1. Materials:

Styrene (St), methyl methacrylate (MMA) and acrylic acid (AA) (Lingfeng Chemical reagent Co. Ltd, Shanghai, China) were distilled and stored at 4 ºC if not used immediately, ammonium persulfate (APS) was recrystallized twice in deionized water before use, α,α'-azoisobutyronitrile (AIBN, Sigma Aldrich) and sodium chloride (NaCl, Merck) were used as received, and water was fresh deionized.

2. Experimental procedure

2.1 Preparation and characterization of monodisperse copolymer particles

The copolymer particles were prepared with surfactant-free emulsion copolymerization of St, MMA and AA, which were carried as following. 100 ml water containing APS of 7.0×10^{-3} mol l^{-1} was added to a four-necked glass reactor (250ml) with an overhead leaf-shaped stirrer paddle and a condenser. Then the mixture consisted of 18.2 g St, 0.8 g MMA and 1.0 g AA was added to the reactor. The mixture was stirred steadily at 200 rpm and left at 70 ºC for 12 h, before it was cooled to room temperature. The average particle size of the copolymer particles is 240±6 nm, as determined from transmission electron microscopy (TEM, JEM-1200EX II, Japan) (Fig. 1). And the solids content was 16.7 wt% as estimated by the feed comonomers content.

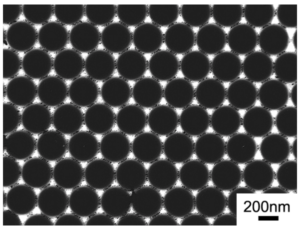


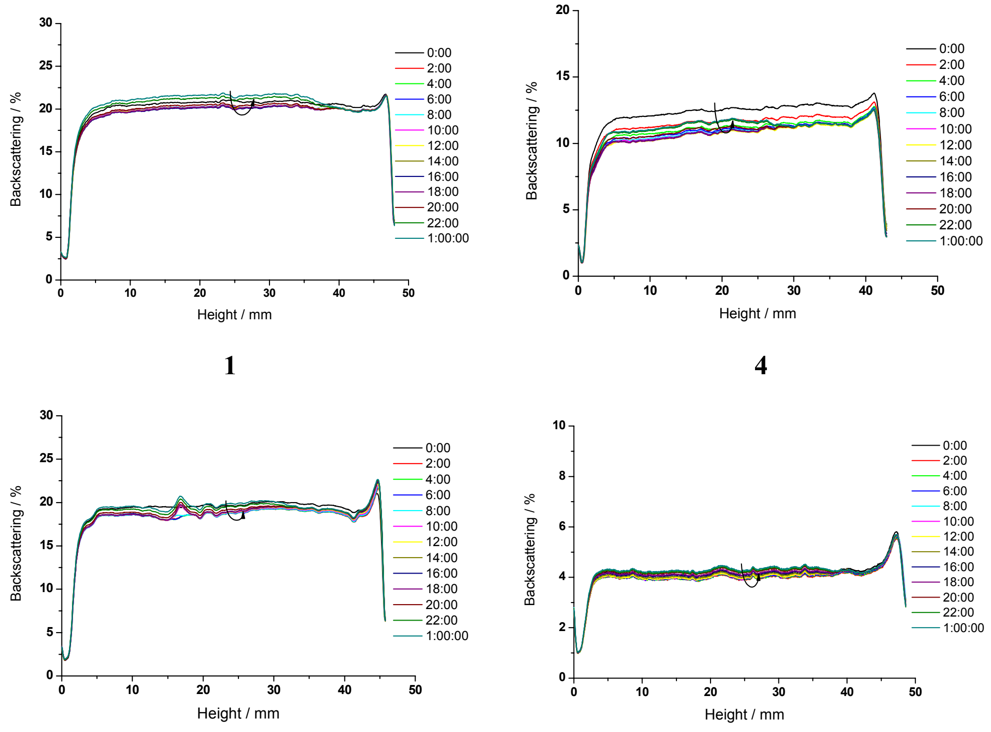
Fig. 1 TEM image of the copolymer particles obtained by surfactant-free emulsion copolymerization of St, MMA and AA in air atmosphere.

2.2 Preparation and characterization of surfactant-free high internal phase emulsions

2.2.1 High internal phase emulsions prepared with addition of 1.0 wt% copolymer particles to the aqueous phase

HIPEs **1**-**9** were prepared with addition of the copolymer particles obtianed in ***2.1*** to the queous phase. HIPEs **1**-**5** with 0.2 mol l^{-1} NaCl aqueous phase were prepared with internal phase volume fraction of 80, 84, 90, 93.3, and 95%, respectively. HIPEs **6** - **9** with 84% internal phase volume were tried to be prepared with 0, 0.1, 0.3, and 6.1 mol l^{-1} NaCl respectively. The total liquid volume of each emulsions in this work was kept at 30 ml. For example, HIPE **1** was prepared as following. 6.0 g MMA containing of 1.0 wt% α,α'-azoisobutyronitrile (AIBN) as organic phase was added to a 100 ml beaker, and stirred with a magnetic stirrer at 400 rpm for 5 min at 25 ºC. The 24 ml emulsion (aqueous phase) containing 1.0 wt% polymer particles was obtained by dilution from the emulsion in ***2.1***. And 0.281 g NaCl was added to the aqueous phase to target 0.2 mol l^{-1} NaCl. Then the aqueous phase was gradually added to the organic phase within 20s. The mixture was stirred for 1min after the addition of aqueous phase was completed.

The preparations of the emulsion **5** and **6** were failed due to the immediate separation of the phase. But HIPEs **1** - **4** and **7** - **9** were stable as evaluation by measuring the backscattering of monochromatic light (λ = 880 nm) from the suspension employing an optical analyzer, Turbiscan Lab Expert (Formulaction, France) (Fig. 2). 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 ºC. The results are presented as the sedimentation profile, i.e., backscattering data versus time.[1]



1 **4**

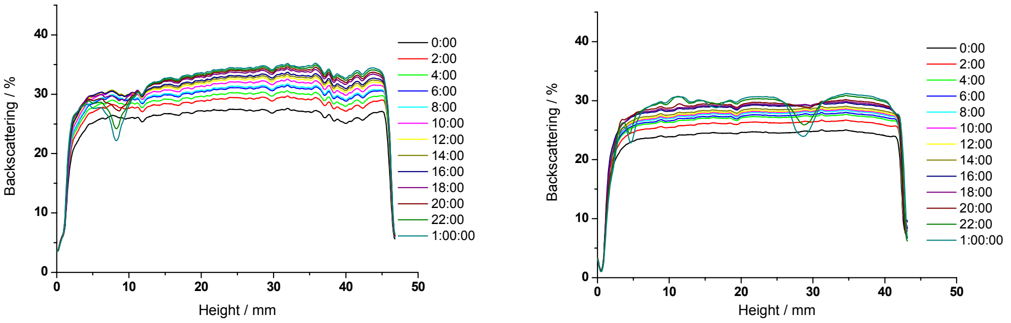
7 **9**

Fig. 2 Backscattering data of water-in-MMA HIPEs which were prepared with addition of copolymer particles to aqueous phase. The particle content of the aqueous phase was 1.0 wt%. The HIPEs were prepared with varied NaCl concentration [NaCl] and water fraction (f_w). (**1**) [NaCl] = 0.2 mol l^{-1}, f_w = 80 vol%; (**4**) [NaCl] = 0.2 mol l^{-1}, f_w = 93.3 vol%; (**7**) [NaCl] = 0.1 mol l^{-1}, f_w = 84 vol%; (**9**) [NaCl] = 6.1 mol l^{-1}, f_w = 84 vol%.

2.2.2 High internal phase emulsions prepared with addition of dry copolymer particles to the organic phase

HIPE **10** – **13** with 0.2 mol l^{-1} NaCl aqueous phase were prepared with internal phase volume fraction of 80, 84, 87, and 90%, respectively. The dry copolymer particles were isolated from the emulsion obtained in ***2.1***, then the dry copolymer particles were added to the organic phase before preparation of the emulsions. The particles content of the MMA in each HIPE was at the level equivalent to 1.0 wt% of its aqueous phase. For preparation of HIPE **11**, Mixture of 4.8 g MMA, 0.048 g AIBN and 0.252 g dry copolymer particles was used as organic phase, and the mixture was stirred with a magnetic stirrer at 400 rpm at 25 ºC. 2 h later, 24 ml water containing 0.2 mol l^{-1} NaCl was gradually added to the organic phase within 20s. The emulsion was stirred for 1 min after the addition of aqueous phase was completed.

HIPEs **10** - **12** were stable as evaluation by measuring the backscattering of monochromatic light (λ = 880 nm) from the suspension employing an optical analyzer, Turbiscan Lab Expert (Formulaction, France) (Fig. 3). 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 ºC. However, the preparation of HIPE **13** having 90% internal volume phase was failed, because of quick phase separation. This phenomena shows that the water-in-MMA HIPEs can be stabilized by the resultant soluble polymer, and the upper limit for internal phase volume of the emulsion stabilized by the dissolved polymer in the continuous phase exists between 87 and 90%. This upper limit is lower than the internal phase volume fraction of the HIPEs obtained with addition of the copolymer particles to the aqueous phase (between 93.3 and 95%).



10 **12**

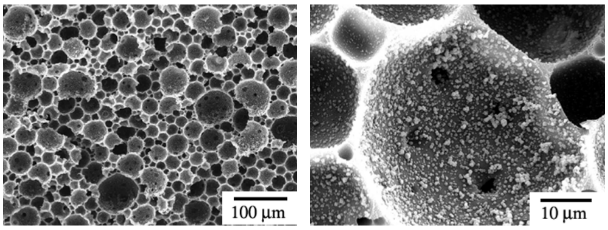
Fig. 3 Backscattering data of water-in-MMA HIPEs **10** and **12.** Both of the emulsions were prepared with addition of the dry copolymer particles to MMA. The particles contents of the MMA were at the level equivalent to 1.0 wt% of their aqueous phase. The internal phase volume fraction of the HIPE **10** and **12** were 80 and 87% respectively, and NaCl concentration of the aqueous phase was 0.2 mol l^{-1}.

2.3 Preparation and characterization of polyHIPEs

The stable HIPEs obtained in ***2.2*** were transferred to sealed glass molds, and polymerized in a 70 ºC bath for 24 h. The polymerized materials were removed from the molds, and dried in a vacuum at 70 ºC for 24 h, then extracted in Soxhlet apparatus with distilled water to remove any impurities, finally, the resulting polymers were dried to constant weight in a vacuum at 70 ºC. The morphology of the resulting polyHIPEs was detected by a JSM-6360LV SEM (Fig. 4, 5 and 6). 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.[2] The average void diameter (R) of each polyHIPE material in this work was achieved as equation (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.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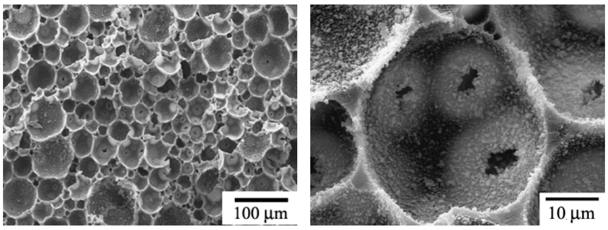
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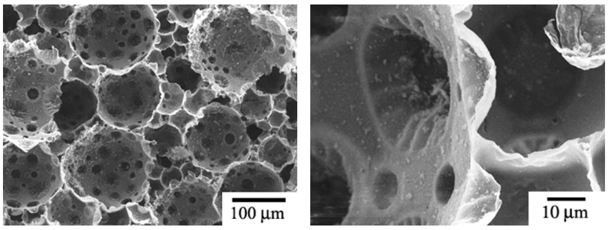
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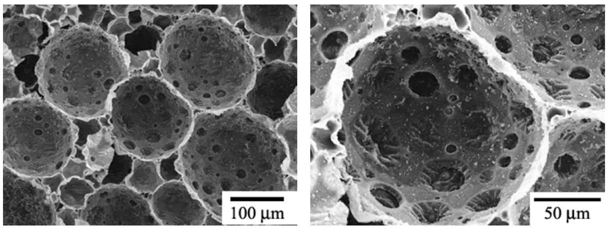
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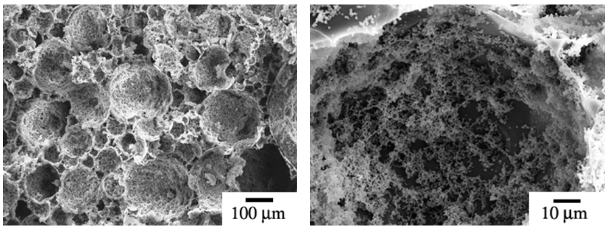
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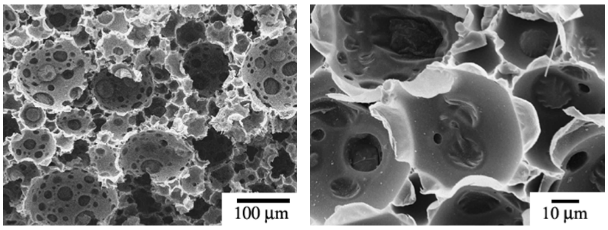
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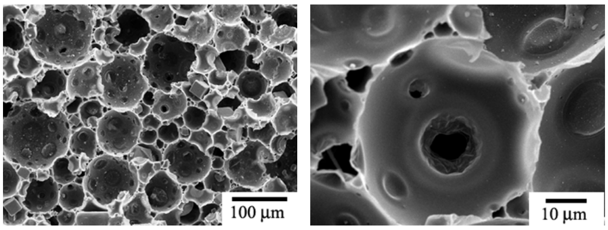

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Fig. 4 SEM images (left, low- and right, high-magnification) of PMMA based polyHIPEs prepared with varied NaCl concentration [NaCl], and water fraction (f_w). The particles content of the aqueous phase of each HIPE was 1.0 wt%. (**1**) [NaCl] = 0.2 mol l^{-1}, f_w = 80 vol%; (**2**) [NaCl] = 0.2 mol l^{-1}, f_w = 84 vol%; (**3**) [NaCl] = 0.2 mol l^{-1}, f_w = 90 vol%; (**4**) [NaCl] = 0.2 mol l^{-1}, f_w = 93.3 vol%; (**7**) [NaCl] = 0.1 mol l^{-1}, f_w = 84 vol%; (**8**) [NaCl] = 0.3 mol l^{-1}, f_w = 84 vol%; (**9**) [NaCl] = 6.1 mol l^{-1}, f_w = 84 vol%.

2.3 The evidences for the copolymer particles survived the polyHIPE preparation.

The emulsion particles survived the polyHIPE preparation was supported by the following observations. Firstly, it was found there were no particles in the polyHIPEs which were obtained with addition of the dry copolymer particles to MMA (Fig. 5). This means that the polymer particles would not be produced during the preparation of the polyHIPEs, when the HIPEs were prepared with addition of the dry copolymer particles to the continuous phase. Secondly, average particle size of the polymer particles found in the resulting polyHIPEs, such as in polyHIPEs **7** (Fig. 6), are comparable to the average emulsion particle size used to prepare the HIPEs (Fig. 7, investigated by JSM-6360LV SEM). So we think that the particles in the resulting polyHIPEs were the emulsion particles survived the polyHIPE preparation.

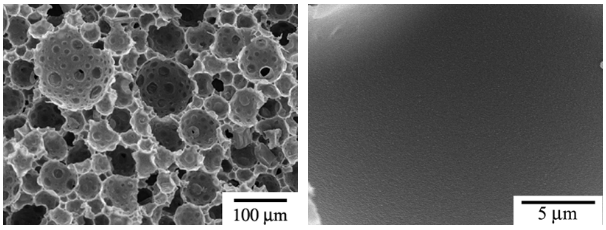

Fig. 5 SEM images of the PMMA based polyHIPE **11** prepared with addition of the dry copolymer particles to MMA. The particles content of the MMA was at the level equivalent to 1.0 wt% of its aqueous phase. The internal phase volume fraction of the HIPE was 84%, and NaCl concentration of the aqueous phase was 0.2 mol l^{-1}.

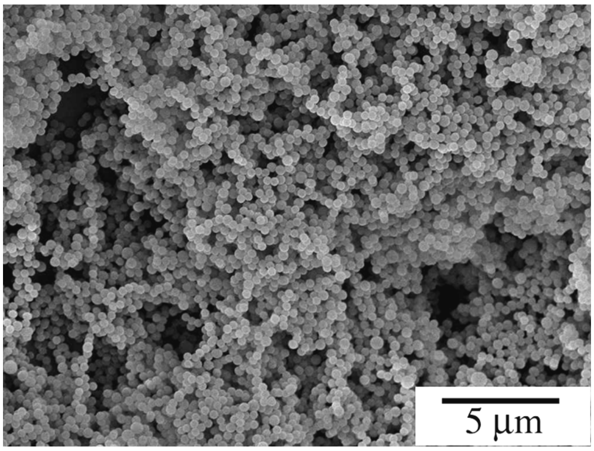

Fig. 6 SEM image of the void wall of polyHIPE **7** which was prepared with addition of copolymer particles to the aqueous phase. The particles content of the aqueous phase was 1.0 wt%. The internal phase volume fraction of the HIPE was 84%, and NaCl concentration of the aqueous phase was 0.1 mol l^{-1}.

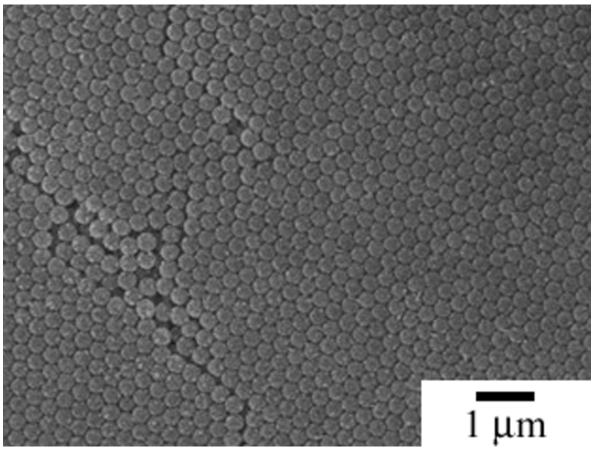

Fig. 7 SEM image of the copolymer particles used to prepare the HIPEs. The particles were produced with surfactant-free emulsion copolymerization of St, MMA and AA in air atmosphere.

Additional references

1. O. Mengual, G. Meunier, I. Cayré, K. Puech and P. Snabre, *Talanta*, 1999, **50**, 445.

2. A. Barbetta and N. R. Cameron, *Macromolecules*, 2004, **37**, 3188.