpm. Once all the water phase was added, the emulsion was further stirred at 700 rpm for a time equal to that spent for adding the water phase. The polymerization was triggered by adding the DMPT accelerator (12 μ L per 1 mL oil phase) to the emulsion under continuous stirring for several minutes. Emulsion samples were left to polymerize in open cylindrical molds in air at room temperature overnight. The polyHIPE samples were purified by Soxhlet extraction with absolute ethanol for 24 hours, then dried in air at room temperature overnight. Alternatively, polyHIPEs were produced by mixing two emulsions, one containing 2 w/v% BPO (as received) and the other 2.38 wt/v% DMPT only, prepared in advance as described above. The polymerization was triggered by mixing equal volumes of both HIPEs.

The samples in thermo-initiated polymerization experiments were prepared as described above with the following modifications. The oil phase was prepared with 1.6 w/v% AIBN (instead of BPO) from purified monomers passed three times through basic alumina to remove the inhibitors and purged with nitrogen before use. The water phase contained 0.12 M CaCl₂ and was degassed under vacuum for 10 minutes before the experiments. Nitrogen was flowing through the flask during the emulsification. The emulsion templates were polymerized in sealed molds inside a preheated to 70°C oven overnight.

2.3. Characterization

The pot life of redox-initiated HIPE templates was determined by measuring the apparent viscosity of the polymerizing samples using a home-built setup (Figure S1, S2 and S3). The porosity was calculated by Equation S1 from the density and volume of the porous samples, and the polymer density. Pore structures were studied by scanning electron microscopy (SEM

EVO 60, Carl Zeiss) of polyHIPE samples coated with 1 nm thick gold layer by using a sputter coater. The sizes of 400 pores and pore throats were measured from the SEM images using Image J software. The median pore throat diameters were determined from their size distribution. The true median pore diameters were determined by stereological analysis following the Saltykov method [20]. The mechanical tests were done with a Mark-10 ESM303 instrument (2.5 kN load cell) at a compression rate of 1.2 mm min⁻¹ at room temperature (see Supporting information).

3. Results and discussion

Examples of typical w/o HIPE samples (M75R – M90R) prepared in our study are shown in Table 1. Stable w/o emulsion templates with 75 – 90 vol% internal water phase were made by stirring deionized water and the oil phase (a mixture of MMA and EGDMA) containing 1 w/v% BPO initiator (as received) and 5 w/v% Pluronic[®] L-121 surfactant as an emulsifier. The polymerization was triggered by adding N, N-dimethyl-p-toluidine (DMPT) accelerator to the stirred emulsion template and conducted in open molds in air at room temperature. We have found that all samples solidified to polyHIPE monoliths without visible defects (Figure 1a-d, insets) within 30 – 35 minutes after adding the accelerator. The maximum temperature reached during the polymerization has monotonically decreased from 35 °C, at 75 vol%, to 26 °C at 90 vol% water phase. This is because the smaller amount of polymerizing monomers produces less heat which is absorbed by the larger amount of water in the more concentrated emulsions. The lower temperature during the polymerization of the HIPEs with larger water content has slowed down their curing rate and prolonged the pot life.

As expected, the porosity of purified dry polyHIPE samples has increased with the water content of the HIPE templates and is in the range 79 – 93 % (Table 1). The SEM images shown in Figure 1 (a) – (d) reveal that the porous materials have an open pore structure of nearly spherical pores connected by circular pore throats. The SEM image analysis has shown that the pores and pore throats have relatively broad size distributions (Figure S4, Table S1

and S2). The median pore diameter increases with the increase of the water volume fraction in the emulsion template, thus suggesting that the size of the template droplets has been bigger in the more concentrated emulsions. This has been supported by optical microscopy observations of the HIPE templates which showed up to 70% increase of the median droplet diameter when the water volume fraction was increased from 75 to 90 vol%. This seems reasonable because the surfactant concentration in the oil phase has been kept constant, hence the total amount of surfactant progressively decreases with the increase of water content. The median pore throat diameter follows the trend observed for the pore size, but its increase is even more significant.

The mechanical tests on purified polyHIPE samples have revealed that the Young modulus and compressive strength decrease with the porosity, as expected [18, 21, 22]. However, Young's moduli of the samples with porosity 88 and 93 % are very close to the estimated expected moduli, E_f , (Table 1) and 50 – 100 times larger than the values reported for PMMA polyHIPEs produced by thermo-initiated polymerization of emulsions with 86 vol% water phase [11]. For better comparison, we have tried to polymerize HIPE templates with the same composition, but using the BPO as a thermo-initiator at 70 – 80 °C, i.e. without adding DMPT to the emulsions. All attempts have failed because the emulsion templates phase separated when heated. We have obtained better results by replacing the BPO with the more efficient and widely used AIBN thermo-initiator in the oil phase. However, the thermo-initiated polymerization of HIPE templates has turned out to be very challenging. We had to purify the monomers by removing the inhibitors, degas and add 0.12 M CaCl_2 to the aqueous phase, use nitrogen atmosphere throughout the HIPE preparation and polymerize them in sealed molds at 70 °C in an oven for several hours. Nevertheless, the w/o HIPE templates with 85 and 90 vol% inner aqueous phase destabilized during the heating and quality polyHIPEs were not produced. The results for samples M75T and M80T with 75 and 80 vol% aqueous content, respectively, are summarized in Table 1 and SEM images of the polyHIPEs are shown in

Figure 1 (e) and (f). In both cases, the polyHIPEs have an open pore structure similar to that of samples produced by redox-initiated polymerization (Figure 1a and b). They have slightly higher porosities but similar pore and pore throat diameters to the respective M75R and M80R samples. The compressive strength of thermo-initiated polyHIPEs is comparable to that of the redox-initiated materials with similar porosity, however, their Young modulus is almost two times lower (e.g. 26 vs 46 MPa at 88 % porosity) and significantly smaller than the estimated expected modulus, E_f , (Table 1). The polyHIPE materials produced by thermo-initiated polymerization were more brittle and crumbled during the compressive tests (cf. insets in Figure 1). This behavior correlates with the observation that the pore walls of polyHIPE samples produced by thermo-initiation have a grainy structure in contrast to the smooth polymer walls in redox-initiated samples (Figure 2). The grainy polymer structure could be due to the fact that the polymerization at 70 °C has occurred faster in a less controllable way in contrast to the redox-initiated polymerization in which the temperature did not exceed 35 °C. The increased water solubility in the oil phase at an elevated temperature could also play a role. The effect of these factors on the polymer microstructure needs further investigation.

Our results demonstrate that the redox-initiation method has significant advantages over the traditional methods of making MMA-based porous materials by thermo- or photo-initiated polymerization of HIPE templates: (i) it considerably simplifies the preparation by eliminating the monomer purification, the use of inert atmosphere and electrolyte in the aqueous emulsion phase; (ii) macroporous polymers with open pore structure and improved mechanical properties are produced without the need of an external source of heating or irradiation. Moreover, we have found that this method also works well when the MMA is replaced by other methacrylate, such as benzyl methacrylate (BeMA) or isobutyl methacrylate, and produces polyHIPEs with morphology similar to the macroporous PMMA materials (Figure 3 and S5). The use of an initiator-accelerator redox couple offers additional

advantages for practical applications by allowing the preparation of two component curing systems which must be mixed to trigger the polymerization [16, 17]. Following this approach, we have formulated two separate HIPE templates: one containing the BPO initiator and the other the DMPT accelerator only. These emulsions can be stored, mixed just before use, then delivered and polymerized in a variety of moulds and spaces with complex geometry to give open pore monoliths ready to be used as porous media shortly after the start of polymerisation. For example, we have used two BeMA-based HIPEs (80 vol% water) for the *in situ* preparation of a filter and a static mixer for foam generation, both functional in less than 20 minutes after mixing the emulsions (Figure 3 and Video S1). The two component MMA-based system gave similar results but the filter preparation took 15 min longer due to slower polymerization (Video S2). However, its curing time was significantly reduced by increasing the crosslinker concentration without compromising the mechanical properties of the polyHIPE (Table S3). The long-term stability of those emulsions was considerably improved by adding electrolyte to the aqueous phase (Figure S6) and they were able to polymerize even at 10 °C (although for a two times longer time), thus showing a potential for their use in the field.

4. Conclusions

In summary, we demonstrate an efficient method for the preparation of open pore polyHIPE materials by using BPO - DMPT redox-initiated polymerization of w/o HIPE templates formulated with MMA or other methacrylates. The method eliminates the need of heating/irradiation and monomer purification, thus reducing the costs without sacrificing the mechanical properties of the porous materials. It also allows of two component HIPE curing systems to be made, stored and used in the field for a rapid preparation of open pore monoliths in spaces with complex geometry. Therefore, the proposed method has a significant potential for further practical exploitation in filtration, separation technology, microfluidics, chromatography and other fields utilizing porous materials.

Supporting Information

Supporting Information is available from the Journal or from the author.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical and time limitations. Data will be made available on request.

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Table 1. Internal phase volume fraction (ϕ_w), curing conditions and pot life (t_p) of w/o HIPE templates, and porosity (P), median pore diameter (d_p), median pore throat diameter (d_t), compressive strength (σ), Young's modulus (E) and the ratio of measured to expected Young's modulus (E/E_f) of the respective polyHIPEs produced by redox-initiated (M75R – M90R) or thermo-initiated (M75T and M80T) polymerization. The continuous oil phase of emulsion templates contains 85 vol% MMA, 15 vol% EGDMA, 5 w/v% Pluronic[®] L-121 surfactant and redox- or thermo-initiator.

Sample	ϕ_w [vol%]	Curing	t_p [min] ^{d)}	P [%]	d_p [μm]	d_t [μm]	σ [MPa]	E [MPa]	E/E_f ^{e)}
M75R ^{a)}	75	room temp. ^{c)}	16 \pm 1	79 \pm 2	16 \pm 1	2.4 \pm 0.2	5.1 \pm 0.1	85 \pm 1	0.6
M80R ^{a)}	80	room temp. ^{c)}	18 \pm 1	84 \pm 2	23 \pm 1	3.7 \pm 0.4	3.2 \pm 0.1	66 \pm 1	0.8
M85R ^{a)}	85	room temp. ^{c)}	22 \pm 1	88 \pm 2	26 \pm 1	4.5 \pm 0.5	1.8 \pm 0.1	46 \pm 1	1.0
M90R ^{a)}	90	room temp. ^{c)}	23 \pm 1	93 \pm 2	29 \pm 2	6.4 \pm 0.6	0.6 \pm 0.1	14 \pm 1	0.9
M75T ^{b)}	75	oven, 70 °C	-	82 \pm 2	17 \pm 1	2.4 \pm 0.2	3.5 \pm 0.4	41 \pm 9	0.4
M80T ^{b)}	80	oven, 70 °C	-	88 \pm 2	17 \pm 1	2.7 \pm 0.2	1.7 \pm 0.1	26 \pm 4	0.6

^{a)}The oil phase contains 1 w/v% BPO initiator (as received) and 1.19 vol% DMPT accelerator, the water phase is deionized water; ^{b)}The oil phase contains 1.6 w/v% AIBN thermo-initiator, the water phase is a degassed 0.12 M CaCl₂ solution; ^{c)}Open molds in air at 23 \pm 2 °C; ^{d)}Time taken for doubling the initial apparent viscosity; ^{e)}The expected Young modulus (E_f) is calculated by^[15] $E_f = E_p (\rho_f / \rho_p)^2$, where ρ_f is the measured porous polymer density, $\rho_p = 1200 \text{ kg m}^{-3}$ and $E_p = 3100 \text{ MPa}$ are the density and Young modulus of PMMA, respectively.^[16]

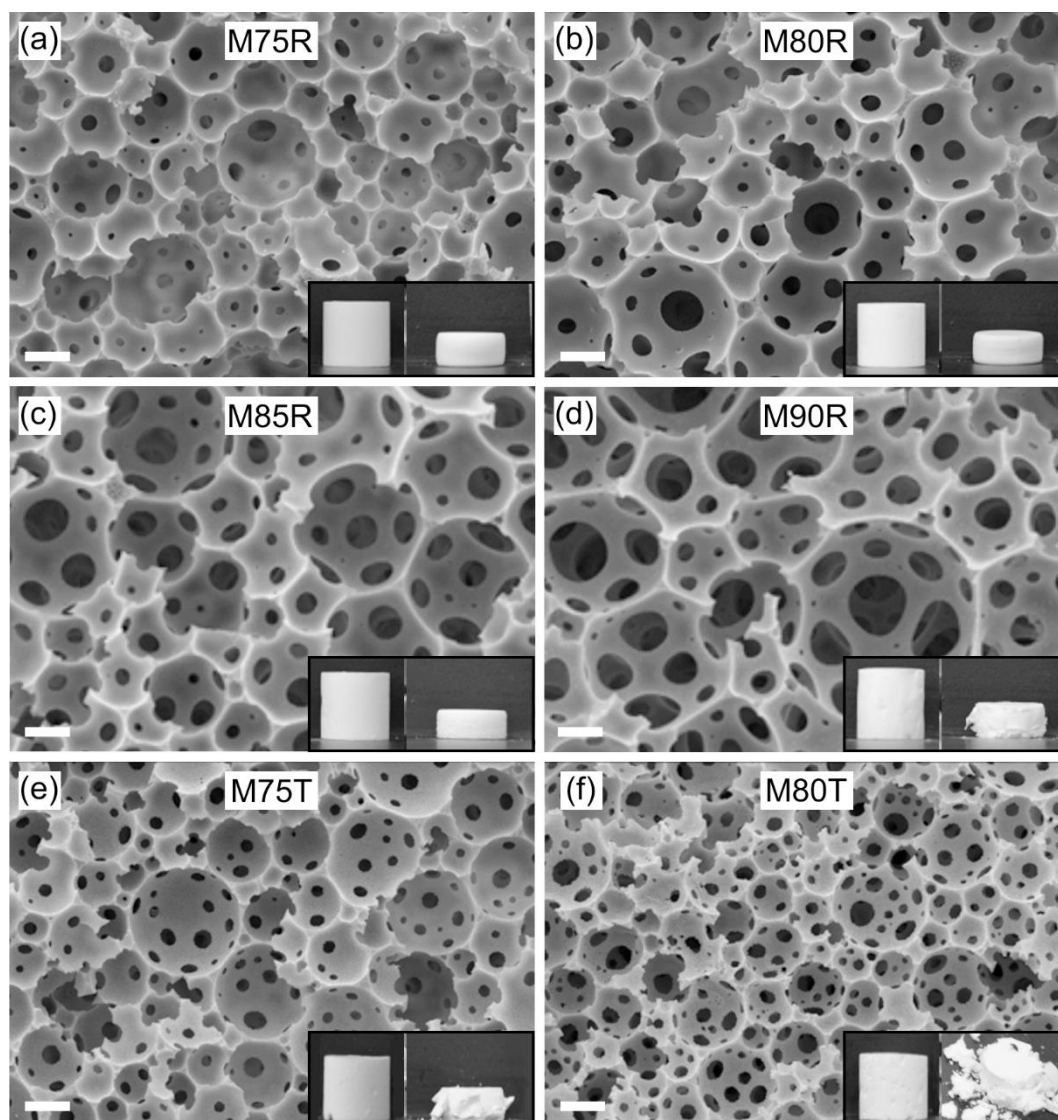


Figure 1. SEM images of polyHIPEs produced by: (a – d) redox-initiated and (e, f) thermo-initiated polymerization (see Table 1). Scale bars are 10 μm . Insets show digital camera images of the respective cylindrical samples (10.3 mm in diameter) taken before (left) and after (right) the compression test.

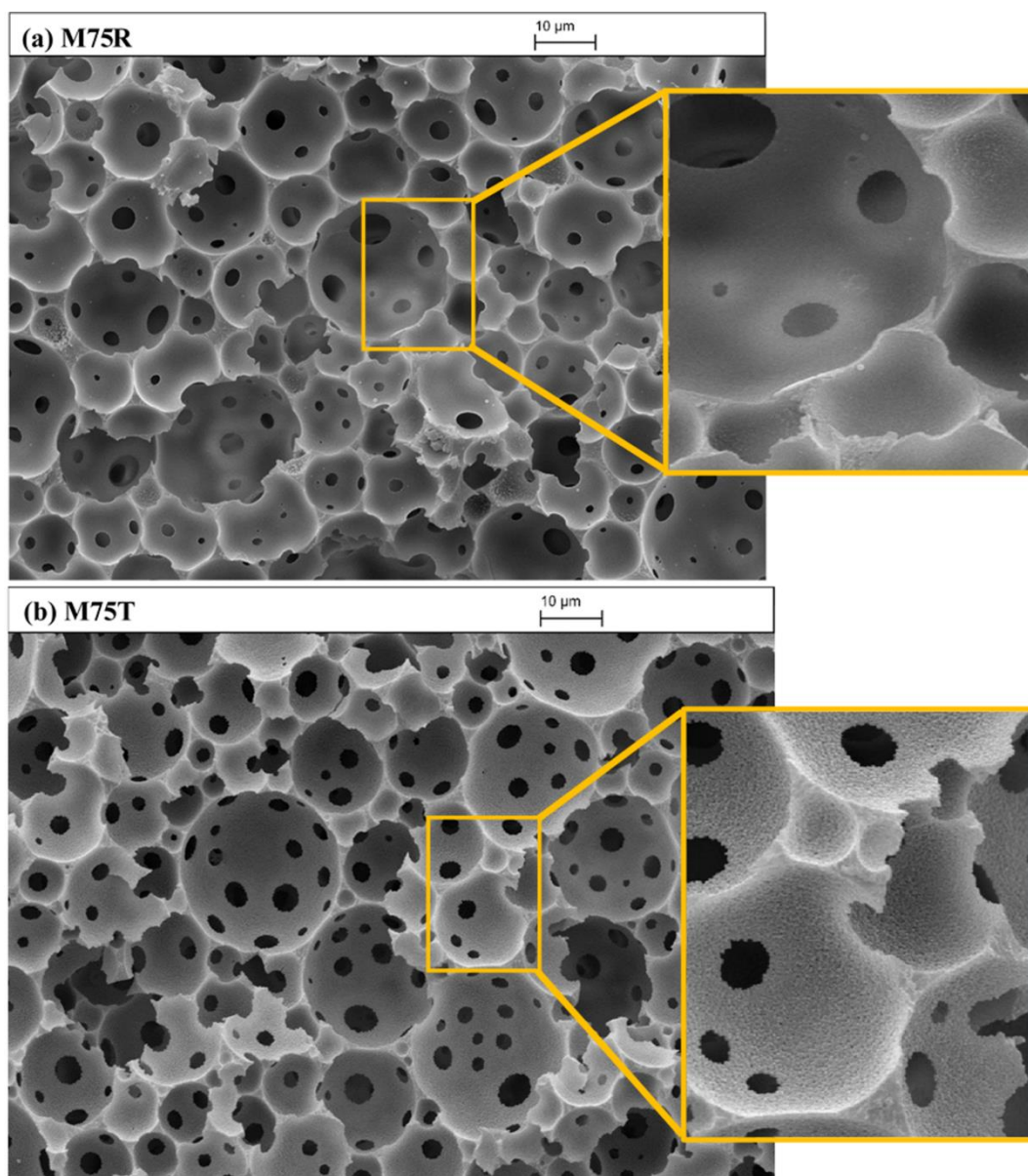


Figure 2. SEM images of polyHIPE samples produced from w/o emulsion templates by (a) redox-initiated and (b) thermo-initiated polymerization (see Table 1). The zoomed areas clearly show that the polymer surface in (a) is smooth while that in (b) has a grainy structure.

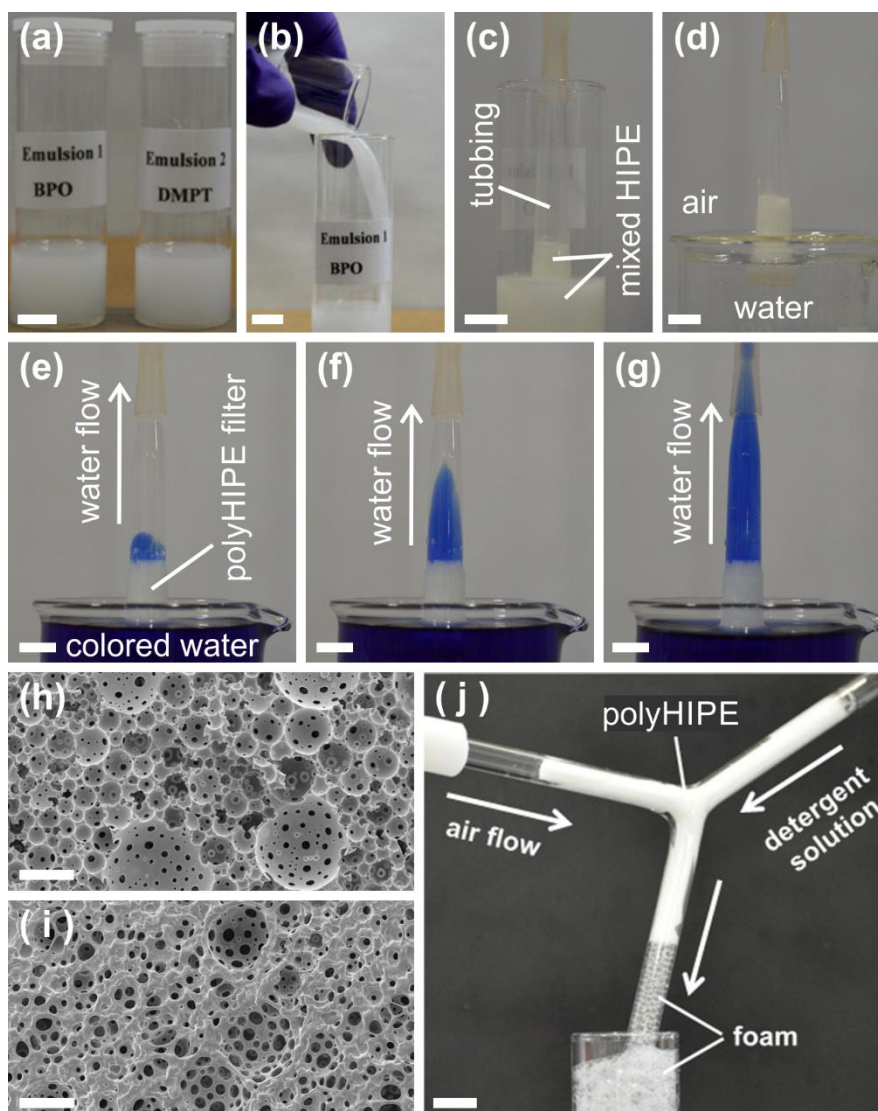


Figure 3. (a – g) *In situ* preparation of a polyHIPE filter: (a – b) mixing of two w/o HIPEs with 20 vol% oil phase (BeMA:EGDMA = 85:15 v/v) containing 5 w/v% Pluronic[®] L-121 and 2 w/v% BPO (as received, emulsion 1) or 2.38 vol% DMPT (emulsion 2); (c) a plug of the mixed HIPE is sucked in a plastic tubing prefilled with water; (d) the plug is left to polymerize immersed in water for 15 min; (e – f) colored water is sucked through the polymerized HIPE plug showing that the polyHIPE is permeable to water; (h, i) SEM images taken (h) inside and (i) at the bottom surface of the polyHIPE confirming its open pore structure. (j) polyHIPE produced in a similar way inside a ‘Y’-shaped glass tubing is used as a static mixer for foam generation. Scale bars are (a – g, j) - 10 mm; (h, i) - 100 μ m. For more details see the Supporting information.

Figure captions

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