Supplementary Information

Characterization of functionalized silica particles

Particle size analysis was carried out by scanning electron microscopy (Figure 1) using a Jeol JSM-5610 LV (Jeol Ltd., Welwyn Garden City, UK). In order to determine the particle size, 1 wt.-% of the oleic acid functionalized silica particles were dispersed by homogenization in styrene in analogue to the procedure used for emulsion preparation. One drop of the suspension was placed directly on a microscope stub and the styrene evaporated via gentle heating. Afterwards, the sample was Au coated and analyzed following the procedure described above. Three individual samples were investigated.

We found that the modified had a silica particle sizes range between 20 and 100 nm in diameter and although the particles fuse together, they can easily be homogeneously dispersed in the organic phase.

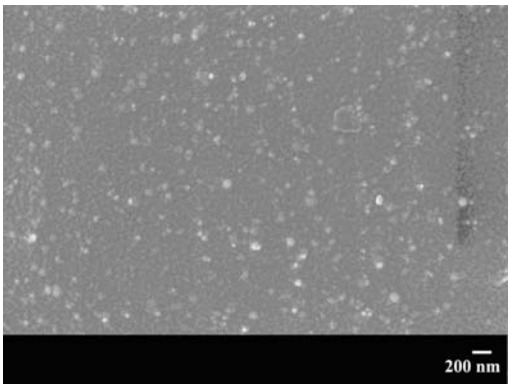

Figure 1. *SEM image showing modified silica particles*

Control experiments: Suitability of oleic acid and unmodified silica particles to act as emulsifier and/or co-emulsifier

An attempt to emulsify 80 vol.-% aqueous phase containing 0.27 M $CaCl_2.2H_2O$ in the monomer phase (1:1 styrene/poly(ethylene glycol) dimethacrylate) by simple stirring using only 3.5 mg oleic

acid as emulsifier resulted in immediate phase separation of the mixture, which proves that the maximum amount of oleic acid that could possibly leach form the modified silica particles (3.5 mg is equivalent to the amount of surface oleic acid adsorbed to 1 wt.-% silica particles used to successfully stabilize w/o HIPEs with respect to the monomers) is not sufficient to stabilize an emulsion (Fig. 2).

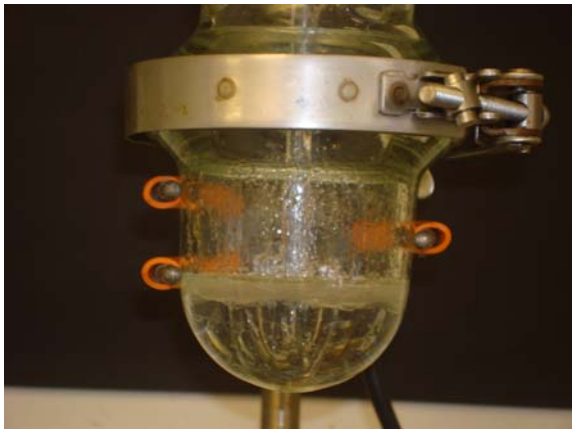

Figure 2. *Photograph of phase separated emulsion (water to oil phase (1:1 styrene/poly(ethylene glycol) dimethacrylate) volume ratio 80:20) demonstrating that oleic acid alone is not a suitable emulsifier to stabilize w/o HIPEs*

Furthermore, we tested 1 wt.-% unmodified (as received) silica particles (which immediately transfer into the water phase even when originally dispersed in the oil phase), only as well as in conjunction with 3.5 mg oleic acid (equivalent to the amount of oleic acid surface coverage of the silica particles) as co-emulsifier system to stabilize an 80 vol.-% internal water phase emulsion. Contrary to the immediate phase separation of the emulsion observed when using oleic acid alone, the emulsions prepared using 1 wt.-% unmodified silica particles alone as well as in conjunction with 3.5 mg oleic acid were rather unstable o/w emulsions as shown in Fig. 3a and b, respectively. These three experiments demonstrate that free oleic acid does act neither as emulsifier for HIPEs nor as co-surfactant in conjunction with unmodified silica particles. Furthermore, unmodified (or in-situ modified) silica particles are not suited to stabilize w/o HIPEs.

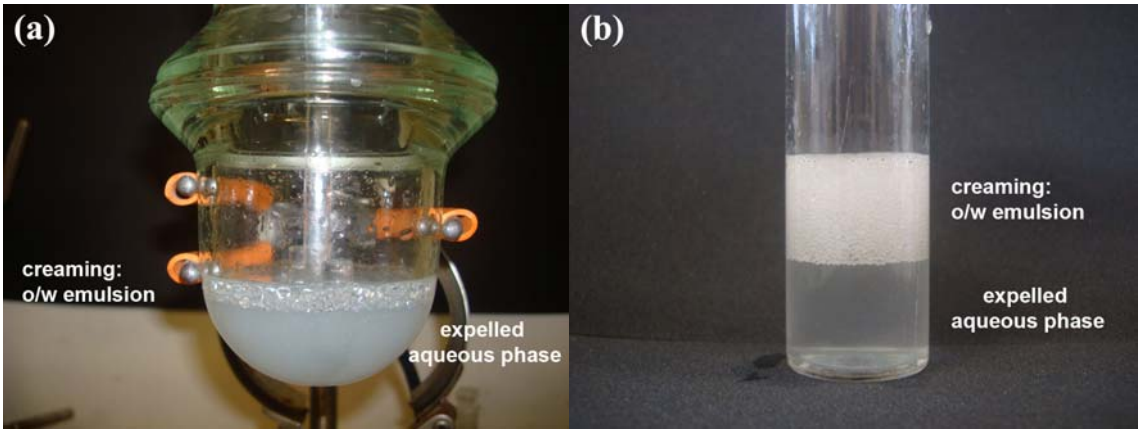

Figure 3. *o/w emulsions(water to oil phase (1:1 styrene/poly(ethylene glycol) dimethacrylate) volume ratio 80:20) a) with unmodified silica particles and b) with unmodified silica particles in conjunction with free oleic acid demonstrating that neither unmodified silica particles alone nor in conjunction with oleic acid are a suitable emulsifiers to stabilize w/o HIPEs*

Influence of the internal phase volume of the emulsion template on pore size of polymerized Pickering-High Internal Phase Emulsions

HIPEs with up to 85 vol.-% internal phase were stabilized using 1 wt.-% (with respect to the organic continuous phase) oleic acid functionalized silica particles and polymerized at 70°C to yield poly-Pickering-HIPEs. Common polyHIPEs are a replica of the emulsion template at the gel point of the polymerizing oil phase, it was concluded from the images in Figure 4 below that droplet size (equivalent to the pore size of the poly-Pickering-HIPE) of the Pickering-HIPE increases with increasing internal phase volume. The increasing amount of internal phase means there is more droplet (w/o interface) area to be covered by the particles. However, as the weight percentage of silica particles (based on the monomer phase) is kept constant, this means that there are effectively fewer particles available (in g/ml emulsion) in an 80 vol.-% HIPE as compared to a 70 vol.-% HIPE and hence the droplet in the emulsion (or pore size in the poly-Pickering-HIPE) increases with

increasing internal phase volume. Above a certain internal phase volume (85 ± 1 vol.-%) the number of particles (when 1 wt.-% particle is used) in the adsorbed layer at the w/o interface is no longer adequate to provide a mechanical barrier against droplet coalescence and thus the emulsion phase separates.

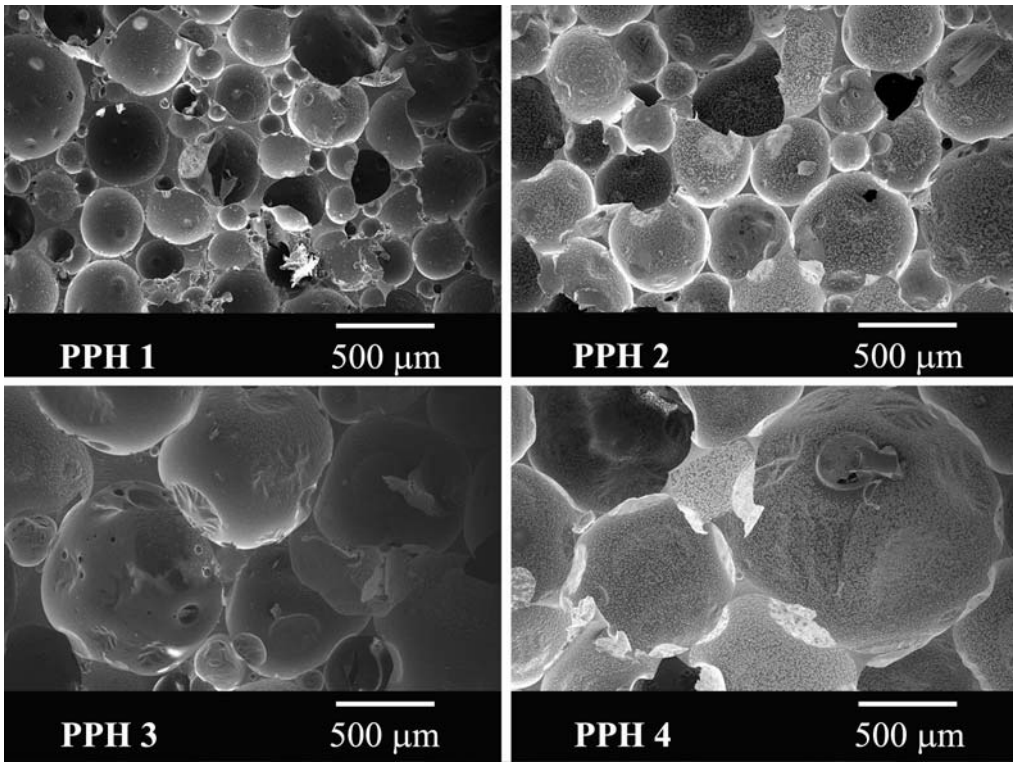

Figure 4. *SEM images showing the pore structure of poly-Pickering-HIPEs synthesized from emulsion templates containing 1) 70 vol.-% internal phase 2) 75 vol.-% internal phase 3) 80 vol.-% internal phase 4) 85 vol.-% internal phase. The Pickering-HIPE templates were stabilized by 1 wt.-% functionalized silica particles.*

Characterization techniques:

Degree of surface coverage of oleic acid functionalized silica particles:

The oleic acid content of the functionalized SP was determined by Thermo Gravimetric Analysis (TGA) (TA Q500 TGA, TA instruments Intl., Delaware, USA). Approximately 8 mg of the particles was placed in a platinum holder and heated to 600°C at a rate of 10°C/min under

an air flow of 20 ml/min. The weight loss was detected as a function of temperature. At least 3 individual samples were investigated.

Droplet size in Pickering-HIPEs:

Microscopy images of the Pickering-HIPEs were taken with an optical microscope (Olympus BX51M). An emulsion sample was placed onto a silanised glass slide in order to avoid heterogeneous emulsion break-down caused by the preferential wetting of the glass by the water phase. The droplet size distribution of the emulsion templates was determined using the software Image tool. At least 100 drops per emulsion were investigated.

Pore structure and pore size in poly-Pickering-HIPEs:

Images of the fractured surfaces of all poly-Pickering-HIPEs produced were taken using a scanning electron microscope (Jeol JSM-5610 LV, Jeol Ltd., Welwyn Garden City, UK). Approximately 1 cm^3 of each sample was rinsed with water to remove any salt that might have been entrapped in the closed pores, dried and fixed to microscope stubs using a double sided carbon sticker and Au coated for 120 s in an argon atmosphere (Scan coat six, Edwards Ltd., Crawley, UK) to achieve the necessary electrical conductivity. The software Image tool was used to determine the pore size distribution of the polymer foams. At least 100 pores form various images taken over the whole sample length were investigated per sample.

Determination of the foam density and porosity of poly-Pickering-HIPEs

Densities and porosities of the poly-Pickering-HIPEs were obtained experimentally. The matrix (polymer or skeleton) density was determined on approximately 300 mg of each polymer foam

using a Helium pycnometer (AccuPyc 1330, Micrometrics Ltd., Limited, Dunstable, UK). Prior to the measurement the foam was crushed into a powder. The envelope or foam density (ρ_f) of each poly-Pickering-HIPE was measured using an envelope density analyzer (GeoPyc 1360, Micrometrics Ltd., Limited, Dunstable, UK). The porosity of the polymer foams was calculated according to the following equation:

$$P = \left(1 - \frac{\rho_f}{\rho_m}\right) \cdot 100 \qquad [\%]$$