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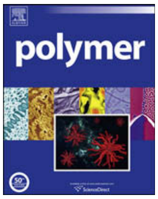

Stability of high internal phase emulsions with sole cationic surfactant and its tailoring morphology of porous polymers based on the emulsions

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ABSTRACT

Stable w/o high internal phase emulsion (HIPE) using cetyltrimethylammonium bromide (CTAB) as the sole surfactant was prepared with long time further mixing of the emulsion after the addition of aqueous phase was completed, although it was generally considered the emulsion would be unstable according to Bancroft rule. The delta backscattering data of these emulsions showed that the further mixing enhanced the stability of the HIPE significantly, because a dram partial of monomers was initiated in the period of preparing the emulsion, which reduced the diffusion of CTAB from the oil phase to aqueous phase and increased the viscosity of the continuous phase. In addition, the morphology of polyHIPEs based on this type HIPEs was tailored. Increasing aqueous phase fraction resulted in the increase of pore volume which could be up to 24.0 ml/g. Increasing the polymerization temperature led to an increase in average void and interconnect diameter in the resulting porous materials. Additionally, the presence of additives, PEG and ethanol, in the aqueous phase was found to increase the average void diameter remarkably. The interconnect diameter of the materials could be controlled at constant pore volume by tuning PEG and ethanol concentration in the aqueous phase. It was suggested that coalescence was the dominant effect in determining the morphology of the polyHIPEs prepared in the presence of PEG, and Ostwald ripening was the major role in tailoring the morphology of the porous materials with ethanol.

1. Introduction

Emulsion templating is a versatile method for the preparation of well-defined open porous monoliths. In general, the technique involves formation of high internal phase emulsion (HIPE) ($\geq$74.05 vol% internal phase, although some recent interpretations suggested lower values) [1–5]. The liquid but highly viscous nature of HIPEs allows the continuous phase to be given any shapes that conform to the shape of the reaction vessels. The polymerization of HIPEs provides a direct synthetic route to a variety of novel, porous monoliths (polyHIPEs) for applications such as biological tissue scaffolds [6–9], sensor materials [10,11], organic synthesis supports [12–15], ion-exchange resin [16] and separation media [17].

Emulsions are colloidal system made of liquid droplets dispersed in another liquid phase. They are produced by shearing these two immiscible liquids, which provides necessary energy to reach a metastable state through fragmentation of one phase into the other. It was realized at the early stages of emulsion research that the volume fractions of oil and water were not so important, and that the emulsion type and stability were determined primarily by the nature of the surfactant [18]. There is an important cornerstone guiding practical emulsion formulation: the Bancroft rule [19,20] which states that the liquid in which the surfactant is predominantly dissolved would form the external or continuous phase [21]. In the past several decades, highly significant advance [3,22–25] on water-in-oil (w/o) HIPE technology has been made with nonionic surfactant or mixing of nonionic surfactant and ionic surfactant, according to the rule.

However, relatively few works have been done on the issue of preparing porous materials using only ionic surfactant. Bass and Brownscombe [26] prepared crosslinked polyHIPEs using mixture of an anionic surfactant and one or more cationic surfactant, but without any explanation of the phenomenon was involved in the patent literature. Recently, we developed a new approach to obtain stable w/o HIPEs involving only cationic surfactant (e.g. cetyltrimethylammonium bromide, CTAB) [27], which contradicted to Bancroft rule. Compared with conventional method, this technique allows the synthesis of the functionalized porous materials based

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on HIPEs in one-step with uniform void and interconnect diameter, and provides an alternative approach to polyHIPEs for use in the green chemistry directly [28]. In this method, the cationic surfactant was dispersed in the oil phase before preparing the emulsion, and further mixing of the emulsion was involved after the addition of aqueous phase was completed. Although several studies [29–32] showed that in some circumstances, if the hydrophilic surfactant is introduced in the oil phase, the system is likely to produce a w/o emulsion upon immediate stirring with the aqueous phase even if Bancroft rule indicates it should be o/w one, because the external phase is the one that temporarily contains the surfactant. Lin et al. [32,33] announced that further long time mixing of the emulsion would result in phase inversion and form o/w emulsion. From what said above, it is important to propose a reasonable explanation concerning the abnormal behaviour of the emulsion obtained in our new method.

Moreover, the average voids and interconnects diameter of the polyHIPEs obtained in this method have been found to increase with increasing the cross-linking reagent [27], which are opposite to the conventional polyHIPEs obtained in the published papers [34,35]. The polyHIPEs were appealed so many applications, in particular as scaffolds for cell culture and tissue engineering, due to not only their highly porous and interconnected structure, but also the possibility of tailoring their morphology by tuning the physical properties of the HIPE prior to curing [36]. There are various methods by which the average void and interconnect diameter of polyHIPEs can be altered [34–38]. Nevertheless, all of these work only involved the HIPEs that obeyed Bancroft rule.

The physical degradation of emulsion is due to the spontaneous trend towards a minimal interfacial area between the dispersed phase and the continuous phase. Minimizing the interfacial area is mainly achieved by two mechanisms: coalescence and Ostwald ripening, which will lead to a coarsening of droplet diameter and a widening of droplet diameter distribution. Ostwald ripening results from the difference in chemical potential between droplets of different diameter. Smaller droplets have greater solubility in the continuous phase than larger droplets, because of Gibbs–Thomson and Kelvin effect [39–41]. The smaller droplets tend to lose their molecules and these molecules diffuse through the continuous phase and re-deposit into larger ones. This leads to an increase of average droplet size with time. Coalescence is considered results from the thinning and rupture of the thin interfacial films between droplets [39]. The nature and concentration of surfactant and the strength of the interfacial film are important parameters in controlling the rate of coalescence. The coalescence and Ostwald ripening will therefore affect the final morphology of porous materials derived from HIPEs.

In this study, a causation of the stability of the HIPEs with CTAB as the sole surfactant was proposed, and methods for controlled emulsion stability were also suggested with the intention of tailoring the morphology of polyHIPEs.

2. Experimental

2.1. Materials

Styrene (St, 99%, Shanghai Lingfeng Chemical Reagent Ltd. Co.) was distilled under a reduced-pressure nitrogen atmosphere. Divinylbenzene (DVB, 80%, the remainder being *m*- and *p*-ethylstyrene, Aldrich) was purified by passing through neutral chromatographic aluminum oxide to eliminate the inhibitor. Ammonium persulphate (APS, 98%, Shanghai Lingfeng Chemical Reagent Ltd. Co.) was purified via recrystallization. Poly(ethylene glycol) (PEG, $\overline{M}_n = 400$, Dow Chemical Company), ethanol (99.7%, Shanghai Zhenxing No. 1 Chemical Plant), CTAB (99%, Shanghai Feixiang Chemical Factory), toluene (99.5%, Shanghai Lingfeng Chemical Reagent Ltd. Co.), hydroquinone (99%, Acros Organics), *p-tert*-butylcatechol (TBC, Acros Organics) and polystyrene (PS, $\overline{M}_W = 24,000$, Aldrich) were used without further purification.

2.2. HIPE preparation and polymerization

An oil phase consisting of 9.0 ml St, 1.0 ml DVB and appropriate CTAB was added to a 250 ml three-necked round-bottomed flask. The mixture was stirred continually at 300 rpm using a D-shaped PTFE paddle connected to an overhead stirrer. After the mixture was stirred steadily for 10–15 min, the aqueous phase consisted of 90 ml distilled water containing APS of 0.0078 mol/l and appropriate additive (PEG or ethanol) was slowly added to the mixture over a period about 2 h using a peristaltic pump. After the addition of aqueous phase was completed, the agitation was kept at constant for more than 5 h at 25 °C. Then the emulsion was poured into a mold and further polymerized at a given temperature over 12 h (at room temperature over 3 months). The polymerized material was removed from the mold, and extracted in a Soxhlet apparatus firstly with distilled water followed by ethanol to remove any impurities, and then dried to constant weight in a vacuum at 70 °C. For studying the effect of the further agitation after the addition of the aqueous phase was completed on the stability of the HIPEs, the following HIPEs with water volume fraction $f_W = 90\%$ were prepared: (1) the 10 ml mixture of St and DVB (9:1 v/v) as oil phase with 5 min further stirring of the emulsion; (2) the 10 ml mixture of St and DVB (9:1 v/v) containing PS of 1.0 wt% as oil phase with 5 min further stirring of the emulsion; (3) 10 ml toluene as oil phase with 5 h further stirring of the emulsion; (4) 10 ml toluene containing 1.0 wt% PS as oil phase with 5 min further stirring of the emulsion; (5) the mixture of St and DVB (9:1 v/v) containing 0.1 wt% TBC (as inhibitor) as oil phase with 5 h further stirring of the emulsion.

2.3. Characterization

The phase behaviour of HIPE was evaluated by measuring the Delta backscattering (Δ backscattering) of monochromatic light ($\lambda = 880$ nm) from the suspension employing an optical analyzer, Turbiscan Lab Expert (Formulaction, France). HIPEs in flat-bottomed cylindrical glass tubes (70 mm height, 27.5 mm external diameter) were placed in the instrument, and the backscattering of light from emulsion was then periodically measured along the height at 25 °C. The results are presented as the sedimentation profile, i.e., Δ backscattering versus time. The monomer conversion was determined by gravimetric method [42]. A HIPE sample was added with hydroquinone solution to stop the polymerization. The contents were dried in vacuum to constant weight. Conversion of this sample can be calculated from the original monomer content and polymer weight obtained.

For analysis, the polyHIPE samples were fractured into millimeter-sized pieces with a scalpel. To get the accurate amount of CTAB in the final polyHIPE, the quantitative analysis of bromine of the polymer sample with or without extraction was performed by Shimadzu Sequential X-Ray Fluorescence Spectrometer (XRF-1800, Japan) at room temperature. 1.6 g of each sample was pressed under 300 N/cm^2 pressure to produce a disc with 3 cm diameter. The disc was then measured by XRF at 95 mA. The CTAB in the extracted polyHIPE was obtained by comparing the net intensity of bromine in the extracted polyHIPEs sample with that in unextracted sample. The CTAB inside the polyHIPE without extraction was 0.8 wt% according to the initial amount of the surfactant. Pore volumes, average interconnect diameters and their distributions were recorded by mercury intrusion porosimeter using a Micromeritics Autopore IV 9500 porosimeter.

Samples were subjected to a pressure cycle starting at approximately 0.1 psia, increasing to 33,000 psia in predefined steps to give interconnect diameter and pore volume information. The morphologies of the porous materials were investigated with a JSM-6360LV SEM. Samples were mounted on aluminum studs using adhesive graphite tape and sputter coated with approximately 5 nm of gold before analysis. The average void diameters of the polyHIPEs were performed using the image analysis software Image J (NIH image). Average diameters measured in this way are underestimates of the real values. Therefore it is necessary to introduce a statistical correction [43]. The average void diameter (R) of each polyHIPE material in this work was achieved as Eq. (1).

$$R = \frac{2}{\sqrt{3}} r \tag{1}$$

where R is the equatorial value of void diameter and r is the diameter value calculated from the SEM image.

3. Results and discussion

3.1. Effect of further mixing of the emulsion

In attempt to determine the effect of further mixing of the emulsion on the emulsion obtained using CTAB as the sole surfactant, two HIPEs with 5 h (Fig. 1a) and 5 min (Fig. 1b) further stirring of the emulsion after the completed addition of aqueous phase were evaluated by measuring the backscattering data using a Turbiscan Lab Expert, respectively. Although both of the samples (Fig. 1a and b) appeared stable in the beginning time when the stirring was stopped, difference of the Δ backscattering data obtained from them has been detected by Turbiscan. Fig. 1a showed that the HIPE prepared with 5 h further stirring was very stable and no separation occurred in the testing time, moreover, the backscattering data of all height of the tested sample increased slowly and then kept constant during the test. The backscattering signal of Fig. 1b in the bottom of test tube increased monotonically (up to 30%) as test time escaped, while the backscattering data of the top

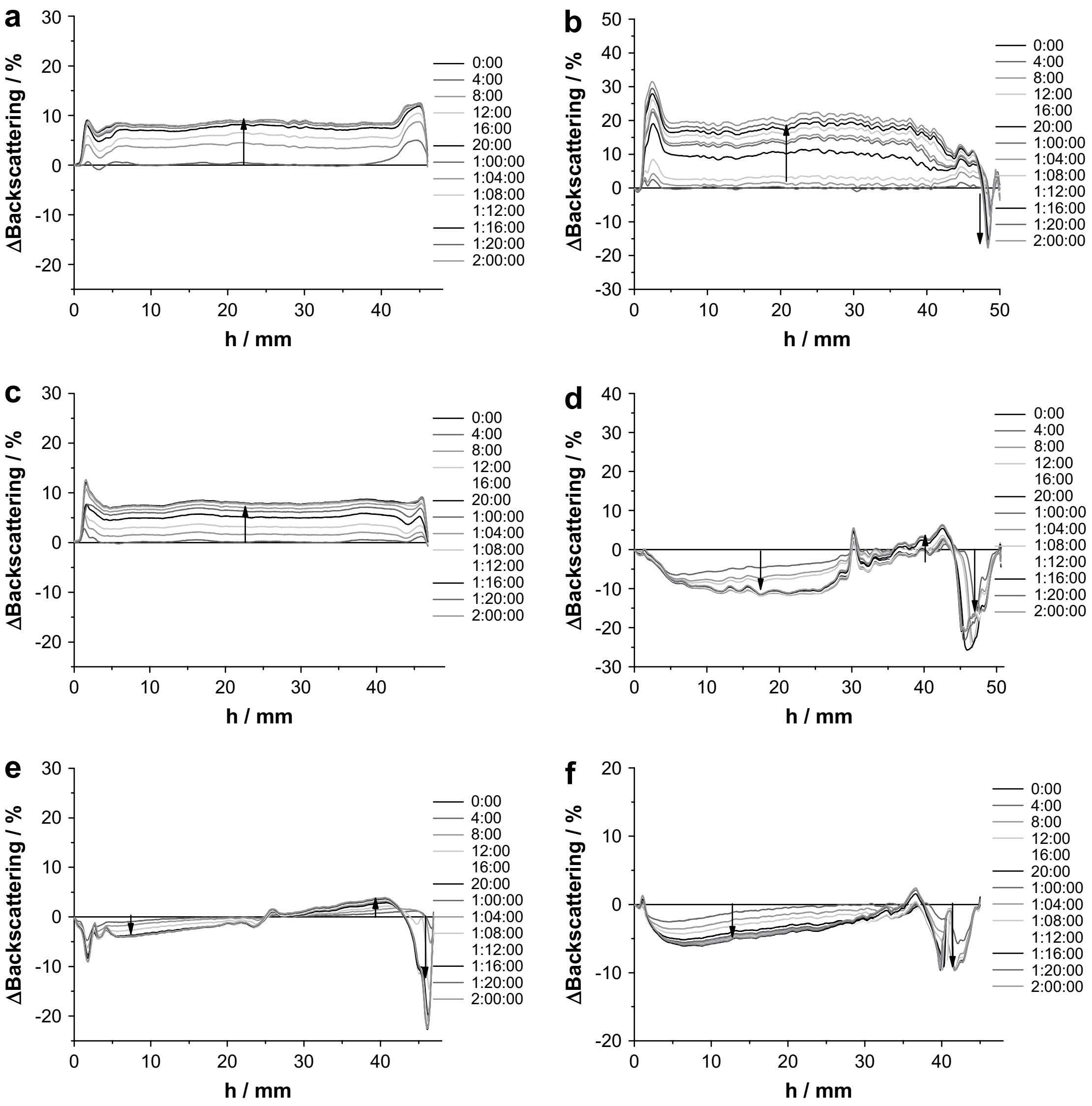

Fig. 1. Δ Backscattering data of w/o HIPEs which were prepared with 90 vol% water and using CTAB as the sole surfactant at 25 °C. (a) Mixture of St and DVB (9:1 v/v) as the oil phase with 5 h further stirring; (b) mixture of St and DVB (9:1 v/v) as the oil phase with 5 min further stirring; (c) mixture of St and DVB (9:1 v/v) containing PS of 1.0 wt% as the oil phase with 5 min further stirring; (d) toluene as the oil phase with 5 h further stirring; (e) toluene containing PS of 1.0 wt% as the oil phase with 5 min further stirring; (f) mixture of St and DVB (9:1 v/v) containing 0.1 wt% *p-tert*-butylcatechol (TBC) as oil phase with 5 h further stirring. These data are represented as a function of time.

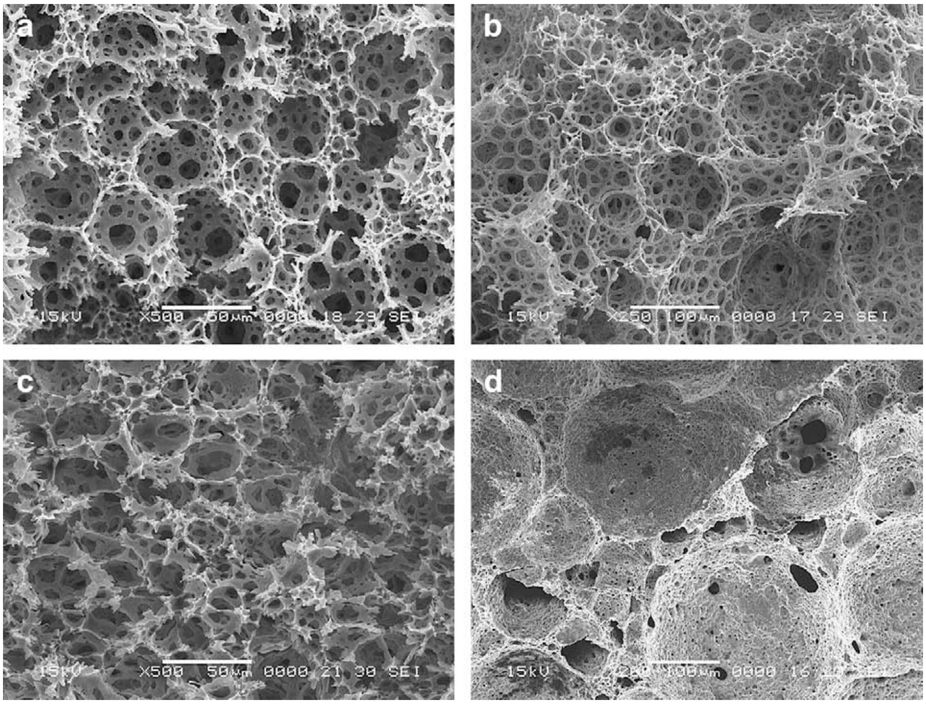

Fig. 2. SEM images of polyHIPEs prepared with different aqueous phase fraction (f_w) and polymerization temperature (T). The CTAB concentration was 0.8 wt%, relative to the organic phase. (a) $f_w = 90.0$ vol%, $T = 70$ °C, scale bar = 50 µm; (b) $f_w = 96.3$ vol%, $T = 70$ °C, scale bar = 100 µm; (c) $f_w = 90$ vol%, $T =$ room temperature, scale bar = 50 µm; (d) $f_w = 90.0$ vol%, $T = 90$ °C, scale bar = 100 µm.

of test tube decreased 20% which meant that there was clarification on the top of the sample (Fig. 1b). The change of the backscattering data of the samples showed that Fig. 1a became more stable and Fig. 1b separated with sedimentation in the test time [44]. In addition, with time further evolution (e.g. one week after the emulsion was prepared) the sample with 5 min further stirring separated completely with organic phase in the top and oil-in-water emulsion in the bottom, whereas, the sample with 5 h further agitation was very stable. This phenomenon showed that further mixing of the emulsion played an important role in preparing stable HIPEs with CTAB as the sole surfactant. The simple gravimetric detection of the HIPEs with 5 h further mixing after the addition of the aqueous phase showed that a dram part of the comonomers (1.0 ± 0.5 wt%) had been initiated during the preparation of the emulsions, however, tiny polymer (could be ignored) was found in the emulsion with only 5 min further agitation. We speculate that the stability of the HIPE with 5 h further agitation was probably caused by the polymerization of a dram part of the monomers during the continuous stirring, and the increase of backscattering data of Fig. 1a was resulted from the further polymerization of the comonomers during the testing period. The presence of polymer molecular in the continuous phase can increase the viscosity of the external phase of HIPE and hence cause the emulsion stability to coalescence and Ostwald ripening [45]. Strong evidence for the speculation was provided by the following experiments. (1) The HIPE (Fig. 1c) formed with mixture of St and DVB (9:1 v/v) containing PS of 1.0 wt% as oil phase was detected by Turbiscan with 5 min further agitation after the addition of aqueous phase was completed. The Δ backscattering data showed the emulsion was stable to sedimentation and the backscattering data increased in all of the height of the sample, which was similar to the change of backscattering data detected of Fig. 1a. It was confirmed that the presence of a small quantity of polymer in the organic phase could enhance the stability of the emulsion. (2) If the stability of the HIPEs in the present study depends on the polymerization of a dram partial of monomers during the preparation, the nature of organic phase will play an important role in the stabilization of the HIPEs. The unpolymerizable organic solvent, toluene, was used to form the w/o HIPE to determine the idea. Although the water-in-toluene HIPE could be prepared, the emulsion separated (formed sedimentation) quickly after the agitation was stopped (Fig. 1d), and transferred to three-phase equilibrium of a bicontinuous microemulsion, excess oil and excess water finally. This phenomena was similar to the typical phase behave of the emulsion disobeyed Bancroft rule [18]. (3) The HIPE (Fig. 1e) obtained with toluene containing PS of 1.0 wt% as the oil phase was prepared with 5 h further agitation. The destabilization of the emulsion occurred during the testing period, although the separating rate of this emulsion was slower than the HIPE that prepared under the same condition but without 1.0 wt% PS in the oil phase (compared Fig. 1e and d). This result implied the addition of PS enhanced the stability of the HIPE, however, the polymerization of the comonomers of the oil phase played more important role in the stabilization of the

Table 1
Morphological parameters of polyHIPEs prepared with different aqueous phase fraction and polymerization temperature.[a]

Temp (°C)	f_w[b] (vol%)	V_{pore}[c] (ml/g)	⟨d⟩[d] (µm)	⟨D⟩[e] (µm)	⟨d⟩/⟨D
70	83	4.5	2.3	21.3	0.11
70	90	7.6	6.7	39.0	0.17
70	95	14.7	19.1	52.2	0.37
70	96.3	24.0	20.8	58.0	0.36
Room temperature	90	8.2	3.9	27.2	0.14
60	90	7.8	6.4	32.2	0.20
80	90	6.9	10.0	42.1	0.24
90	90	6.3	10.5	119.2	0.09

[a] The CTAB concentration was 0.8 wt%, relative to organic phase.
[b] Relative to total liquid volume.
[c] Pore volumes determined by Hg porosimetry.
[d] Average interconnect diameter determined by Hg porosimetry.
[e] Average void diameter determined by SEM.

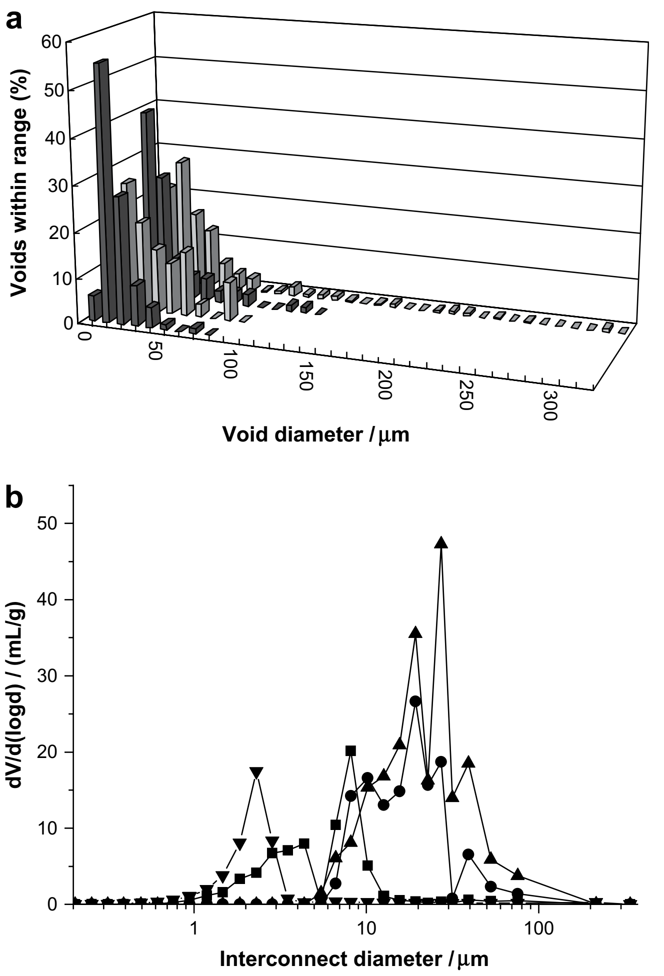

Fig. 3. Influence of water fraction (f_w) on void diameter distribution (a) and interconnect diameter distribution (b) of the resulting polyHIPEs obtained at 70 °C. (a) f_w (from front to back): 83.0, 90.0, 95.0, and 96.3 vol%; (b) f_w: 83.0 vol% (▼), 90.0 vol% (■), 95.0 vol% (•), 96.3 vol% (▲).

emulsion. (4) The HIPE (Fig. 1f) was prepared with the mixture of St and DVB (9:1 v/v) containing 0.1 wt% TBC (inhibitor) as oil phase, and was detected by Turbiscan. The change of the backscattering data showed that coalescence occurred, and there were sedimentation and clarification in the bottom and top of sample (Fig. 1f). (5) The polyHIPE (Fig. 2d) obtained by polymerization of the HIPE at room temperature in a relatively long period (e.g. in three months) showed that the comonomers could be initiated during the process of preparing HIPEs at 25 °C.

Although it was generally considered that further mixing of the emulsion after addition of the aqueous phase was completed would lead to instability of the w/o emulsion prepared with sole hydrophilic surfactant, the above experimental results indicated the further mixing in the present study played an important role in preparing stable HIPE, because partial comonomers in the oil phase was initiated during the agitation. The presence of polymer molecular in the continuous phase has been confirmed to increase the viscosity of the external phase of HIPE and hence cause the emulsion stability to coalescence and Ostwald ripening [45]. Moreover, the X-Ray Fluorescence Spectrometer analysis of polyHIPE obtained from the polymerization of the HIPE with 0.8 wt% CTAB (relative to the comonomers) showed that up to 70% of the initial amount of CTAB remained in the polymer which was extracted in a Soxhlet apparatus firstly with distilled water followed by ethanol. This meant that the major CTAB existed in the oil phase even after long time further stirring of the emulsion, although it was generally thinking that most of the CTAB should transfer from oil phase into aqueous phase during the agitation [32,33]. The abnormal surfactant behaviour was also due to the initiated comonomers. The resulting polymer molecules in the oil

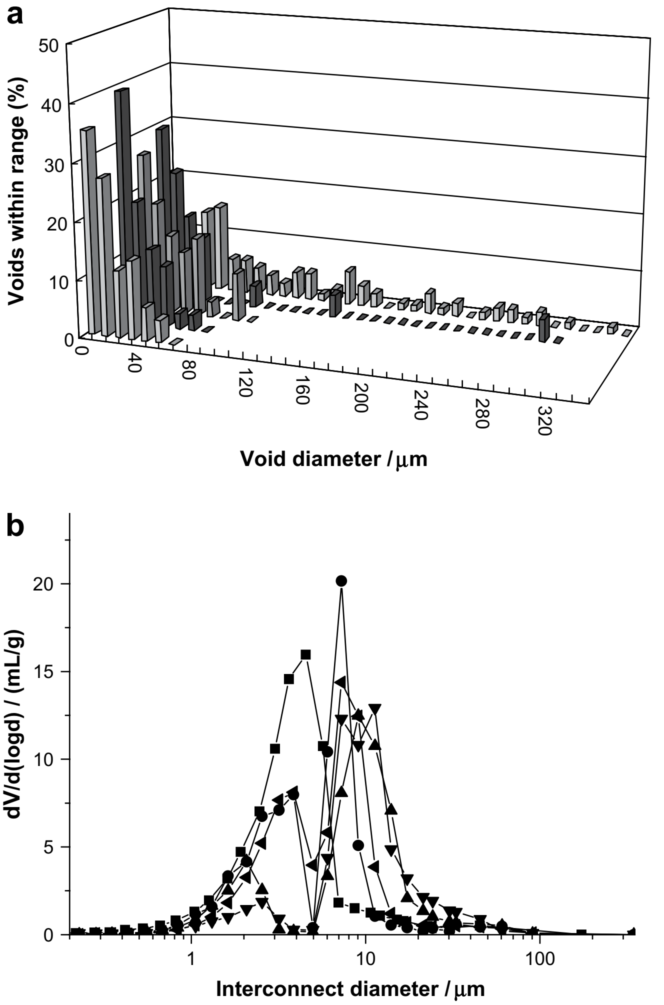

Fig. 4. Influence of polymerization temperature (T) on void diameter distribution (a) and interconnect diameter distribution (b) of the resulting polyHIPEs obtained with water fraction of 90.0 vol%. (a) T (from front to back): room temperature, 60, 70, 80, and 90 °C; (b) room temperature (■), 60 °C (◄), 70 °C (•), 80 °C (▲), 90 °C (▼).

Table 2
Morphological parameters of polyHIPEs prepared with different aqueous phase additives.

Additive (%)[a]	C_s[b] (wt%)	V_{pore}[c] (ml/g)	⟨d⟩[d] (μm)	⟨D⟩[e] (μm)	⟨d⟩/⟨D⟩
PEG (4.0)	0.8	8.6	9.1	43.0	0.21
PEG (13.4)	0.8	8.5	8.0	43.5	0.18
PEG (20.0)	0.8	8.5	5.1	57.8	0.09
PEG (25.0)	0.8	6.5	12.0	262.8	0.05
PEG (25.0)	1.6	8.2	6.6	77.1	0.09
Ethanol (1.0)	0.8	8.6	3.9	40.0	0.10
Ethanol (5.0)	0.8	8.3	4.5	42.1	0.11
Ethanol (8.0)	0.8	8.2	7.3	233.4	0.03
Ethanol (8.0)	1.6	8.3	7.0	222.2	0.03

[a] Polymerization temperature = 70 °C, aqueous phase additives (PEG and Ethanol) expressed as wt%.
[b] Relative to organic phase.
[c] Pore volumes determined by Hg porosimetry.
[d] Average interconnect diameter determined by Hg porosimetry.
[e] Average void diameter determined by SEM.

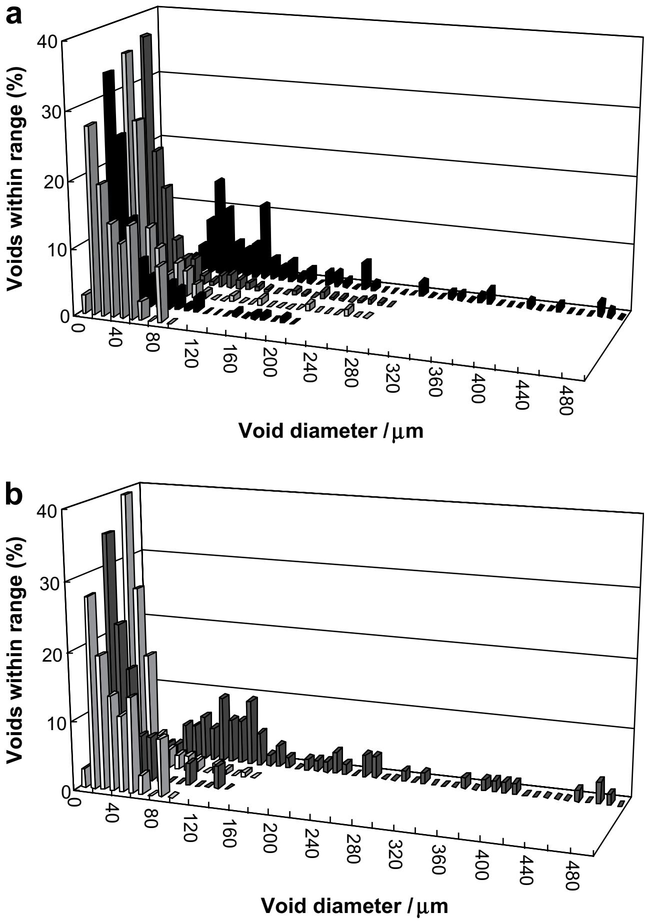

Fig. 5. Void diameter distribution plots of the polyHIPEs obtained with different aqueous phase additives at 70 °C. The aqueous phase volume fraction of the emulsions used as template was 90%. (a) PEG (from front to back: no PEG, 4.0 wt%, 13.4 wt%, 20.0 wt%, 25.0 wt%); (b) ethanol (from front to back: no ethanol, 1.0 wt%, 5.0 wt%, 8.0 wt%).

phase reduced the diffusion of CTAB from the continuous phase and interface into the aqueous phase due to the polymer–surfactant interaction [21,46]. And the containing of surfactant in the oil phase (continuous phase) enhanced the stability of the HIPE.

3.2. *Effect of water fraction*

Increasing the water volume fraction (f_w) of the HIPEs from 83 to 90, 95 and 96.3% was found to cause materials with more open, porous structure (Fig. 2a–b). The average void diameter ($\langle D\rangle$) increased steadily (Table 1), and the void diameter distributions became broad (Fig. 3a). With increase of f_w, the surfactant was required to stabilize an increasingly large interfacial area, simultaneously the surfactant concentration was kept constant relative to the monomer phase, thus the average water droplet size became correspondingly larger and the average void diameters increased. At the same time the skeletal framework (continuous phase in HIPEs) of the solid polyHIPEs became progressively thinner, which caused a concomitant thinning of the film of continuous phase around the aqueous droplets. As a result, increasing f_w caused increase in interconnect size (Table 1). As the f_w increased, the interconnect diameter with a broader distribution at higher value and a tail extending in the lower diameter range existed (Fig. 3b).

The ratio of the average interconnect diameter ($\langle d\rangle$) and void diameter ($\langle D\rangle$) provides a measure of the degree of interconnection. The values of the ratios for the materials prepared in this work are shown in Table 1. As f_w increased, the degree of interconnection ($\langle d\rangle/\langle D\rangle$) of the polyHIPE material increased, which was brought about by the larger increase in interconnect diameter compared to void diameter. This also suggested that increasing f_w caused instability of the emulsion.

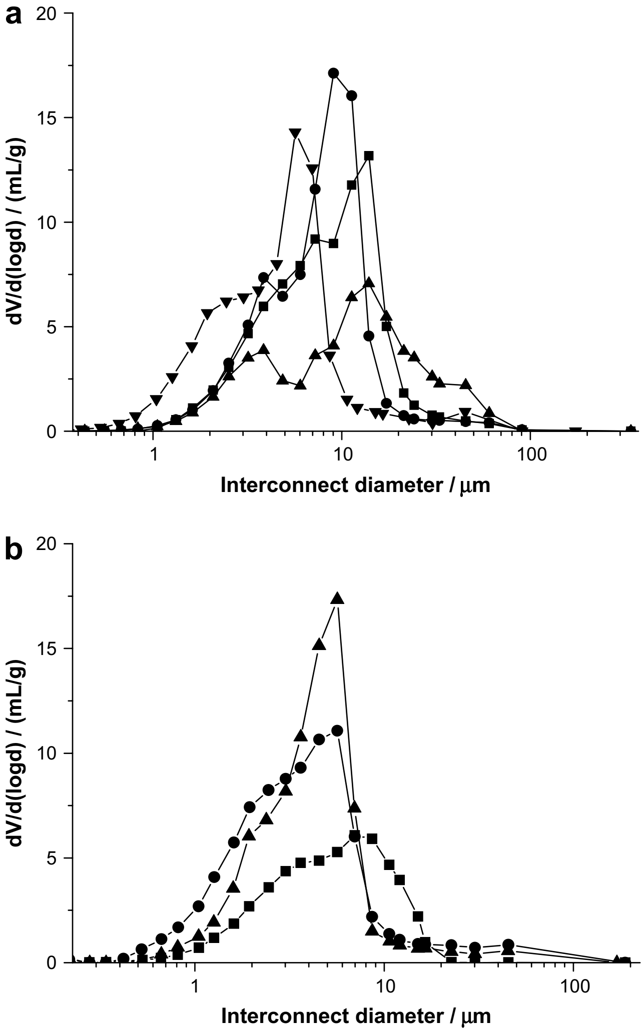

Fig. 6. Interconnect diameter distribution of the polyHIPEs produced using different aqueous phase additives at 70 °C. The aqueous phase volume fraction of the emulsions used as template was 90%. (a) PEG: 4.0 wt% (■), 13.4 wt% (•), 20.0 wt% (▼), 25.0 wt% (▲); (b) ethanol: 1.0 wt% (•), 5.0 wt% (▲), 8.0 wt% (■).

As shown in Table 1, with increasing of the water fraction, the pore volumes of these polyHIPEs increased rapidly and could be up to 24.0 ml/g, which suggests that the tuning of f_w can tailor both of the pore volume and interconnect diameter of this type polyHIPE material simultaneously.

3.3. *Effect of polymerization temperature*

Increasing the polymerization temperature in the range of room temperature to 90 °C was found to cause a striking increase in both the average interconnect and void diameter of the polyHIPEs (Table 1 and Fig. 2c–d). Increasing the polymerization temperature will increase thermal agitation and the frequency of contact of the water droplets, and hence results in a higher probability of droplet coalescence [40]. It is also noticed that as the emulsion temperature increases, the viscosity of the HIPE decreases, which will increase

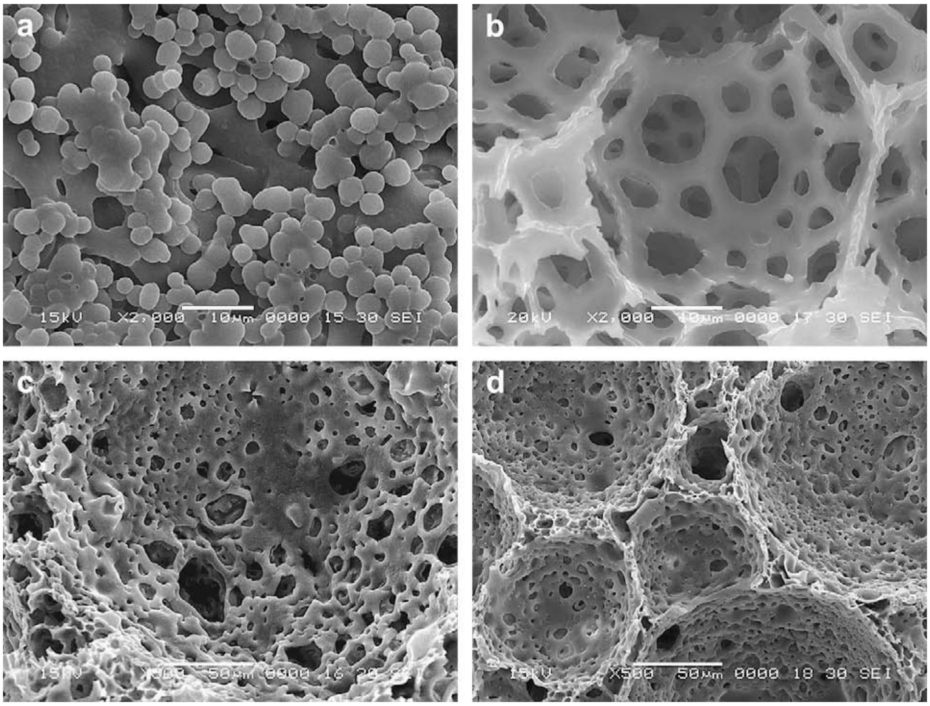

Fig. 7. Influence of surfactant concentrations (C_s) on the morphology of the polyHIPEs which was prepared with different aqueous phase additives at 70 °C. The aqueous phase volume fraction of the emulsions used as template was 90%. (a) PEG 25.0 wt%, $C_s = 0.8$ wt%, scale bar = 10 μm; (b) PEG 25.0 wt%, $C_s = 1.6$ wt%, scale bar = 10 μm; (c) ethanol 8.0 wt%, $C_s = 0.8$ wt%, scale bar = 50 μm; (d) ethanol 8.0 wt%, $C_s = 1.6$ wt%, scale bar = 50 μm.

surfactant diffusion from oil phase and interface to aqueous phase. This will promote droplet coalescence and cause phase separation of the emulsion. The opinion was supported by the fact that increasing CTAB concentration from 0.8 to 1.6 wt% resulted in remarkable decrease of the average void diameter (from 119.2 to 46.2 μm) of the polyHIPEs obtained at 90 °C.

It has been described that the gradual coarsening process would broaden the droplet size distribution of the emulsion with a tail extending towards larger droplet sizes [47]. Fig. 4a shows the distribution of the void diameters became broad with its tail towards larger void diameter with increasing polymerization temperature. This reinforces the idea that coalescence was the main mechanism of destabilization of the HIPE with increase of the emulsion temperature. The differential plot of intrusion versus interconnect diameter (Fig. 4b) shows that increasing the polymerization temperature resulted in increase of the average interconnect diameter and the narrower distribution of the interconnected diameters with a tail extending in the lower interconnected diameter.

It was also found that increasing the polymerization temperature resulted in increase of average interconnect and void diameter, however decrease of pore volume (Table 1).

3.4. *Effect of additives*

PEG and ethanol were chosen as the water-miscible organic additives to tailor the morphology of the polyHIPEs prepared by our method. Each of PEG and ethanol was added to HIPEs in increasing quantities until phase separation occurred. It was found that the emulsion could accept much higher quantities of PEG in aqueous phase (25.0 wt%) than ethanol (8.0 wt%).

Comparing with ethanol, the effect of PEG was much less observably on the emulsion due to the greater partitioning of PEG into the aqueous phase. As shown in Table 2, each additive produced an increase in the average void size. SEM image analysis indicated that increasing PEG and ethanol caused broader distribution of void diameter with a tail extending towards larger void diameters (Fig. 5).

The interconnect diameter distribution curves were quite different in nature between adding PEG and ethanol, but similar for all PEG and ethanol, respectively (Fig. 6). When PEG was used as the additive, the average interconnect diameter values decreased steadily with increasing PEG concentration from 4.0 to 13.4, and 20.0 wt%, then increased sharply with further increasing PEG concentration from 20.0 to 25.0 wt% (Table 2). Unlike PEG as an additive, the interconnect diameter decreased markedly following initial addition of ethanol (1.0 wt%) (comparing entry 6 in Table 2 with entry 2 in Table 1). As the concentration of ethanol was increased further, there was a tendency towards materials with a higher average interconnect diameter and a narrower diameter distribution.

The addition of PEG and ethanol to the aqueous phase also provided two good ways to tailor the average interconnect diameter at a given pore volume. The interconnect diameter decreased steadily, and the pore volume kept constant when the PEG increased from 4.0 to 13.4, and 20.0 wt% (Table 2). With increase of the ethanol concentration from 1.0 to 5.0, and 8.0 wt%, the interconnect diameter increased gradually, and the pore volume of materials was almost unchanged (Table 2). Essentially, these mean that the interconnect diameter can be controlled easily without changing the pore volume of polyHIPEs.

The degree of interconnection ($\langle d \rangle / \langle D \rangle$) decreased following addition of the ethanol by 1.0 or 5.0 wt% compared with that without additive (comparing entry 6 and 7 in Table 2 with entry 2 in Table 1), which was brought about by a little increase of average void diameter and large decrease of average interconnect diameter. While further increasing ethanol in the aqueous phase led to sharp decrease of the degree of interconnect because of much more increase of average void diameter than that of the average interconnect diameter (Table 2). In the case of PEG, the degree of interconnection decreased steadily, when PEG concentration increased (Table 2).

The presence of organic additives in the aqueous phase can cause the destabilization of the emulsion due to their partial solubility in both the continuous phase and disperse phase of the emulsion, which can enhance diffusion of water molecules from droplet to droplet and thus enhance Ostwald ripening [1,48]. Some works [9] have announced that the increase in void diameter of polyHIPEs with addition of a co-solvent or additive was solely due to Ostwald ripening. However, some researchers [1] reported that addition of co-solvents could disrupt the interfacial film and cause some of the surfactant to migrate in the bulk phase, hence promoting coalescence of the emulsion droplets. It is possible that the rate of both Ostwald ripening and coalescence are enhanced by addition of co-solvents to the emulsion, and that one process may dominate depending on the exact system. Fig. 7a and c show there were many micro-particles in the wall of the voids of the polyHIPEs with PEG of 25 wt%, however, there were many small holes in the walls of the one with ethanol of 8.0 wt%. The interesting morphologies of walls of the voids may explore the potential application of this new type polyHIPEs. The different phenomenon discovered above implied that there was different mechanism (Ostwald ripening and coalescence) dominated the two systems respectively.

To investigate whether Ostwald ripening or coalescence dominated the destabilization of the emulsion, the polyHIPEs with different C_s values were prepared using PEG (25.0 wt%) or ethanol (8.0 wt%) as additives. Increasing C_s from 0.8 to 1.6 wt% in PEG containing HIPE led to more open nature of the material with decrease of the void diameter (Table 2), and smooth walls of the voids (Fig. 7b). The results suggested that coalescence was the major cause of the increased void diameter in the presence of the PEG, since increasing C_s had great influence on the average void diameter of the polyHIPE material. However, when ethanol was used as an additive, the coalescence was not the major cause of increase of the void diameter, because there was no real discernible effect on void diameter and morphologies of the void walls of the material by increasing C_s in HIPEs, (comparing Fig. 7c with Fig. 7d). To explain the results obtained with 8.0 wt% ethanol when the surfactant concentration increased, we suppose that Ostwald ripening dominated the process. The idea supported the morphology of the wall in void of the materials with relative high ethanol concentration (Fig. 7c and d), suggesting that the large quantity of holes were produced by a great deal of w/o micelles in the interior of the continuous phase.

4. Conclusions

Stable w/o HIPEs were prepared using CTAB as the sole surfactant and with 5 h further mixing of the emulsion after complete addition of the aqueous phase, although it was generally considered the emulsions would be unstable according to Bancroft rule. The abnormal phase behaviour of the emulsions was studied by Turbiscan analysis. The Δ backscattering data of these emulsions suggested that the further mixing of HIPE after the addition of aqueous phase enhanced the stability of the HIPE significantly, because a dram partial of monomers was initiated in the period of preparing the emulsion. The resulting polymer molecules in the oil phase increased the viscosity of the continuous phase, and enhanced the stability of the emulsions. Moreover, the presence of polymer molecules in the oil phase would reduce the diffusion of CTAB from the oil phase to aqueous phase due to polymer–surfactant interaction.

The polymerization of this type HIPEs was carried out, and the morphology of the resulting polymers (polyHIPEs) was tailored with changing the aqueous phase volume fraction, polymerization temperature and adding additives to the aqueous phase. Increasing aqueous phase volume fraction resulted in the increase of both interconnect diameter and the pore volume of this type polyHIPEs simultaneously, The pore volume can be up to 24.0 ml/g. Increasing the polymerization temperature led to an increase in average void and interconnect diameter in the resulting porous materials. It is suggested that coalescence was major cause for the instability of the emulsion in this process, because increasing of the system temperature aqueous increased phase droplet collision, and enhanced surfactant diffusion from the oil phase to the aqueous phase.

The presence of additives, PEG and ethanol, in the aqueous phase was found to increase the average void diameter remarkably, and the interconnect diameter of the materials could be controlled by tuning the PEG and ethanol concentration in the aqueous phase at constant pore volume. The addition of PEG and ethanol affected not only the void and interconnect diameter but also the morphologies of the wall of the voids in the polyHIPEs. When the surfactant was kept at 0.8 wt% based on continuous phase, many micro-particles in the wall of the voids of the materials were observed with addition of PEG 25.0 wt%, and many micron-sized holes were detected in the wall with addition of ethanol 8.0 wt%. The interesting morphologies of walls of the voids may explore the potential application of this new type polyHIPEs. The different morphologies of the walls of the voids and the effect of the surfactant concentration on the morphologies of the porous materials suggested that coalescence was the dominant effect in determining the morphology of the polyHIPEs prepared in the presence of PEG, and Ostwald ripening was the major role in tailoring the morphology of the porous materials with ethanol.

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