Supporting Information

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

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Curing dynamics of polymerizing samples

The curing process of polymerizing samples was studied by a home-built experimental setup shown in Figure S1. A cylindrical sample tube (inner diameter 16.2 mm) loaded with the HIPE sample (5 mL) sits on a precision balance (Sartorius Entris 64-1S) connected to a computer. A cylindrical PTFE probe with a diameter of 3.175 mm is partially immersed in the sample at a depth of 10 mm. The probe is firmly attached to a motor driven platform which can be moved up or down at a constant speed by a step motor controlled by the computer. The step motor is used to oscillate the probe at a constant amplitude of 0.6 mm and period of 6 s. This generates oscillations in the weight measured by the balance which are recorded by the computer. A K-type thermocouple mounted inside the probe (with its tip protruding 5 mm out from the probe) is used to monitor the temperature inside the sample using a digital thermometer (HH306A, Omega) also connected to the computer. Another thermocouple is used to not shown).



Figure S1. Experimental setup for studying the curing dynamics of polymerizing samples.

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The main contribution to the amplitude of weight oscillations (A_c) corrected for buoyancy $(A_b \sim 0.005 \text{ g})$, $A_c = A_w - A_b$, is from the viscosity of the sample. In order to relate the amplitude of weight oscillations, A_c , to the liquid viscosity, measurements with seven silicone oils with increasing viscosity in the range 48 mPa s to 1048 Pa s have been made. The A_c measured for those silicone oils is plotted against their dynamic viscosity in a double logarithmic scale in Figure S2. The data fit very well a power function.



Figure S2. Amplitude of weight oscillations corrected for buoyancy, A_c , for silicone oil samples measured by the setup shown in Figure S1 at 25 °C and plotted against the dynamic viscosity of the oil. The probe oscillated with amplitude $a_p = 0.6$ mm and a period of 6 s during the measurements. The solid line is the best power function fit.

Typical plots of weight and amplitude of oscillations versus time recorded during the polymerization of a HIPE sample (80 vol% water phase) using an oscillating probe are shown in Figure S3a. The apparent viscosity and temperature versus time during the polymerization are shown in Figure S3b.



Figure S3. (a) Typical plots of weight oscillations (left axis) and amplitude, A_w , versus time recorded during the polymerization of a w/o HIPE sample (80 vol% water phase) using an oscillating probe. The probe immersed at 10 mm in the sample oscillated with a constant amplitude $a_p = 0.6$ mm and a period of 6 s. The amplitude of weight oscillations, A_w , increases with time because the viscosity increases due to polymerization. (b) Apparent viscosity and temperature of the sample during polymerization. The vertical arrows point to the pot life, t_p (the time for doubling the initial viscosity) and the time at $\eta_a = 1000$ Pa s adopted by us as the gel time, t_{gel} . The small dip in the viscosity curve near the time of temperature maximum is observed because the sample has solidified. Therefore, the values at longer times do not have a meaning of viscosity, but are due to the friction of the PTFE probe sliding over the polymer lubricated by the water. The zero time corresponds to the moment when the DMPT accelerator has been added to the sample to initiate the polymerization.

Pore size and pore throat size distributions



Figure S4. (a) A SEM image of the polyHIPE sample M90R. The scale bar is 10 μ m. (b) Cumulative (circles and squares) and relative (diamonds and triangles) frequencies of pore diameters constructed from 400 measurements. Blue squares and red triangles correspond to the true diameters determined from the measured size distributions (circles and diamonds) by stereological analysis following the Saltykov method.^[1] The vertical arrows show the respective diameters do.1 (10% of diameters are smaller than do.1), do.5 (median diameter) and do.9 (90% of diameters are smaller than do.9). (c) Cumulative (circles) and relative (diamonds) frequencies of pore throat diameters constructed from 400 measurements.

Table S1. Pore diameters (d_{0.1}, d_{0.5} and d_{0.9}) determined from SEM images of polyHIPE samples produced from w/o emulsion templates with varying volume fraction of water (ϕ_w) by redox-initiated (M75R – M90R) or thermo-initiated (M75T and M80T) polymerization (see Table 1). Span = (d_{0.9} - d_{0.1})/d_{0.5}. The diameter errors shown correspond to the 95 % confidence interval determined by using a nonparametric Bootstrapping method with 1000 resamplings.^[2]

Sample	\$\$ _w [vol%]	d _{0.1} [µm]	d _{0.5} [µm]	d _{0.9} [µm]	Span
M75R	75	12 ± 1	16 ± 1	30 ± 4	1.1 ± 0.3
M80R	80	16 ± 2	23 ± 1	37 ± 3	0.9 ± 0.2
M85R	85	19 ± 2	26 ± 1	40 ± 3	0.8 ± 0.2
M90R	90	22 ± 2	29 ± 2	49 ± 6	0.9 ± 0.3
M75T	75	12 ± 1	17 ± 1	25 ± 2	0.8 ± 0.2
M80T	80	11 ± 1	17 ± 1	25 ± 2	0.8 ± 0.2

Table S2. Pore throat diameters (d_{0.1}, d_{0.5} and d_{0.9}) determined from SEM images of the polyHIPE samples shown in Table S1.

Sample	φ _w [vol%]	d _{0.1} [µm]	d _{0.5} [µm]	d _{0.9} [µm]	Span
M75R	75	1.3 ± 0.2	2.4 ± 0.2	4.1 ± 0.3	1.2 ± 0.2
M80R	80	1.8 ± 0.3	3.7 ± 0.4	7.1 ± 1.0	1.4 ± 0.4
M85R	85	2.0 ± 0.3	4.5 ± 0.5	8.5 ± 1.0	1.4 ± 0.3
M90R	90	3.1 ± 0.4	6.4 ± 0.6	11.8 ± 1.1	1.4 ± 0.3
M75T	75	1.5 ± 0.1	2.4 ± 0.2	3.9 ± 0.3	1.0 ± 0.2
M80T	80	1.6 ± 0.2	2.7 ± 0.2	4.8 ± 0.5	1.2 ± 0.3

Porous materials produced from isobutyl methacrylate-based HIPEs



Figure S5. An image of a typical polyHIPE produced by redox-initiated polymerization of a w/o HIPE template with 80 vol% inner water phase (deionized water) and an oil phase containing 85 vol% isobutyl methacrylate (IBMA), 15 vol% EGDMA, 5 w/v% Span 80 surfactant, 1 w/v% BPO initiator (as received) and 1.19 vol% DMPT accelerator. The HIPE is prepared and polymerized in air at room temperature.

In situ preparation of polyHIPE filters by redox-initiated polymerization of two component HIPE systems

Two w/o HIPEs with the same inner phase (80 vol% deionized water) were prepared. The oil phase of both emulsions contained 85 vol% monomer (MMA or BeMA), 15 vol% EGDMA crosslinker and 5 w/v% Pluronic[®] L-121 surfactant. 2 w/v% BPO initiator (as received) was added to the oil phase of emulsion 1, while 2.38 vol% DMPT was added to the oil phase of the second emulsion. The polymerization was triggered by mixing equal volumes of the two emulsions and vigorous hand stirring using a stainless-steel spatula for 1 minute. Then, 0.5 mL of the mixed emulsion were sucked in a plastic tube (a pipettor tip) connected to a syringe pump via plastic tubing prefilled with water. The tube was transferred to a beaker filled with water and left to polymerize. Water colored with blue ink was sucked through the polyHIPE to confirm its open pore structure and suitability for filtration applications.

The filter preparation is shown in Video S1 (BeMA system) and Video S2 (MMA system). The oil phase in MMA-based HIPEs was colored with a small amount of So-Strong® Red oil soluble colorant (Smooth-On Inc., USA). The BeMA containing system polymerized much quicker (a pot life of 3.5 minutes) than the MMA-base system.

The polyHIPE filter used as a static mixer for foam generation was prepared in a similar way. A small amount of the mixed emulsion was sucked in the middle section of 'Y'-shaped glass tubbing prefilled with water and left to polymerize. Then, air and water solution of a liquid detergent (Fairy washing liquid) were simultaneously pumped through two of the 'Y'-junction arms and the foam flowing out from the 3rd arm was collected as illustrated in Figure 2j.

Porosity and mechanical testing of polyHIPEs

Purified cylindrical polyHIPE samples with diameter 10.3 mm were cut to a length of 10 mm using a home-built low speed cutter with a diamond disc. The dimensions and mass of each sample were measured and the density of the porous material, ρ_f , determined. The porosity was calculated by Equation S1 using 1.20 ± 0.01 g cm⁻³ for the polymer density, ρ_p ,^[3] and averaged over at least 8 samples.

$$P(\%) = \left(1 - \frac{\rho_f}{\rho_p}\right) \times 100 \tag{S1}$$

The same samples were used in the compressional mechanical tests done according to the ASTM D1621 standard on a Mark-10 ESM303 force test stand (2.5 kN Series 5 load cell) at a compression rate of 1.2 mm min^{-1} at room temperature.

Effect of the crosslinker concentration

Table S3. Pot life (t_p) and gel time (t_{gel}) of w/o HIPE templates with 80 vol% water phase (deionized water) and different concentrations of EGDMA crosslinker and MMA in the oil phase (shown) containing 1 w/v% BPO initiator (as received) and 1.19 vol% DMPT accelerator. The porosity (P), compressive strength (σ) and Young's modulus (E) of the respective polyHIPEs produced by redox-initiated polymerization are also shown.

EGDMA [vol%]	MMA [vol%]	t _p [min] ^{a)}	t _{gel} [min] ^{a)}	P [%]	σ[MPa]	E [MPa]
10	90	20 ± 1	35 ± 1	83 ± 2	3.6 ± 0.1	70 ± 3
15	85	18 ± 1	27 ± 1	84 ± 2	3.2 ± 0.1	66 ± 1
30	70	11 ± 1	15 ± 1	84 ± 2	3.2 ± 0.1	63 ± 1

^{a)}Defined in Figure S3b.





Figure S6. Median diameter of emulsion droplets versus time after the preparation of w/o HIPE templates with 80 vol% inner aqueous phase of deionized water (circles, blue dashed line) or 0.12 M CaCl₂ aqueous solution (triangles, red line). The external oil phase contains 85 vol% MMA, 15 vol% EGDMA and 5 w/v% Pluronic[®] L-121 surfactant. The droplet diameters were determined from the cumulative size distributions constructed by measuring 400 droplets from optical microscope images using Image J software. The diameter of deionized water droplets (circles) increases significantly 2 hours after preparation due to Ostwald ripening. The presence of electrolyte in the droplets (triangles) slows down the Ostwald ripening and improves considerably the long-term stability of the emulsion template. The smaller initial size of droplets with CaCl₂ suggests that the electrolyte also improves the surface activity of the surfactant, thus adding extra stability to the emulsion. A similar electrolyte effect has been observed in w/o HIPEs stabilized by a nonionic Span 80 surfactant.^[4]

References

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