Emulsions

DOI: 10.1002/anie.200902103

High Internal Phase Emulsions Stabilized Solely by Microgel Particles**

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High internal phase emulsions (HIPEs) are often defined as very concentrated emulsions in which the volume fraction of the internal phase exceeds 0.74.[1] Conventional HIPEs consisting of a continuous organic phase and an internal aqueous phase (water-in-oil, w/o emulsion) are commonly stabilized by large amounts of surfactant.[2,3] If the continuous phase contains one or more monomeric species that are polymerizable, HIPEs can be used as templates for the fabrication of highly porous materials. Highly porous materials have proven to be useful in a variety of applications, including filtration membranes for molten metals and hot gases, bioreactors, catalyst carriers, and scaffolds for bone replacement and tissue engineering.[4–6]

In addition to surfactants, colloidal particles have also been used to stabilize HIPEs and produce macroporous materials after drying and sintering.[7,8] The concept of using particle-stabilized, or Pickering, emulsions as templates to manufacture porous materials provides a number of benefits that are not achievable using low-molecular-weight surfactants. Firstly, the particles used as stabilizers in Pickering emulsions are irreversibly adsorbed at the interface of emulsions because of their high energy of attachment, which makes the resultant Pickering emulsions extremely stable with shelf-life stabilities of months or even years.[9] Secondly, the use of Pickering emulsion droplets as templates can functionalize the cell walls of the porous materials with a layer of solid particles, which could, for example, contain functional groups and lead to a variety of further applications. The stability and type of Pickering emulsions depend on the hydrophilicity of the particles.[9]

While considerable progress has been made on the fabrication of porous materials by Pickering HIPE templating, one important limitation has still remained. All previous reports on Pickering emulsions deal with emulsions for which the volume fractions of the dispersed phases are less than 0.70. On the basis of the developed thermodynamic model, Kralchevsky et al.[10] have predicted that Pickering emulsions will phase-invert above an internal phase volume fraction of 0.5. In practice, phase inversion is usually observed at a volume fraction of 0.70 after kinetic factors are considered. Binks and co-workers[11,12] have experimentally demonstrated that Pickering emulsions phase-invert between volume fractions of 0.65 and 0.70, which means that the majority phase becomes the continuous phase. The formation of HIPEs stabilized solely by solid particles seems to be impossible. Menner et al.[13] reported on the first successful preparation of an HIPE stabilized solely by carbon nanotubes with 60% internal phase volume. Akartuna et al.[14] also reported on the preparation of macroporous materials from Pickering HIPE templates stabilized by inorganic particles, but about 35 vol% particles were needed to stabilize the emulsions with internal phase fractions of 72–78%. Recently, using titania or silica particles, stable Pickering HIPEs with an internal phase volume fraction greater than 90% could be prepared.[15,16] However, the hydrophilicity of the particles should be tailored through prior chemical treatment. Furthermore, to avoid the collapse of the emulsion structure during the production of porous materials, consolidation of the HIPEs by gelation of the continuous phase requires additional strict control over the reaction chemistry, which may be challenging. Hence, the fabrication of porous materials using the Pickering HIPE templating approach that would not need chemical reactions and could be easily extended to a wide variety of chemical compositions is highly desirable.

We report herein the stabilization of Pickering hexane-in-water (o/w) HIPEs with volume fractions as high as 0.9 by soft poly(*N*-isopropylamide)-*co*-(methacrylic acid) (PNIPAM-*co*-MAA) microgel particles at concentrations as low as 0.05 wt%. Microgel particles are adsorbed at the oil–water interface to hinder extensive droplet coalescence. Excess microgel particles simultaneously form a gel in the continuous phase to trap oil droplets in the gel matrix, which in turn can inhibit creaming of the oil droplets and enhance the emulsion stability. Evaporation in air of the gelled continuous phase of the HIPEs directly leads to porous materials without any chemical reactions. Furthermore, the porosity of the final structure can be tailored by simply changing the microgel particle concentration.

Fluorescent PNIPAM-*co*-MAA microgel particles were synthesized using surfactant-free precipitation polymerization as described before.[17] The details are provided in the Supporting Information (Figures S1–S4). The resultant microgel particles have an average hydrodynamic diameter of 248 nm at room temperature with a solution pH value of 7.5, as determined by dynamic laser light scattering (see the

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[**] The financial support of this work by the Hong Kong Special Administration Region (HKSAR) Earmarked Project (CUHK402707, 2160324) and the Direct Grant for Research 2006/07 of the Chinese University of Hong Kong (CUHK 2060303) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200902103.

Supporting Information, Figure S1). Recently, it has been well demonstrated that emulsions can be effectively stabilized by such microgel particles alone at high pH values ($\mathrm{pH} > 6$) and low temperature ($T < 32\,^{\circ}\mathrm{C}$).[17–19] For polar oils such as octanol, a catastrophic phase inversion of the emulsion from o/w to w/o was observed when the internal oil volume fraction increased above 0.60.[17] As the nature of the oil phase plays an important role in Pickering emulsions, microgel particles will be used herein to stabilize hexane-in-water emulsions with an internal oil volume fraction greater than 0.80.

Microgel-stabilized emulsions were prepared by mechanically shearing a mixture containing the dispersed phase, hexane, and an aqueous dispersion of microgel particles for 30 s with an Ultra Turrax T25 homogenizer (10 mm head) operating at 13500 rpm. The appearance of emulsions after 12 h is shown in Figure 1. The continuous phases of all mixtures consisted of 2 wt% microgel particles, while the amount of the dispersed phase in the final emulsion varied from 20 to 91 vol%. All microgel-stabilized emulsions are o/w emulsions, in contrast to the usual water-in-oil (w/o) HIPEs.[15,16,20] Note that for a dispersed phase fraction lower than 60 vol%, emulsions are stable but undergo creaming slowly over 12 h after preparation. For internal phases between 80 and 90 vol%, the emulsions not only exhibit remarkable stability against extensive coalescence but also inhibited creaming of the oil droplets, indicating that soft microgel particles are suitable for stabilizing HIPEs. No change is observed in the size of emulsion droplets within a time period of more than three months after the preparation. Increasing the internal phase volume up to 91 vol%, however, results in phase separation of the emulsion.

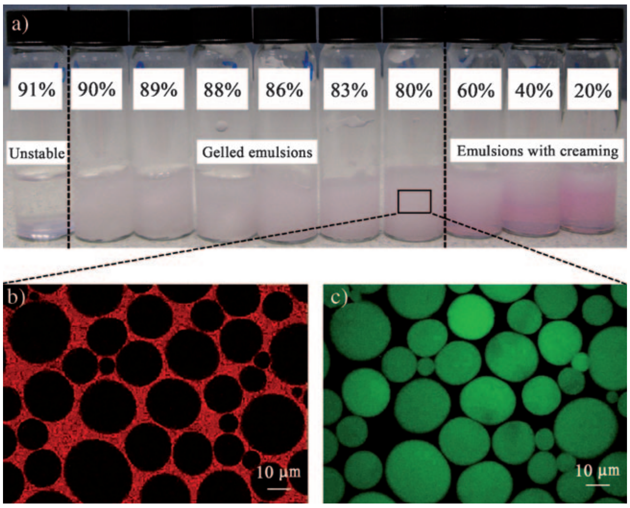

Figure 1. a) Photograph of microgel-stabilized emulsions having an internal oil phase volume from 20 to 91% at room temperature, where the continuous phases of all mixtures consist of 2 wt% microgel particles in the initial dispersion with a solution pH value of approximately 6.0. b, c) Confocal images of the emulsion with 80 vol% hexane oil stabilized by 2 wt% microgel particles excited by lasers with wavelengths of 408 and 543 nm, respectively.

From the confocal images of the fluorescent microgel-stabilized emulsions (Figure 1b), we originally attributed the remarkable stability of HIPEs to the strong adsorption of soft microgel particles at the oil–water interface, which provides a steric hindrance to droplet–droplet coalescence. A recent study by Brugger et al.,[19,21] however, suggested that emulsion stability is not only dependent on the microgel packing, but that the viscoelastic properties of the adsorbed microgel layer are also responsible for emulsion stability, because charged microgels at the interface can provide pronounced elastic behavior, which probably retards the rate of film drainage between coalescing droplets. More importantly, Figure 1b also reveals that the excess microgel particles surprisingly form a gel in the continuous phase, at the same time separating oil droplets in the gel matrix, which in turn inhibits creaming and phase inversion. It is worth mentioning that emulsions with a gelled continuous phase are often produced using a two-step process, in which oil is first dispersed in the continuous phase consisting of monomers and cross-linkers and reactions are then carried out to trap oil droplets in the gel matrix.[22] To our knowledge, this is the first example for the preparation of emulsions with a gelled continuous phase in a single step. We conjecture that the self-gelation of the soft microgel particles in the continuous phase may be due to the specific and highly cooperative hydrogen bonding that exists between charged microgel particles (at $\mathrm{pH} > 6$), which leads to aggregation of microgels. This phenomenon has been observed and reported recently.[21,23] Confocal imaging (Figure 1c) of pyrene-loaded emulsions confirms the presence of polydisperse hexane oil droplets, whose size varies from around one micrometer to tens of micrometers.

Figure 2 shows the appearance of HIPEs with an internal phase of 80 vol% stabilized by different amounts of microgel particles in the initial dispersion. Interestingly, microgel particles at concentrations as low as 0.05 wt% are sufficient to prepare a stable Pickering HIPE. This finding is in contrast to conventional HIPEs, for which large fractions of expensive surfactants (5–50%) are often required to stabilize HIPEs effectively.[2,14] Confocal microscopy images (Figure 3a–c) taken 30 min after the preparation of emulsions show that the microstructures of the emulsions stabilized by different amounts of microgel particles look quite similar. Unprece-

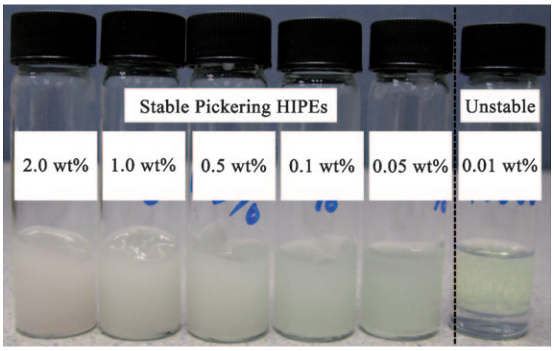

Figure 2. Appearance of the HIPEs formed by varying the amount of microgel particles in the initial dispersion at room temperature, where the dispersed phases of all mixtures have an internal oil phase volume of 80%.

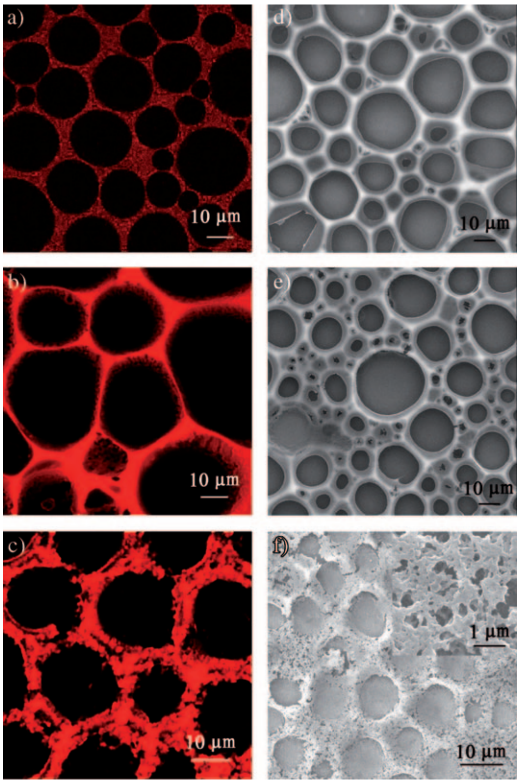

Figure 3. Microstructures of emulsions and porous materials prepared with different concentrations of microgel particles. a–c) Oil-in-water emulsion with 80% hexane and 2 (a), 0.5 (b), or 0.05 wt% (c) particles in the initial dispersion. d–f) SEM images of porous materials obtained after drying the corresponding emulsions (a–c) at room temperature. Note that Figure 3a is the same as Figure 1b.

dentedly, decreasing the amount of microgel particles in the initial dispersion from 2 to 0.05 wt% does not lead to larger droplets, suggesting that the size of the oil droplet is independent of microgel concentration. This result can be ascribed to the fact that during the adsorption of microgel particles to the oil–water interfacial area produced by the forceful mixing process, the microgel particles also form a gel in the continuous phase. In this way, the formed oil droplets are trapped inside the gel network as soon as agitation is stopped, so that even partially covered droplets will not raise the droplet size by undergoing the coalesce. It seems likely that the size of droplets only depends on the input shearing rate. Despite the fact that microgel particles with a concentration of 0.05 wt% can effectively prohibit oil droplets from further coalescence, the stability against creaming increases progressively with increasing particle concentration, as shown in Figure 2. Moreover, confocal imaging also reveals that one advantage of using relatively high concentrations of microgel particles is the formation of a strong gel network in the continuous phase to separate oil droplets, which in turn can lead to the formation of a uniform film after drying in air, as shown below.

After emulsification, the wet HIPEs with an internal phase of 80 vol% stabilized by different amounts of microgel particles were dried in air to remove oil and water. The relatively high vapor pressures of hexane and water (20.2 and 2.34 kPa, respectively, at 25 °C) allow for the evaporation of the emulsion droplets at room temperature. Drying directly leads to the macroporous materials. The corresponding SEM images are depicted in Figure 3d–f. Note that no chemical reactions are involved before oil removal. The average cavity sizes in the porous structures are comparable to the oil droplet diameters of the precursor emulsions, thus suggesting that these cavities result from a loss of the oil component. Therefore, the microgel-stabilized HIPEs used as initial templates are sufficiently strong to withstand the high capillary stresses developed during drying without the distortion of their internal structures. Moreover, the high-magnification images (see inset of Figure 3 f and Supporting Information, Figure S5) show that the microstructures of resultant porous materials exhibit different degrees of pore interconnectivity between neighboring droplets. For example, decreasing the microgel particle concentration in the initial dispersion to 0.05 wt% leads to the formation of more open windows between touching droplets, which suggests that the microgel-stabilized HIPEs enable us to further tailor the pore porosity between touching droplets by simply changing the particle concentration in the initial dispersion. These porous materials should have a great potential for encapsulation applications.

In conclusion, we have shown that stable Pickering HIPEs with an internal phase of up to 90 vol% can be prepared using soft PNIPAM-*co*-MAA microgel particles with very low concentrations (0.05–2 wt%). The microgel particles are effectively adsorbed onto the oil–water interface to hinder droplet coalescence. At the same time, the excess particles form a gel in the continuous phase to trap oil droplets in the gel matrix, which in turn inhibits creaming and phase inversion in Pickering HIPEs. Such Pickering HIPEs therefore have a longer shelf life and can better fulfill aesthetic requirements. In addition, Pickering HIPEs stabilized by microgel particles enable their processing into porous structures in a very straightforward manner without any chemical reactions. The cell walls of the final structures are densely packed with a layer of PNIPAM-*co*-MAA microgel particles, which are pH- and temperature-sensitive. This aspect adds great flexibility to tune the surface properties for specific requirements. We thereby believe that such porous materials have great potential for applications in chemical and biological separation, as catalyst supports, and as scaffolds for tissue engineering.

Experimental Section

Microgel particle synthesis: PNIPAM microgel particles were synthesized using surfactant-free precipitation polymerization.[17] Typically, *N*-isopropylacrylamide (NIPAM; 3.0893 g), *N*,*N'*-methylene bisacrylamide (MBAA; 0.1075 g), methacrylic acid (MAA; 0.1072 g), and the fluorescent dye methacryloxyethyl thiocarbamoyl rhodamine B (MRB; 0.0014 g) were dissolved in deionized water (140 mL) in a 250 mL two-neck reactor fitted with a nitrogen bubbling inlet and outlet and a reflux condenser and stirred with a magnetic stir bar. Then the solution mixture was adjusted to pH 10.88 with sodium hydroxide solution. Note that a recent study showed that a high pH value is not suitable for the synthesis of microgels with high MAA content.[19] After stirring the solution for 40 min at 70 °C under nitrogen bubbling, the polymerization was initiated by addition of potassium persulfate (KPS; 0.031 g) dissolved in deionized water (10 mL). The reaction mixture was kept at 70 °C for 7 h. The resultant microgels were purified by ultracentrifugation and dialyzed for seven days to remove the lower molar mass polymer and unreacted reagents. The size of the microgel particles was measured using laser light scattering (LLS) at an angle of 20°. The apparatus used for LLS measurements was an ALV-5000 goniometer setup (ALV Laser) equipped with a helium–neon laser and a digital correlator.

Microgel-stabilized HIPEs were prepared by homogenizing the microgel dispersion with proper amounts of *n*-hexane using an Ultra Turrax T25 homogenizer (10 mm head) operating at 13500 rpm for 30 s. The total emulsion volume was 5 cm^3. The emulsion type was determined by measuring the conductivity (Jenway). The confocal microscopy images were taken on a Nikon Eclipse Ti inverted microscope (Nikon, Japan). Lasers with wavelengths of 543 and 408 nm were used to excite the fluorescent microgel particles and pyrene molecules, respectively. An oil immersion objective (60×, NA = 1.49) was used to view the samples. The HIPEs were placed on the cover slides and a series of *x*/*y* layers were scanned. The temperature was kept at 25 °C. For SEM observation, emulsions were dried at room temperature for 24 h and then coated with Au before imaging on a FEI Quanta 400 FEG microscope operating at 10 kV.

Received: April 20, 2009

Keywords: emulsions · gels · mesoporous materials · particle-stabilized emulsions

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