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Highly Porous Open-Cellular Monoliths from 2-Hydroxyethyl Methacrylate Based High Internal Phase Emulsions (HIPEs): Preparation and Void Size Tuning

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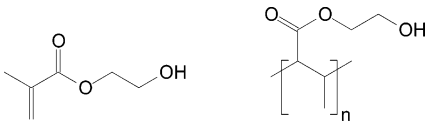
ABSTRACT: Preparation of highly porous (up to 80% pore volume) open-cellular monolithic cross-linked polymers from 2-hydroxyethyl methacrylate is reported. Oil-in-water and water-in-oil high internal phase emulsions are applied as porosity templates, resulting in an interconnected porous structure with void diameters between 550 nm and 18 μm. Significantly larger voids were obtained in the case of oil-in-water emulsions (between 5 and 18 μm) as opposed to water in oil emulsions (approx 600 nm). Controlled coarsening exploiting limited kinetical stability of emulsions was used to obtain monoliths with larger voids, diameters being enlarged 3-fold.

Introduction

Biocompatible materials based on 2-hydroxyethyl methacrylate (HEMA; Scheme 1) are of interest due to numerous applications, especially in the biomedical field.[1] PolyHEMA is a known biocompatible material, used in the production of contact lenses,[2] medical implants,[3] drug delivery material,[4] dental composites,[5] and scaffolds for tissue engineering.[6] While hydrogels are usually produced from HEMA to suit the biomedical applications, materials with permanent porosity are applied for the purposes like three-dimensional tissue engineering scaffolds[7] and supports for chromatography.[8] Furthermore, polyHEMA with permanently porous structure would be useful as a support for solid-phase organic synthesis, possessing a hydroxy reactive moiety for further functionalization. The ability to control the porous properties and morphology of polyHEMA is very important because specific applications require unique pore sizes. Especially in the case of supports for living cell growth this is crucial.[9] Interconnectivity of pores is also essential for biomedical applications as well as for the permeability of material when used as a support in a flow-through reactor. A way to produce highly porous polymers with connected pores, tunable pore size, and distribution is to employ a high internal phase emulsion (HIPE), where the volume fraction of the discontinuous phase is very high (it is generally accepted that, in a HIPE, the volume fraction of the internal phase is larger than 74.05%, which is maximum space occupiable by uniform spheres, although some recent interpretations suggest lower values).[10] Polymer materials prepared by the polymerization of the continuous phase of a water-in-oil (w/o) HIPE are well established[11] and have been applied as supports for organic synthesis,[12] filtration media,[13] chromatographic columns,[14] and scaffolds for tissue engineering.[15] On the other hand, less research has been published on the "inverse" oil-in-water (o/w) polyHIPEs, where the aqueous phase is continuous and contains monomers. Such an emulsion is more appropriate for the preparation of hydrophilic materials. Cooper et al. have applied super-critical carbon dioxide in water HIPEs for the preparation of polyacrylamide polyHIPEs.[16] Same technique was used to prepare poly(2-hydroxyethyl acrylate), while the attempts to produce polyHEMA in such a manner failed.[17] We were able to apply o/w HIPEs, using toluene as the oil phase, to prepare mechanically stable poly(acrylic acid) polyHIPEs.[18] Barbetta et al. described the use of o/w HIPEs for the preparation of gelatin-based porous materials as tissue engineering scaffolds.[19] HIPEs including polymers prepared by self-assembly of colloidal systems[20] and selective casting[21] have been reported by Kramer et al. Recently, protein-in-oil emulsions were applied to produce foam structures by cross-linking protein films at the phase boundaries.[22] In this paper, we are reporting the preparation of polyHIPE materials based on HEMA using w/o and o/w high internal phase emulsions. The influence of emulsion type on the void size inside the material is also reported. A method of coarsening by controlled droplet coalescence exploiting limited emulsion stability is described.

Scheme 1. HEMA and PolyHEMA Formulas



Experimental Section

Materials. 2-Hydroxyethyl methacrylate (HEMA, Aldrich) and ethyleneglycol dimethacrylate (EGDMA, Aldrich) were passed through a Al_2O_3 column prior to use to remove the inhibitors. *N*,*N*′-Methylene bisacrylamide (MBAA, Fluka) was recrystallized from methanol before use. Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic F68; Aldrich), polyethylene/polypropylene glycol (Pluronic L121; Gerbu), Polyoxyethylene(40) isooctylphenyl ether (Triton X-405, Aldrich), 4-(1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol solution (Triton X-705 70%, Aldrich), ammonium persulfate (APS, Fluka), *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TEMED, Fluka), cyclohexane (Kemika), 1,4-dioxane (Kemika), 2-propanol, calcium chloride hexahydrate (Merck), *n*-heptane (Kemika), and hexane (Fluka) were all used as received.

Preparation of HEMA/MBA PolyHIPE from Oil-in-Water High Internal Phase Emulsion. For the sample **A1** (75% pore volume, 13% cross-linking): 2.20 g (16.90 mmol) of HEMA was added to 5.20 g of deionized water. The cross-linker MBAA (0.40 g, 2.59 mmol), initiator APS (0.07 g, 0.31 mmol), and surfactant Pluronic F68 (1.50 g) were dissolved in the above HEMA solution.

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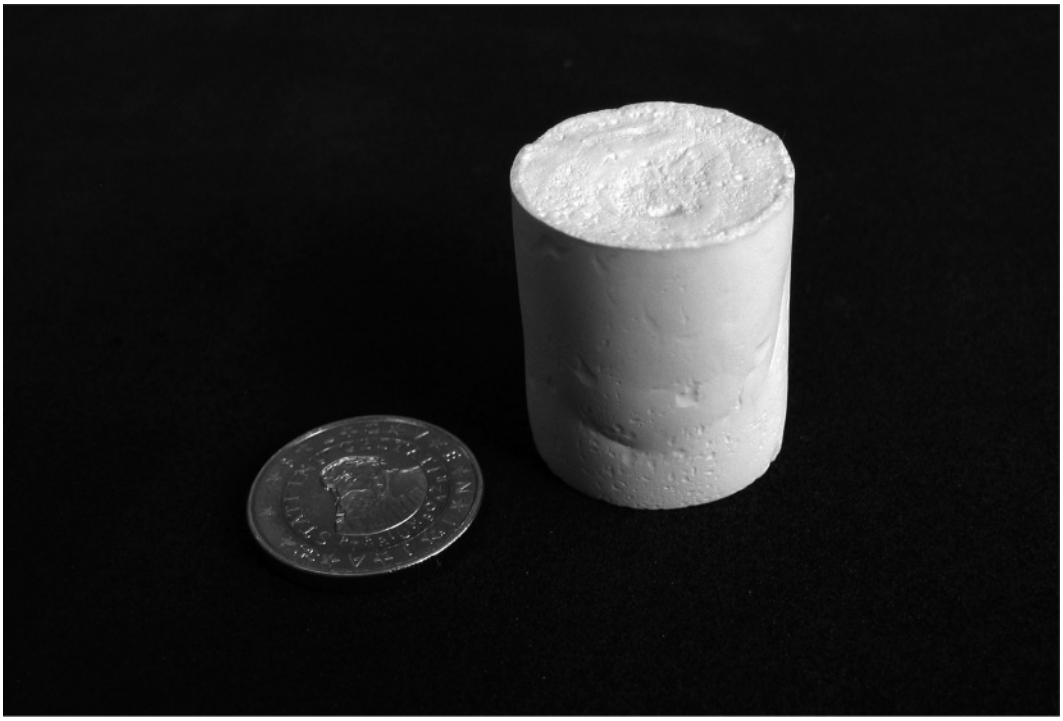


Figure 1. Photograph of the monolith **A1**.

Cyclohexane (22 mL) was added dropwise to the monomer solution under constant stirring with an overhead stirrer at 350 rpm. Once all cyclohexane has been added, stirring was continued for a further 30 min to produce a uniform O/W emulsion. Stirring of the emulsion was then reduced to 20 rpm, and the reducing agent TEMED (0.06 mL, 0.52 mmol) was added. After 3 min of additional stirring at 20 rpm, the emulsion was transferred to the mould (polyethylene container) and cured at room temperature for 1 h. The resulting monolith was immersed in 2-propanol for 24 h, purified via Soxhlet extraction with 2-propanol for 24 h, and dried under vacuum at 60 °C.

Preparation of HEMA/EGDMA PolyHIPE from Water-in-Oil High Internal Phase Emulsion. For the sample **B1** (75% pore volume, 10% cross-linking): 2.30 g (17.67 mmol) of HEMA, 0.39 g (1.97 mmol) of EGDMA, and 2.4 g of Pluronic L121 were added to 4.5 g of dioxane. The aqueous phase, consisting of 0.08 g (0.35 mmol) of APS and 0.24 g of calcium chloride hexahydrate in deionized water (21 mL), was added dropwise to the organic phase while stirring with an overhead stirrer at 400 rpm. Once all the aqueous phase had been added, stirring was continued for a further 30 min to produce a uniform w/o emulsion. Stirring was reduced to 20 rpm, and 0.06 mL (0.52 mmol) of TEMED was added. The emulsion was transferred to the mould (polyethylene container) and cured at room temperature for 1 h. The resulting monolith was immersed in 2-propanol for 24 h, purified via Soxhlet extraction with 2-propanol for 24 h, and then dried under vacuum at 60 °C.

Time-Dependent Droplet Coalescence Experiments. Precursors HIPEs for the samples **A2**−**A4** were stirred at 20 rpm for 1, 2, or 12 h. For each HIPE, an optical micrograph was recorded. Emulsion was cured by the addition of 0.06 mL (0.52 mmol) of TEMED at room temperature for 1 h and purified via Soxhlet extraction with 2-propanol for 24 h.

Structural Characterization of the Monoliths. FTIR spectra were recorded on a Perkin-Elmer FTIR 1650 spectrometer (KBr pellets), optical microscope images were taken on a Carl Zeiss microscope with a digital camera, scanning electron microscopy (SEM) pictures were taken on a FEI Quanta200 3D, and mercury intrusion porosimetry was performed on a Pascal 440 porosimeter (ThermoQuest Italia, Rodano, Italy). The average droplet sizes of emulsions were measured from optical microscope image by the use of SemAfore software (version 4.01). At least 150 droplets were counted, analysis was repeated three times, and the average droplet size was calculated. The same procedure was performed for calculating average void sizes of monoliths from SEM pictures, using a correction factor of $2/(3^{1/2})$ to compensate for the statistical error.[23]

Table 1. Emulsion Composition Data

	crosslinker[b]				internal phase	
a	type	degree (mol %)	surface active agent[c]	CT[d] (h)	type	PV[e] (vol %)
A1	MBAA	11	Pl. F68	0	cyclohexane	75
A2	MBAA	11	Pl. F68	1	cyclohexane	75
A3	MBAA	11	Pl. F68	2	cyclohexane	75
A4	MBAA	11	Pl. F68	12	cyclohexane	75
A5	MBAA	11	Pl. F68	0	cyclohexane	85
B1	EGDMA	17	Pl. L121	0	1,4-dioxane	75
B2	EGDMA	30	Pl. L121	0	1,4-dioxane	75

[a] Sample **A1**−**A5**: from o/w emulsion; **B1**−**B2**: from w/o emulsion. [b] MBAA = *N*,*N*′-methylenebisacrylamide; EGDMA = ethyleneglycol dimethacrylate. [c] Pl. = Pluronic. [d] CT = Coarsening time in hours. [e] PV = Pore volume is the volume fraction of the internal phase.

Results and Discussion

Oil-in-Water HIPEs as Templates. The kinetic stability of a HIPE guides, in a great deal, the polymerization procedure in obtaining a polyHIPE material. As opposed to hydrophobic polyHIPEs prepared from a w/o HIPE, such as poly(4-vinylbenzyl chloride (VBC)) and polystyrene, the preparation of a more hydrophilic polyHIPE from an o/w HIPE usually requires more careful emulsion stabilization and polymerization. The preparation of poly(acrylic acid-co-methylenebisacrylamide) (MBAA), for instance, required the use of a redox initiating pair of *N*,*N*,*N*′,*N*′-tetramethylethylendiamine (TEMED) and ammonium persulfate (APS).[18] Attempts to prepare an o/w HIPE, using toluene as the organic phase (as used with poly(acrylic acid) polyHIPE) did not yield a stable emulsion, experimenting with various nonionic surfactants (poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol); Pluronic F68, polyoxyethylene(40) isooctylphenyl ether; Triton X405, 4-(1,1,3,3,-tetramethylbutyl) phenyl-polyethylene glycol solution; Triton X705). Toluene, which has an appreciable

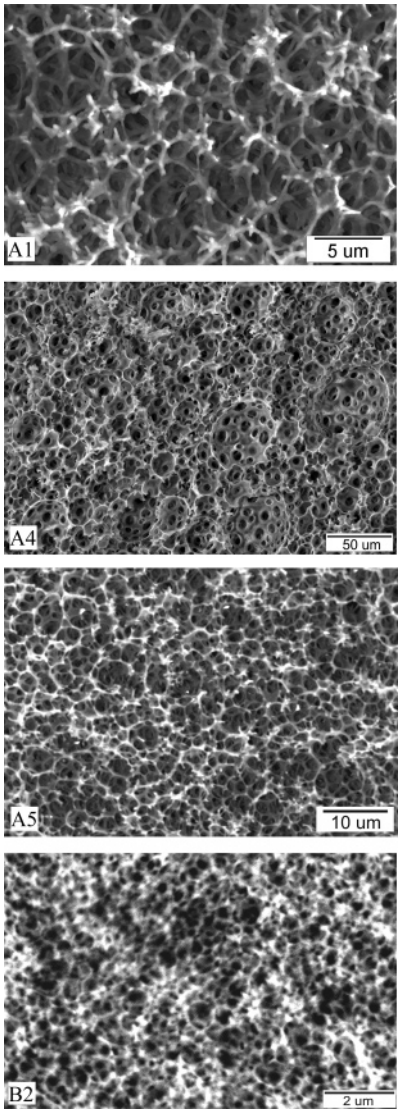


Figure 2. SEM pictures of polyHIPEs **A1**, **A4**, **A5**, and **B2**.

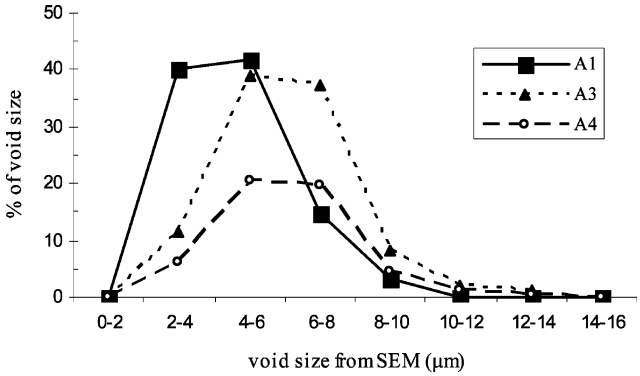


Figure 3. Void size distribution of PolyHIPEs **A1**, **A3**, and **A4**.

dipole moment (0.31 D at 20 °C), is partially miscible with HEMA, and emulsions based on HEMA and toluene were insufficiently stable to make polyHIPE materials. To overcome this problem, nonpolar solvents were used in place of toluene. The use of *n*-heptane (dipole moment 0) and hexane (dipole moment 0.08 D) did not result in an emulsion stable enough to yield solid polymers (phase separation occurred prior to polymerization), while the use of cyclohexane (dipole moment 0) yielded kinetically stable HIPE (75% pore volume, cross-linked with 11 mol % MBAA), which led to, after the addition

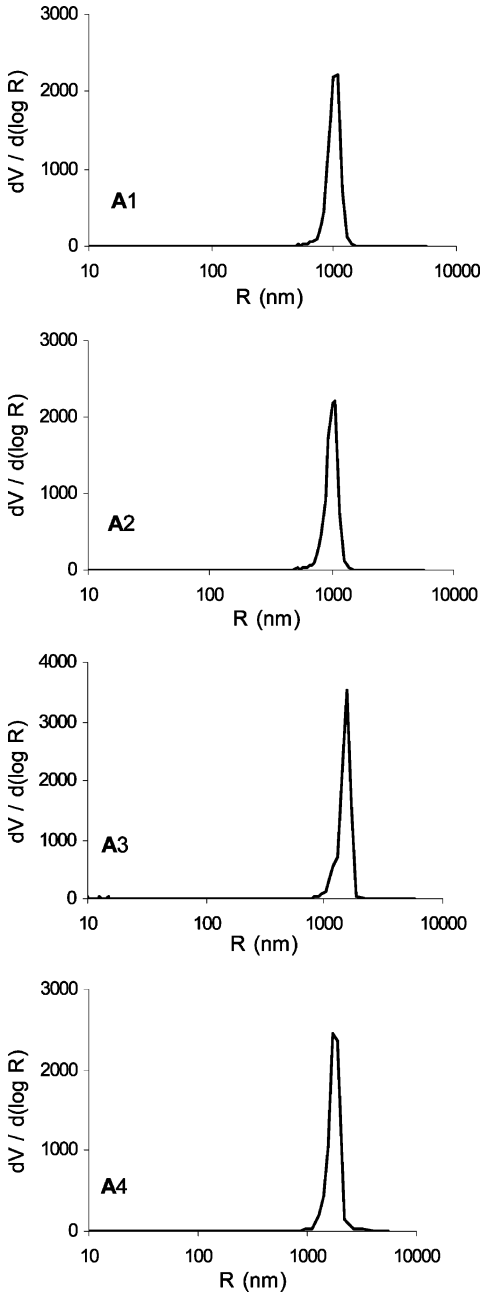
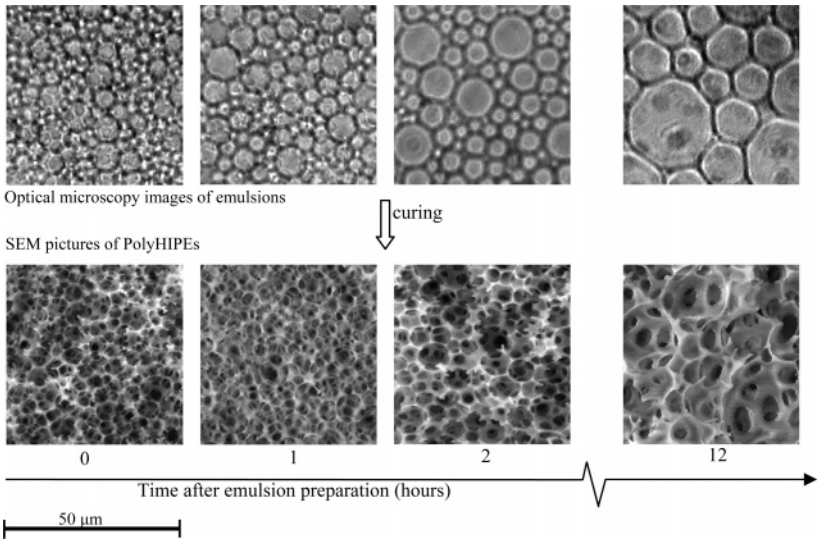


Figure 4. Mercury porosimetry data for PolyHIPEs.

of the initiator (TEMED and APS), a solid monolithic polymer (**A1**, Figure 1). With respect to the material preparation, it has to be mentioned that the structure of the surfactant plays a vital role in stabilizing the emulsions. For o/w HIPEs surfactants, high hydrophilicity−lipophilicity balance (HLB) values are normally applied. Triton X-405 (HLB = 17.9) worked best for o/w acrylic acid polyHIPES, while in the case of HEMA, a surfactant with an even higher HLB, namely Pluronic F68 (HLB = 24) had to be applied (Table 1). Upon SEM analysis of **A1** (Figure 2), open cellular structure was evident, the voids being approximately 5.5 μm in diameter and the connecting pores approximately 2 μm in diameter. Void sizes were determined by SEM image analysis, while the interconnecting pore sizes were determined by mercury porosimetry and SEM image analysis. Achieving a narrow void size distribution in a polyHIPE material can be a difficult task because the highly concentrated emulsion tends to have a wider droplet size distribution so that a more efficient packing is achieved.[24] In our case (sample **A1**), approximately 51% of all voids were

Scheme 2. Influence of Time-Dependent Droplet Coalescence on the Morphology of PolyHIPEs



between 4.0 and 6.0 μm, while approximately 69% of all voids fell between 3.5 and 6.5 μm (Figure 3). Mercury porosimetry was used to determine the average pore size; however, the results of mercury porosimetry for polyHIPE samples have to be taken with some reservations due to the specific morphology of polyHIPE materials. We believe the mercury porosimetry data to actually give the interconnecting pore size as the average pore size (Figure 4), as we already discussed in our previous work.[14] When sufficient pressure of mercury is achieved, it penetrates through the interconnecting pores and fills the entire void immediately. Therefore, the entire void volume is assigned to the pore diameter of the interconnecting pore. From SEM images, it is difficult to give a correct evaluation of the interconnecting pore size because the pores are inside the material and are photographed at various angles. The figures resulting from SEM image analysis were, in our case, close to the ones from the mercury porosimetry; however, the porosimetry figures were used for further discussions and material characterization. FTIR spectroscopy confirmed the chemical composition (for hydroxyl group at 3400 cm^{-1}, acrylate carbonyl group at 1727 cm^{-1}, amide carbonyl group at 1676 and 1532 cm^{-1}). The observed shrinkage of the material after drying was approximately 20% in all directions. The dried sample **A1**, when immersed in water, had swollen to approximately 1.5× size of the dried piece while uptaking 10.95 g of water per gram of polymer. To further enhance the porosity, more organic phase was added, up to 85%. Stable emulsion was formed and polyHIPE structured monolith resulted (**A5**; Figure 2; average void size 4.6 μm, average windows size 1.5 μm). However, the material shrinkage upon drying was more noticeable than for the 75% pore volume sample **A1**, suggesting poorer mechanical properties of the more porous material.

Water-in-Oil HIPEs as Templates. Because HEMA is also miscible with some more polar organic solvents, we experimented with obtaining a HEMA monolithic polyHIPE using a w/o HIPE, monomers being in the oil phase and using the aqueous phase as the porosity template. 1,4-Dioxane (dipole moment 0.45 D) was found to be an appropriate medium for the continuous phase, with a 0.8% aqueous solution of $CaCl_2$ as the internal emulsion phase. Again, the choice of surfactant was very important. Sorbitan monooleate, used for styrene and VBC w/o HIPEs was not convenient for this system, so we tested at first sorbitan trioleate (HLB = 1.8); however, the emulsion was most efficiently stabilized using Pluronic L121 (HLB = 0.5), yielding sample **B1** (75% pore volume, 17 mol % of crosslinker ethyleneglycol dimethacrylate (EGDMA)). However, after the purification and drying, the shrinkage of the material was significant (approximately 60%). Upon employing more cross-linker (EGDMA), increasing the amount to 30%, the sample **B2** was obtained, exhibiting almost no shrinkage after drying and the internal open porous architecture was retained (Figure 2). When compared to sample **A1** (o/w HIPE), the void and interconnecting pore size is much smaller (average void size approximately 0.64 μm, average interconnecting pore size approximately 0.19 μm as opposed to 5.5 and 2.0 μm for **A1**). The higher cross-linking degree also influenced the swelling behavior. The sample **B2** showed no significant swelling upon immersion in water while still uptaking 7.59 g of water per gram of polymer.

Void Size Tuning. Because of different applications of polyHIPE materials requiring specific pore size, it is important to be able to control the parameters of morphology (void and interconnecting pore size). The use of polyHIPEs as supports for catalysts, scavengers, or reagents for organic synthesis will require smaller pores, thus enlarging the surface area and site accessibility however large enough to enable convective flow in the case of flow through applications.[25] On the other hand, the use of polyHIPEs as living tissue fabrication scaffolds normally requires void sizes bigger than 10 μm depending on the size of the specific cell it is to support.[9] The void size and void size distribution is largely dependent on the stability of the emulsion, while the interconnecting pores are created during the shrinkage of the material through the polymerization of the continuous phase and depend on, among other things, the concentration of monomers in the continuous phase.[24] To be able to control the void size means to control the stability of the precursor HIPE as the smaller droplets of the internal phase coalesce and bigger droplets are formed. Cameron et al. described a method of adding a small amount (approximately 2 vol % of the continuous phase) of both phase miscible solvents to the emulsion, thus causing a limited droplet coalescence and achieving up to 2.8-fold increase in the void size.[23] We found it difficult to control the void size with this method, as the stability was compromised to a degree of complete phase separation. However, because a rapid initiation system has been used for the polymerization of both o/w and w/o type HIPEs, we simply applied limited kinetical stability to achieve void size enlargement. The prepared o/w HIPE (75% pore volume,

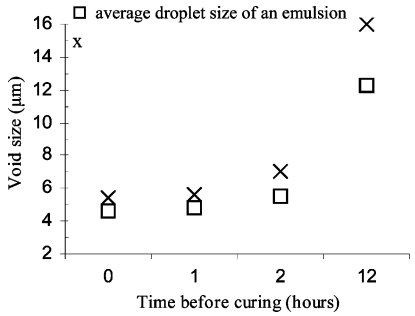


Figure 5. Influence of coarsening time on void size of PolyHIPEs.

Table 2. Morphology Characteristics of PolyHIPEs A1, A2, A3, A4

sample[a]	D^a (μm)	d^b (μm)	d/D
A1	5.45	2.00	0.37
A2	5.66	2.42	0.43
A3	6.99	2.90	0.41
A4	15.95	3.41	0.21

[a] D = average void size, determined from SEM images. [b] d = average interconnecting pore size determined by Hg porosimetry.

cross-linked with 11 mol % MBAA) was left almost unstirred (kept at 20 rpm for the ability to introduce TEMED) and monitored via optical microscopy. In the case of o/w HIPE, the time profile between 0 and 12 h showed an enlargement of the droplets of approximately 30% every 2 h, being enlarged from 5.5 μm at the end of stirring up to 16.0 μm after 12 h (Figure 5). The polymerization of "intermediate" HIPEs resulted in polyHIPEs with void sizes corresponding almost completely to precursor HIPEs, a factor of 1.05× (polymer void size/emulsion droplet size) can be observed (Scheme 2) reproducibly. The prolongation of coarsening time further than 12 h resulted in substantial inhomogeniety in droplet size and consequently in a material with a wider void size distribution. We expected the void size distribution to be broadened by allowing the droplet coalescence to occur. Indeed, a broadening trend can be observed; however, the broadening of void size distribution is not dramatic. Sample **A2** (1 h of coarsening time) has approximately 44% of voids of the diameter between 4 and 6 μm (in the interval of 2 μm) as opposed to 51% for the immediately cured **A1** and approximately 69% of the diameter between 3.5 and 6.5 μm (in the interval of 3 μm) as opposed to 69% for **A1**. While the void size distribution for **A3** (2 h coarsening time) is similar (in terms of wideness) to the distribution of **A2** (1 h time), the distribution gets wider for sample **A4**, which was cured 12 h after the emulsion preparation. Twenty-two percent of voids lie between 14 and 17 μm (in the interval of 3 μm) and approximately 62% of voids between 10 and 18 μm (in the interval of 8 μm; see Figure 3 for the presentation of void size distributions). The ratio of void size and interconnecting pore size is also a figure telling about the morphology of the material. For samples **A1**−**A3**, this ratio remains between 0.35 and 0.45 (Table 2), while for 12 h coarsening sample **A4**, it is lowered to 0.21, indicating smaller interconnecting pores compared to voids.

Conclusion

It has been shown that highly porous open cellular polyHEMA monolithic polymers can be obtained by employing a high internal phase emulsion, either o/w or w/o type. The material does not significantly shrink after drying, and the process of drying is reversible; the dried material can uptake solvent. The void and interconnecting pore size can be tuned within the interval of 0.5−14 μm for voids and 0.2−5 μm for the interconnecting pores, which is an important ability having different applications in mind. Limited kinetic stability allows the void size enhancement up to 3.5 times without the addition of solvents. Further work will be devoted to enhancing the ability to control the pore size within an even wider interval, applying a combination of added solvents and time-dependent coarsening methods. Concentrated emulsions can be a good alternative to other methodes like the application of sintered beads or the adsorption of silica particles for the preparation of highly porous materials.

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