Pore Structure of Macroporous Polymers Using Polystyrene/Silica Composite Particles as Pickering Stabilizers

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ABSTRACT: A novel approach for the preparation of interconnected macroporous polymers with a controllable pore structure was reported. The method was based on the polymerization of water-in-oil Pickering high internal phase emulsion (HIPE) stabilized by polystyrene (PS)/silica composite particles. The composite Pickering stabilizers were facilely obtained by mixing positively charged PS microspheres and negatively charged silica nanoparticles, and their amphiphilicity could be delicately tailored by varying the ratio of PS and silica. The droplet size of Pickering HIPEs was characterized using an optical microscope. The pore structure of polymer foams was observed using a scanning electron microscope. The interconnectivity of macroporous polymers was evaluated upon their gas permeability, which was greatly improved after etching PS microspheres included in the Pickering stabilizers with tetrahydrofuran. As a result, fine tailoring of the pore structure of polymer foams could be realized by simply tuning the ratio of PS to silica particles in the composite stabilizer.

INTRODUCTION

Porous polymers have been widely used in many fields such as catalysts, separation, storage, tissue engineering scaffolds, and sound and heat insulation owing to their low density and high porosity. Various applications of porous polymers are heavily relied on their pore structures. Although many methods have been reported for the fabrication of porous polymers, emulsion templates attract great attention owing to the facile tailoring of pore size and size distribution of the resulting polymer materials. With a minimum internal phase volume fraction of 74%, high internal phase emulsions (HIPEs) are often used as templates to produce high porosity polymers.

Conventional HIPEs are commonly stabilized by surfactants such as cetyltrimethylammonium bromide, sorbitan monooctanoate (Span 80), and amphiphilic polymers, which are toxic and not environmentally friendly. A large amount of surfactant is required to produce stable HIPEs (5–50 wt % relative to the continuous phase), which gives rise to the additional production costs. Moreover, macroporous polymers prepared from HIPEs generally show undesirable mechanical strength. Hence, these polyHIPEs are obviously restricted for further applications, especially in biomedical materials.

Instead of molecular surfactants, solid particles with appropriate surface property, such as silica, titania, and iron oxide nanoparticles can also stabilize HIPEs, which are often referred to as Pickering HIPEs. However, the pristine solid particles are often too hydrophilic or too hydrophobic to effectively stabilize HIPEs, and thus they still need to be modified using certain surfactants, thus making the modification process more tedious. Many efforts have been devoted to obtaining stable Pickering HIPEs using surfactant-free stabilizers.

Colloidal celluloses and various cellulose derivatives were found to be capable of stabilizing simple oil-in-water systems. Some other colloidal particles, including chitosan nanocrystals, protein particles, fat crystals, and wax microparticles could also successfully stabilize HIPEs. However, these reports mostly focus on the stability of Pickering HIPEs rather than the pore structures of polyHIPEs, which have rarely been explored.

Polymer foams with interconnected pores have been reported in the systems where HIPE templates are stabilized by surfactants. In the case of Pickering HIPEs, although a small quantity of pores are interconnected by pore throats formed during the polymerization process, control over the interconnectivity in poly-Pickering HIPEs still remains challenging. Thus, applications of such macroporous polymers in the fields of adsorption, filtration, and tissue engineering scaffolds are restrained. There have been only several reports on Pickering HIPEs concentrating on the formation of an open-cell structure so far. Interconnected porous polymers are formed by introducing the molecular surfactants or by drawing the solid particles from the interface through monomer–particle reactions. Recently, we prepared polymer foams with open-pore structures by extracting the thin monomer layer between two adjacent emulsion droplets using the flocculation process with a lipophilic core. It is also an effective method to form pore throats using the monomer with high polymerization shrinkage.

In this study, a surfactant-free composite Pickering stabilizer is facilely prepared only by mixing positively charged polystyrene...
(PS) microspheres and negatively charged silica nanoparticles. The wettability of the composite stabilizer is easily tailored by varying the ratio of PS microspheres and silica nanoparticles. Stable water-in-oil (w/o) HIPEs with controllable droplet size can be produced when the PS/silica composite particles are used as Pickering stabilizers. Open-cell macroporous polymers are achieved after the polymerization of Pickering HIPEs with relatively high PS microsphere concentration, and their interconnectivity is further improved by etching with tetrahydrofuran (THF).

**EXPERIMENTAL SECTION**

**Materials.** Silica hydrosols (28 nm, 40.0%) were supplied by Fujian Sanbang Chemical Co., Ltd (China). THF (99%) was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Styrene (St, 99%), divinylbenzene (DVB, 80%), [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MATMAC, 75%), 2,2′-azobis (2-methylpropionamide) dihydrochloride (AIBA, 99%), and 2,2′-azobis(isobutyronitrile) (AIBN, 99%) were provided by Aladdin Chemistry Co., Ltd. St and DVB were purified by distillation under vacuum, and AIBN was recrystallized with ethanol before use. Deionized water was used throughout the experiments.

**Synthesis of PS/Silica Composite Pickering Stabilizers.** PS microspheres were prepared using a soap-free emulsion polymerization method. In a typical procedure, AIBA (0.05 g) was dissolved in water (107.5 g) in a 250 mL three-necked flask equipped with magnetic stirring and nitrogen protection, and then St (9.375 g) and MATMAC (0.277 g) were added. After heating at 70 °C for 12 h, PS microspheres dispersed in water were obtained. Cross-linked PS microspheres were prepared in a similar manner; only instead of 9.375 g of St, a mixture of 80 vol % of St and 20 vol % of DVB was dissolved in the oil phase before the preparation of Pickering HIPEs.

**Preparation of Pickering HIPEs.** Pickering emulsions were prepared using PS/silica composite particles as the stabilizers. The oil phase (1.25 mL) consisting of 80 vol % of St and 20 vol % of DVB was added to 5 mL of aqueous phase containing the PS/silica composite Pickering stabilizer. The mixture was then vigorously emulsified with Vortex-BE1 at 500 rpm for 10 min to form Pickering HIPEs.

**Preparation of Poly-Pickering HIPEs.** Initiator AIBN (1.0 wt %) was dissolved in the oil phase before the preparation of Pickering HIPEs when the samples would undergo polymerization. The Pickering HIPEs were transferred into centrifuge tubes, sealed, and placed in a 65 °C oil bath for 24 h. The polyHIPEs were then obtained after drying in a convection oven at 60 °C for 48 h.

**Characterization.** Both hydrodynamic diameter and zeta potential of silica nanoparticles and PS colloidal particles were measured on a Malvern ZS90 analyzer. The hydrodynamic diameter was measured in a PS cell at 25 °C. The zeta potential was measured in a universal dip cell in a PS cuvette for potential measurements at 25 °C under pH 7. The concentration of the suspension was 0.1 wt %.

Photographs of Pickering HIPEs, PS colloidal particles, and silica hydrosols were taken using a Sony Xperia Z5 digital camera. The morphology of the Pickering emulsion droplets was observed using an EVS680 optical microscope. The type of Pickering emulsions (w/o or o/w) was assessed by the drop test.

The pore structure of the macroporous polymers was observed using a Zeiss Ultra 55 field-emission scanning electron microscope (FE-SEM). All samples were placed onto the carbon-coated lacy substrates, and the polymer samples were sputtered with gold before observation. The mean pore size of the poly-Pickering HIPEs was obtained by averaging the size of at least 100 pores estimated from SEM images.

The permeability of the poly-Pickering HIPE was characterized by measuring the flow rates of nitrogen passing through the sample at 5000 Pa. The macroporous polymers were cut into cylinders with a length of 10 mm and a diameter of 14 mm. Each sample was measured three times.

**RESULTS AND DISCUSSION**

**Preparation of PS/Silica Composite Pickering Stabilizers.** A silica hydrosol is normally too hydrophilic to stabilize Pickering emulsions, and thus surfactants are used to tailor its amphiphilicity. 25,30,51 PS microspheres obtained via a soap-free emulsion polymerization method are also very hydrophilic because of the charges on their surface. The charge neutralization of negatively charged silica nanoparticles and positively charged PS microspheres hereby is developed as a new way to endow the composite particles with appropriate amphiphilicity for the subsequent stabilization of Pickering HIPEs.

The average diameters of PS microspheres and silica nanoparticles are 103 and 57 nm, respectively (see Figure 1). The white flocculation is clearly observed when silica hydrosols are dropped into PS microsphere aqueous dispersion, indicating the strong electrostatic attraction between the polymer and inorganic particles (see Figure 2). The zeta potentials of PS particles and silica nanoparticles are measured to be +49.7 ± 0.6 and −20.0 ± 0.8 mV, respectively. Obviously, the zeta potential of PS/silica composite particles decreases gradually as increasing content of silica nanoparticles, and approaches zero when the concentration of silica reaches 60 wt % (see Figure 3). Therefore, the extremely hydrophilic surface of PS particles can be suitably hydrophobized via this facile and efficient route for the subsequent preparation of

**Table 1. Recipes for the Preparation of PS/Silica Composite Pickering Stabilizers**

<table>
<thead>
<tr>
<th>sample</th>
<th>silica particles (wt %)</th>
<th>PS microspheres (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.80</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.70</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>5</td>
<td>0.40</td>
<td>0.60</td>
</tr>
<tr>
<td>6</td>
<td>0.45</td>
<td>0.55</td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>0.55</td>
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*With respect to the aqueous phase.*

Figure 1. Size distribution of (a) silica nanoparticles and (b) PS microspheres in water.
optimal stabilization effort for HIPEs. However, when extremely large aggregations of silica and PS are produced, the zeta potential approaches minus, meaning that the surfaces of PS microspheres are fully covered by hydrophilic silica particles. It has been reported that solid particles with extreme hydrophilicity or hydrophobicity are unable to stabilize Pickering emulsions.32–35 Meanwhile, the gravity of such large aggregates cannot be neglected anymore at the oil/water interface, which is bad for the stabilization of Pickering emulsions. Therefore, PS/silica composite particles with very high silica content (sample 8, Table 1) are not able to stabilize HIPEs (Figure 4h).

Pickering HIPEs stabilized by PS/silica composite particles was observed using an EV5680 optical microscope. As shown in Figure 5a–d, the droplet size of Pickering HIPEs decreases with an increase in the silica/PS ratio in PS/silica composite particles from 1:3 to 2:3. Notably, a further increase in the silica/PS ratio to 9:11 or more (1:1) leads to a larger droplet size of formed HIPEs, instead (see Figure 5ef). We attribute the size difference in emulsion droplets to the different stabilization effects of composite Pickering stabilizers. As demonstrated above, weak flocculation of the oppositely charged PS microspheres and silica nanoparticles can vary the PS surface from extremely hydrophilic to amphiphilic owing to charge neutralization, which facilitates the effective stabilization of HIPEs. However, over flocculated composite particles sacrifice their surface amphiphilicity because of full coverage of the PS surface by hydrophilic silica nanoparticles, indicating a poor stabilization for w/o HIPEs. In short, the size of Pickering HIPEs could be adjusted effectively by varying the ratio of silica to PS in the composite particles.

**Preparation of Poly-Pickering HIPEs.** After the polymerization of Pickering HIPE templates, porous polymers are obtained, as shown in Figure 6. The pore size of macroporous polymers are measured by averaging the size of at least 100 pores estimated from SEM images and plotted in Figure 7. It decreases first and then increases with the content of silica in the composite stabilizer. The pore size of poly-Pickering HIPEs is in good agreement with the droplet size of the original emulsions, indicating that the coalescence of adjacent droplets is suppressed during the polymerization procedure. Interestingly, some pore throats are clearly observed, as shown in Figure 6a–d. To our knowledge, the polymerization of Pickering HIPEs mainly produces closed-cell pores. Although some pores are interconnected by pore throats, the interconnectivity is still out of control because the solid particles around the emulsion droplets by acting as barriers.16,55,56 Considering that PS/silica composites play as Pickering stabilizers of HIPEs in our system,
PS microspheres are swollen by St before polymerization. Thus, the monomer layer between two emulsion droplets becomes thinner initially, and the pore throats are then produced because of the split on the weak walls when polymerization shrinkage occurs.

To verify the formation mechanism of pore throats, cross-linked PS microspheres, which are hardly swollen by a monomer, were prepared in comparison with uncross-linked ones. As shown in Figure 8, there is no obvious difference in appearance between the uncross-linked and the cross-linked PS microsphere powders. Besides, the size and the morphology of the microspheres are almost the same (see Figure 9). However, the solution of uncross-linked PS microspheres in a monomer becomes transparent and the viscosity increases a lot, whereas a turbid dispersion is obtained when the cross-linked PS particles are mixed with a monomer. This result again confirms that the uncross-linked PS microspheres are easily swollen by St, but the cross-linked ones are not. Cross-linked PS colloidal particles are also mixed with silica hydrosols as the recipe of sample 2 in Table 1 to prepare the Pickering stabilizer and the subsequent Pickering HIPEs. In our case, the size of uncross-linked PS microspheres after swelling is larger than that of cross-linked ones that are hardly swollen by a monomer. It has already been demonstrated that larger Pickering stabilizer often stabilizes larger emulsion droplets and vice versa.57 Therefore, the smaller droplet size of HIPEs and the smaller pore size of poly-HIPEs is anticipated when substituting cross-linked PS/silica composite particles for

Figure 5. Optical microscopy images of Pickering HIPEs stabilized by composite particles with different weight ratios of silica particles to PS microspheres: (a) 1:3, (b) 3:7, (c) 7:13, (d) 2:3, (e) 9:11, and (f) 1:1 (samples 2–7, Table 1).

Figure 6. SEM images of poly-Pickering HIPEs stabilized by composite particles with different weight ratios of silica particles to PS microspheres: (a) 1:3, (b) 3:7, (c) 7:13, (d) 2:3, (e) 9:11, and (f) 1:1 (samples 2–7, Table 1).

Figure 7. Pore sizes of poly-Pickering HIPEs stabilized by composite particles with different concentrations of silica nanoparticles in PS/silica composite stabilizers (samples 2–7, Table 1).
uncross-linked PS/silica composite particles as a Pickering stabilizer (see Figure 10a,b). Moreover, as shown in Figure 10b, few open throats are observed, which is significantly different from the pore structure in the previous case (see Figure 6a). We think one possible reason is that the oil layer between two water droplets is too thick to be torn up during polymerization because cross-linked PS microspheres cannot extract a monomer from the oil phase. Gas permeability test (Figure 11) confirms that the interconnectivity of poly-Pickering HIPEs is greatly improved by using the uncross-linked PS/silica composite stabilizers.

The results above have demonstrated that the polymer foams with interconnected pore structures can be achieved when uncross-linked PS/silica composite particles are used as Pickering stabilizers. Because THF is a good solvent for dissolving uncross-linked PS, which is immobilized initially at the monomer/water interface and then at the pore wall after polymerization, more and larger pore throats would be expected when exposing the poly-Pickering HIPEs to THF. Figure 12 shows the morphology of poly-Pickering HIPEs after treatment with THF. It is clearly seen that the samples have many larger pore throats compared with those before THF treatment as shown in Figure 6. The amount of pore throats decreases with decreasing content of PS microspheres in the composite particles. However, etching the poly-Pickering HIPE stabilized by cross-linked PS/silica composite particles with THF, there was no obvious difference before (Figure 10b) and after (Figure 10c) THF treatment, indicating that the cross-linked PS microspheres are hardly washed away. The interconnectivity of polymer foams before and after THF etching is also characterized by the gas permeability test, and the result is plotted in Figure 13. It is clear that the permeability of macroporous polymers is enhanced obviously after THF treatment, especially for those using the composite stabilizer with a high PS content. This is in good agreement with the SEM images. In a word, both gas permeability and SEM results suggest that the interconnectivity of macroporous polymers can be facilely tailored by simply varying the weight ratio of the uncross-linked PS in the composite particles upon treatment with THF.

**CONCLUSIONS**

Environmental friendly PS/silica composites are facilely prepared by mixing positively charged PS colloidal particles and negatively charged silica nanoparticles as a Pickering stabilizer to produce stable w/o HIPEs without any other surfactants. The amphiphilicity of the composite stabilizer is tailored by varying the ratio of PS to silica, and thus the droplet
size of Pickering HIPEs and the pore size of poly-Pickering HIPEs are tuned conveniently. Dominantly over other Pickering stabilizers, PS/silica composite particles immobilized on the oil/water interface can extract a monomer from the continuous phase, thus thinning the monomer layer between adjacent water droplets and finally producing an open-cell structure owing to the split of the weak interface during polymerization. The interconnectivity of polymer foams can be further improved by etching with THF, especially for the samples with a high PS content in the composite stabilizer. This kind of polymer/silica composite Pickering stabilizers probably opens a new gateway for tailoring the pore structure, especially the interconnectivity of polymer foams, meeting the requirements of various applications.

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