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Synthesis of open porous emulsion-templated monoliths using cetyltrimethylammonium bromide

Shengmiao Zhang, Jianding Chen*

School of Materials Science and Engineering, East China University of Science and Technology, P.O. Box 289, 130 Meilong Road, Shanghai 200237, PR China

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Abstract

In recent years, open porous materials (polyHIPEs) have attracted more and more attention because of their specific properties and applications in biological tissue scaffolds, catalysis supports and ion-exchange resin. However, the surfactants used in this type material were limited to nonionic surfactants or the mix of nonionic surfactant and ionic surfactant. In this work, firstly well-defined polyHIPEs were synthesized by W/O emulsions with ionic surfactant alone (e.g., CTAB). Furthermore, the polyHIPEs with much higher pore volume (14.7 $cm^3\ g^{-1}$), uniform pore diameter and cell size were obtained by this method. Both the median pore diameter and average cell size of the polyHIPEs rose with increase of DVB concentration and/or water fraction.

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1. Introduction

Emulsion templating is a versatile method for the preparation of well-defined open porous monoliths. In general, the technique involves forming a high internal phase emulsion (HIPE) (≥60% v/v internal phase) [1–10]. 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 [10]. The polymerization of HIPEs (W/O) provides a direct synthetic route to a variety of novel, porous monoliths (polyHIPEs) for applications in biological tissue scaffolds [11–15], sensor materials [16], catalysis supports [17–19], ion-exchange resin [20]. Over the past two decades, highly significant advance on polyHIPE technology has been made and several groups have continued this till now. However, the surfactants they used were limited to nonionic surfactants or the mix of nonionic surfactant and ionic surfactant [1–21]. Furthermore, it is considered unsuitable to prepare HIPE (W/O) with only ionic surfactant [22], because ionic surfactants (e.g., cetyltrimethylammonium bromide (CTAB)) are water-soluble, which contradict the Bancroft rule. The rule states that the liquid in which the surfactant is more soluble would form the external or continuous phase [23].

In this work, a new method was demonstrated to obtain polyHIPEs with cation surfactant such as CTAB. Interestingly, the pore volume of the polyHIPEs was much higher than that of the previous work [24–27], which was very important for many applications (e.g., microbioreactor) [28]. The method was inspired by recent investigations on mechanism of continuous stirring inversion which have demonstrated that the stirring time played an important role in forming inversion emulsion [29,30] and the testing was proved to produce the polyHIPEs by long time stirring with ionic surfactant concentration in this work. The monomers chosen here were styrene (St) and divinylbenzene (DVB).

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* Corresponding author. Tel./fax: +86 21 64253375.
E-mail address: jiandingchen@ecust.edu.cn (J. Chen).

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2. Experimental

2.1. Materials

St (99%, Shanghai Linfeng Chemical Reagent Ltd. Co.) was distilled under a reduced-pressure nitrogen atmosphere; 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; CTAB (99%, Shanghai Feixiang Chemical Factory) was used as supplied.

2.2. Synthesis

The polyHIPEs were prepared by inverse emulsion polymerization. Appropriate St, DVB and CTAB were added to a three-necked flask fitted with an addition funnel and an overhead D-shaped stirrer paddle. The mixture was stirred steadily for 10–15 min and then the aqueous phase containing APS (0.07 mol/L based on monomers phase) as initiator was slowly added to the stirring mixture. To obtain a highly viscous emulsion, the stirring rate was kept constant for more than 5 h after the adding at 25 °C. Then the reaction liquid was poured into a mold and further polymerized at 70 °C over 12 h. The polymerized sample was removed from the mold, extracted in a Soxhlet apparatus firstly with distilled water followed by ethanol to remove any impurities, and dried to constant weight in a vacuum at 70 °C. The polyHIPEs conformed closely to the interior of the molds and no significant shrinkage was observed during the polymerization of the HIPEs, although some shrinkage always occurred when the polymers were dried.

2.3. Characterization

The HIPE stability was evaluated by measuring the back scattering using a Turbiscan Lab Expert (Formulaction, France). As soon as the stirring was stopped, the HIPE was transferred to a test tube and the HIPE stability was obtained from the back scattering data change of the test tube with elapsed time at 25 °C. The lower the change rate of the back scattering data is the more stable the HIPE will be [31,32]. For analysis, the polymer samples were fractured into millimeter-sized pieces with a scalpel. Pore volumes, median pore sizes and its 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 60,000 psia in predefined steps to give pore size/pore volume information. The morphologies of the monoliths 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 cell size of the polyHIPEs calculated from the microscopic images is underestimates of the real values. Therefore it is necessary to introduce a statistical correction [33]. The average cell size (R) of each monolith in this work was achieved from Eq. (1) [34].

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

where R is the equatorial value of cell size and r is the diameter value calculated from the confocal microscopic image.

3. Results and discussion

First of all, the emulsification of water and St was studied (temperature = 25 °C, volume fraction of water = 83%, CTAB and APS concentrations = 0.022 mol/L and 0.07 mol/L based on St, respectively). Milky-white O/W emulsion was formed and significantly stable after stirring was ceased at 25 °C, and no settling occurred even after extended periods (i.e., several days, see Fig. 1). The result suggested that this system was suitable for emulsion templating because the free-radical polymerization chemistry would be expected to occur before the emulsion became destabilized.

Fig. 2a and b show the SEM images of sample 1 and sample 2 in Table 1, respectively. A dramatic decrease was observed in average cell size (from 80.8 μm to 6.0 μm) and median pore diameter (from 8.2 μm to 0.4 μm) with the increase of CTAB concentration from 0.011 mol/L to 0.022 mol/L (based on monomer phase). It is believed that the emulsion was more stable at higher CTAB concentration and partial droplet coalescence was stopped, which caused the decrease of the average cell size (inferentially, the average water emulsion droplet size). The significant reduction of the average droplet size of the internal phase causes the decrease of the average area of contact point of the deformed neighboring droplets [35–37]. The polymerizable phase film is considered to be especially thin in the area of contact points of the deformed neighboring droplets, and the thickness of the area of contact points is crucial in order to produce open porous polymer foams during the

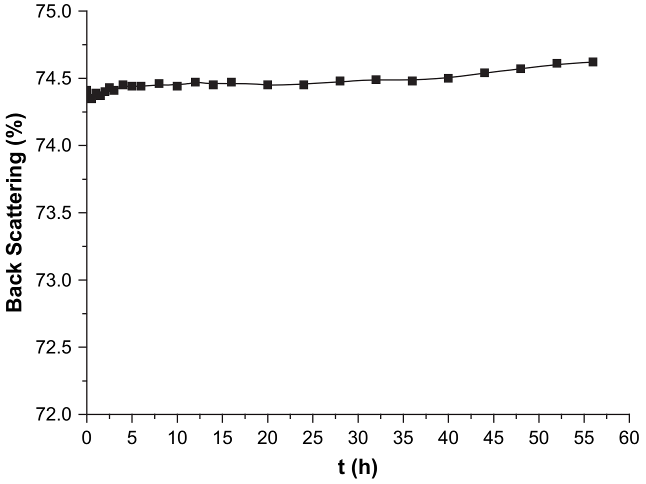

Fig. 1. Back scattering data of W/St emulsions stabilized with CTAB. The data are represented as a function of time (0:00–56:00 h) and of sample height (0.163–51.2 mm).

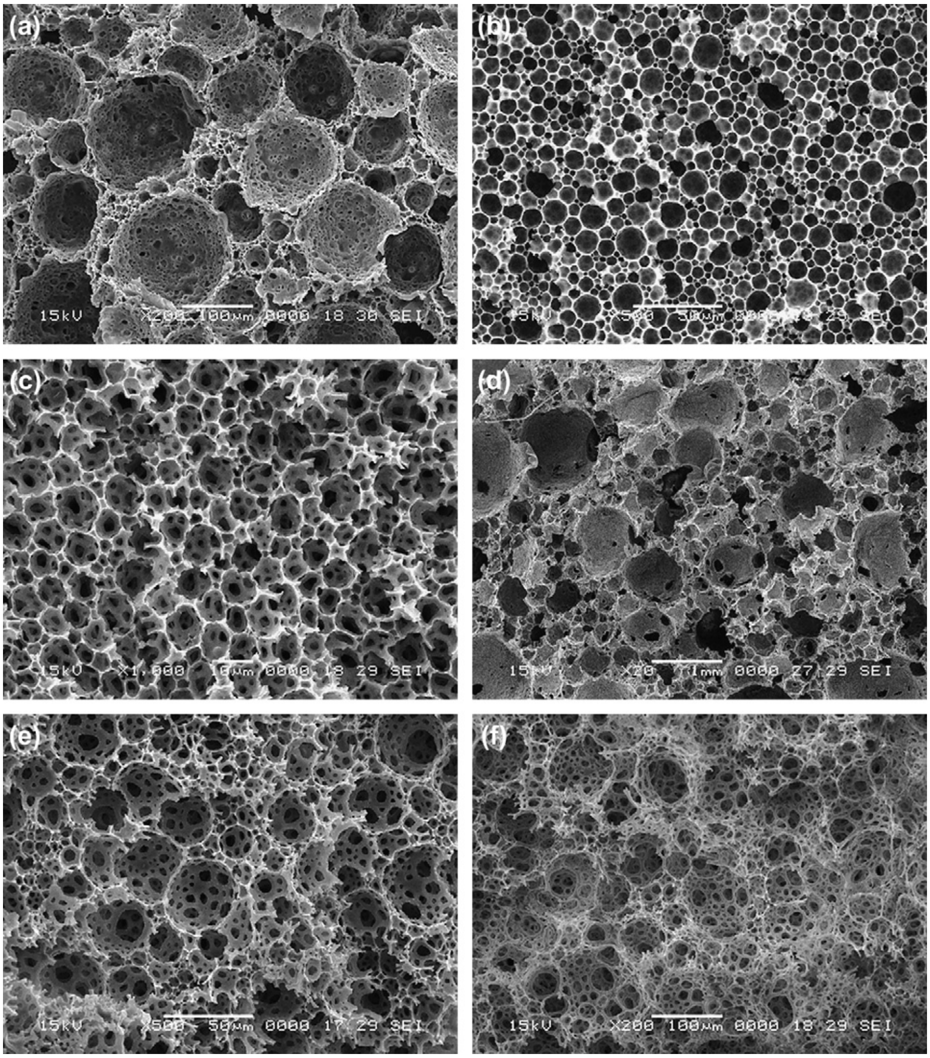

Fig. 2. SEM images of templated polyHIPEs produced from W/O emulsions with CTAB as surfactant. (a) Sample 1, scale bar = 100 μm; (b) sample 2, scale bar = 50 μm; (c) sample 3, scale bar = 10 μm; (d) sample 5, scale bar = 1 mm; (e) sample 6, scale bar = 50 μm; (f) sample 7, scale bar = 100 μm.

polymerization of the continuous phase of the HIPEs [38–41]. Besides, the pores in the materials of this type are believed to form by a mechanical action, which leads to the rupture of the thin polymer films covering the faces between the closest neighboring droplets during the purification and removal of the locked internal phase from the synthesized polyHIPEs [42]. The film of contact of the neighboring droplets becomes the weak point that fractures during the polyHIPE purification process and removal of the locked internal phase from the synthesized polyHIPEs. Thus, the increase of the CTAB concentration led to the reduction of the average area of the weak points and the average pore diameter. With the increase of CTAB concentration from 0.011 mol/L to 0.022 mol/L (based on monomer phase), an increase from 2.6 $cm^3\ g^{-1}$ to 4.9 $cm^3\ g^{-1}$ in pore volume was also noticed.

Various DVB concentrations (0–20% v/v based on monomer phase, samples 2–5) were investigated to control the morphologies of the polyHIPEs. Fig. 2b–d shows that the median pore diameter and cell size increased significantly with the fraction of DVB increased from 0% to 20%, which is contrary to the polyHIPEs using nonionic surfactant (e.g., Span80 or Span60, which is water-insoluble). This paper supposes it may be due to the water-soluble nature of the CTAB. Because

Table 1
Emulsion templating using W/O emulsions

Sample[a]	Volume fraction DVB[b] [%]	Volume fraction water [%]	V_{pore}[c] [$cm^3\ g^{-1}$]	Median pore diameter[c] [μm]	Average cell size[d] [μm]
1	0	83	2.6	8.2	80.8
2	0	83	4.9	0.4	6.0
3	10	83	5.6	2.0	14.3
4	15	83	2.4	3.0	21.5
5	20	83	1.3	40.4	415.9
6	10	90	7.6	3.0	23.8
7	10	95	14.7	12.8	58.7

[a] Sample 1: CTAB 0.011 mol/L, based on monomer phase; samples 2–7: CTAB 0.022 mol/L, based on monomer phase.
[b] Based on total monomers.
[c] Characterized by mercury intrusion porosimeter.
[d] Determined by SEM.

DVB is more hydrophobic than St [40], CTAB is more difficult to dissolve in DVB than in St. With the increase of the DVB ratio in the oil phase, the emulsion became less stable and partial droplet coalescence was occurred, which caused the increase of the average cell size. As illustrated above, the increase of the droplets' size was contributed to the increase of the median pore diameter. So the morphology of the polyHIPEs of this type can be controlled by DVB concentration. Meanwhile, sample 3 exhibited much higher pore volume (5.6 $cm^3 g^{-1}$) than the other samples. The physical basis of the phenomenon was not yet understood. One possible interpretation was that this result due to both uniform cell size and much more open porous structure (see Fig. 2c).

In attempt to investigate the effect of water fraction on the morphologies of the polyHIPEs with this method, the volume fraction of the water internal phase was increased from 83% to 90% (sample 6, Fig. 2e) and 95% (sample 7, Fig. 2f). Even under such concentrated conditions, it was possible to form W/O emulsions that filled the entire reaction vessel. Polymerization of these W/O HIPEs led to materials with an even more open, porous structure, and with total pore volumes as high as 14.7 $cm^3 g^{-1}$ (sample 7, higher than the pore volumes of all polyHIPEs that have been reported) [24–27]. Sample 7 exhibited a much larger median pore diameter (12.8 μm) and average cell size (58.7 μm) than the other samples (containing DVB 10% v/v based on total monomers), probably because the concentration of CTAB was kept constant relative to the external monomer phase while the volume fraction of the internal water phase was increased. Thus, the surfactant was required to stabilize an increasingly large interfacial area and the average water droplet size and median pore diameter became correspondingly larger.

Although, not all of the cell size and pore diameter of the samples were monodispersed, sample 3 suggested that it was possible to synthesize emulsion-templated porous monoliths with well-defined cell size and pore diameter distributions with the technique, as shown in Figs. 2c and 3, which will much enlarge the applications of this type materials [43,44].

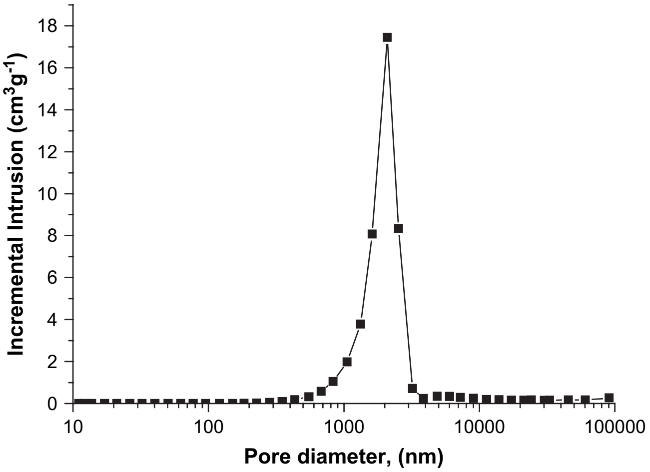

Fig. 3. Mercury intrusion porosimeter data for sample 3; median pore diameter = 2.0 μm, total intrusion volume = 5.6 $cm^3 g^{-1}$.

4. Conclusions

In this work, a new method has been developed for producing well-defined open porous materials by W/O emulsions with ionic surfactant (e.g., CTAB). In contrast to the methods which involved nonion-surfactants, this approach not only did use only ionic surfactant firstly, but also could get polyHIPEs with much higher pore volume (14.7 $cm^3 g^{-1}$) and uniform pore diameter and cell size. The median pore diameter and average cell size of the polyHIPEs increase with an increase of DVB concentration and water fraction. The influence of DVB concentration on the median pore diameter of polyHIPEs was opposite to the previous. Future work will focus on the extension of this approach to a wider range of materials and on achieving fine control over porous structure by tuning the surfactant concentration, cross-linker amount, volume fraction of the water internal phase, etc.

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