



## Antagonistic effect of particles and surfactant on pore structure of macroporous materials based on high internal phase emulsion



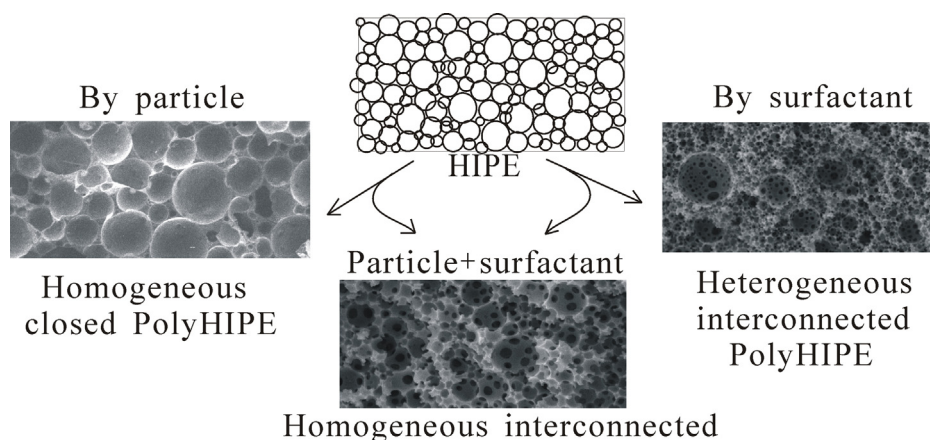
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### HIGHLIGHTS

- Antagonistic effect of nanoparticles and nonionic surfactant on the pore structure of PolyHIPE was investigated.
- Particles-stabilized HIPE result in PolyHIPE with homogeneous closed voids, while heterogeneous interconnected voids were formed in surfactant system.
- A compromise is necessary to obtain PolyHIPE with homogeneous interconnected void.
- Interconnectivity was assessed by loading and releasing property of PolyHIPE.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Herein we present a systematic study of the antagonistic effect of nanoparticles and nonionic surfactant on pore structure of polymerized high internal phase emulsion (polyHIPE). Interconnected polyHIPE with small voids and large RSD in void size was obtained by surfactant-stabilized emulsion, while a close-cellular polyHIPE with large voids and low RSD in void size was prepared by particles-stabilized emulsion. This antagonistic effect was originated from the different stabilizing mechanism of two different stabilizers. Particles improve the stability of HIPE, and resultantly, endow the polyHIPE with excellent homogeneity; On contrary, surfactant lead to the formation of interconnected void. To obtain polyHIPE with interconnected homogeneous voids, an optimal ratio of surfactant/particle is necessary. The interconnectivity of polyHIPE was first investigated by the loading and releasing property of polyHIPE.

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### 1. Introduction

High internal phase emulsion (HIPE) is an emulsion with internal phase volume greater than 74 vol%, the maximum volume that

may be occupied by uniform spheres [1,2]. As template for macroporous monolith, HIPE has received increasing attention due to the ease of synthesizing porous monoliths with controllable structures and physical properties [3,4]. Beside solvent evaporation [5] and in situ gelation [6] in HIPE template, polymerization of monomers in continuous phase, followed by removal of internal phase and surfactant, gives a highly porous monolith with interconnected windows. Such monolith, termed polyHIPE, have been the subject

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of intense interest due to their wide applications, such as chromatography separation [7,8], absorbent [9], tissue engineering [10], supports for reactor [11], and porous material precursor [12].

Pore structure of polyHIPE is a decisive parameter for different application. Two important characteristics lie in the interconnectivity and pore homogeneity. For example, highly open-porous polymer foams are very attractive materials for a wide range of applications such as absorbent or separation material, while polyHIPE used as thermal insulating material or precursor of carbon material should be closed-celled [13,14]. As to the size homogeneity of void, polyHIPE for chromatography separation should be uniform in void to limit the dispersion of chromatographic band [15,16]. So an efficient strategy for controlling pore structure and homogeneity of polyHIPE is crucial for the application of polyHIPE.

Conventionally, HIPEs are stabilized by surfactants with low hydrophilic-lipophilic balance values between 2 and 6, such as span 80 [17,18] and hypermer B246 (HLB = 4.9) [19]. This conventional polyHIPE possess many unique properties, such as low foam density and interconnected pore structure. A typical polyHIPE structure consists of spherical voids, in place of the droplets, and high density of interconnecting windows. This characteristic, however, leads to a disadvantage of poor mechanical property. To target this problem, particle-stabilized HIPEs, also known as Pickering HIPEs [20], have been used as templates to prepare highly porous polymers termed poly-Pickering HIPEs [21–23]. Unfortunately, these monoliths exhibit a highly closed-cell structure and low interconnectivity [24].

An existing strategy, particles and surfactants were used simultaneously to balance the interconnectivity and mechanical properties of polyHIPE monolith [25–27]. Whereas amphiphilic surfactant reduces the oil-water interfacial tension, the solid particles form rigid shells that surround the dispersed phase and prevent coalescence [28,29]. Although increasing attention has been focused on this topic, there lacks a quantitative investigation to the effect of stabilizer mixture on pore structure of polyHIPE.

In this paper, we focused on the relationship between pore structure and stabilizer employed. The interconnectivity was evaluated by the loading and releasing properties of polyHIPE, rather than by size of windows or back pressure as traditional method is. The results verified that the interconnectivity and homogeneity of void can be regulated by changing the ratio of span80/particle.

## 2. Experimental

### 2.1. Materials

Fumed SiO<sub>2</sub> particles with an average diameter of 15 nm were produced by Wacker Silicones (Germany). Styrene (St, 99 wt%), divinylbenzene (DVB, 80 wt%), benzoyl peroxide (BPO, 99 wt%) and rhodamine B (RB, 99 wt%) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Dichlorodimethylsilane, CaCl<sub>2</sub> and sorbitan monooleate (span80) were purchased from Fucheng Chemical Reagent Co. (Tianjing, China). All chemicals were used as received.

### 2.2. Preparation of emulsion and polyHIPE

Fumed SiO<sub>2</sub> particles were modified by dichlorodimethylsilane according to the method in our reported paper [30]. A typical emulsion with a 74 vol% aqueous internal phase was prepared as follows. The stabilizer, modified SiO<sub>2</sub> or/and span80 (depend on the recipe), was dispersed in the oil phase which is consisted of St, DVB (25 wt% to St) and initiator BPO (1.0 wt% to monomer). To this oil phase, CaCl<sub>2</sub> aqueous solution (1.0 wt%) was added dropwise under constant stirring at 3000 rpm. Once all aqueous phase has been added,

stirring was continued for a further 5 min to produce a uniform milky W/O HIPE. Then HIPE emulsion was filled into a glass tube (100 × 10 mm I.D.) and polymerized in a 60 °C water-bath for 24 h to cure a polyHIPE monolith. Finally, prepared polyHIPE was cut into pieces of about 3–5 mm in size and reflux extracted in ethanol to remove surfactant and other impurities.

### 2.3. Characterization

For microscopy, a drop of the emulsion was diluted in its continuous phase on a glass microscope slide with a dimple and gently covered with a cover slip. Images of emulsion drops were taken using a microscope fitted with a digital camera (CAIKON, China). The average diameter of emulsion droplets was calculated from 100 individual drops according to the scale of microscopic image. Morphology of polyHIPE was characterized by scanning electron microscope (SEM, Oxford VEGA3 TESCAN) equipped with a field emission electron gun. Prior to the test, the polyHIPE was fixed to substrate via a carbon sticker and sputtered with gold. The size of 50 voids in SEM image was estimated and the RSD of void size was calculated to characterize the homogeneity. The porosity of polyHIPE was obtained by reported method [31] with a modification of using ethanol, instead of paraffin oil, as immersed chemical.

### 2.4. Drug loading and in vitro release of polyHIPE

The polyHIPE pieces were immersed into rhodamine B solution (1.0 mg g<sup>-1</sup> in ethanol) and reflux incubated for 8 h. The loaded amount of rhodamine B was determined by UV–vis spectrophotometer at 550 nm [32]. Then the rhodamine B-loaded polyHIPEs were transferred into a colourimeter tube containing ethanol and incubated at 25 °C water-bath. At each pre-determined time interval, the percentage of released rhodamine B was detected by UV–vis spectrophotometer. Each experiment was performed in triplicate, and the average value was reported.

## 3. Results and discussion

### 3.1. SiO<sub>2</sub> modification and emulsion preparation

In this study, hydrophilic SiO<sub>2</sub> particles were modified by dichlorodimethylsilane. By modification, nano-SiO<sub>2</sub> was endowed with moderate hydrophilicity to be adsorbed irreversibly at the oil-water interface. To determine the contact angle of particles, SiO<sub>2</sub> particles were compressed into a slide by a compressor under 15 MPa. A drop of water (about 2 μL) was dropped on the slide. The image by a contact angle goniometer is shown in Fig. 1. The contact angle increase from 23° to 83°, showing an excellent hydrophobicity after modification.

Fig. 2 shows the digital photograph and optical micrograph of prepared HIPE stabilized by different stabilizer. Prepared HIPE was stable and sticky, as typical HIPE presents. All the droplets were spherical in shape. The size distribution of emulsion droplet is shown in Fig. 2b. With span80 as stabilizer, the emulsion was milky in appearance and extremely high in viscosity. The droplets range typically from 2 to 4 μm. SiO<sub>2</sub> stabilized emulsion presents a lower viscosity and larger droplet size of tens of micrometers. Pickering emulsion is stabilized by mechanical apartment of particles-formed film around the droplet. Larger size of SiO<sub>2</sub> particles than surfactant results in large droplet size of Pickering emulsion than surfactant-stabilized emulsion. When span80 and SiO<sub>2</sub> were employed, the emulsion is still low in viscosity and the droplet size decrease to 10 ~ 30 μm typically.

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