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High internal phase emulsion gels (HIPE-gels) from polymer dispersions reinforced with quadruple hydrogen bond functionality†

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A convenient route to organogels templated by high internal phase emulsions has been developed. Key is the use of a waterborne polymer latex loaded with a multiple hydrogen bond (MHB) functionality that becomes disentangled and transfers across the oil–water interface forming a gel network in the oil phase *via* hydrogen bond interactions.

One speaks of a high internal phase emulsion (HIPE), for example water droplets dispersed in oil, when the total volume fraction of droplets exceeds the value of 74% by volume (maximum packing fraction of monodisperse hard spheres). HIPEs are widely used in gels and creams in cosmetic products, petroleum gels for safety fuels, and the food and bio-related industries.[1] HIPEs are commonly stabilized by molecular surfactants, which include amphiphilic block copolymers.[3] In recent years, HIPEs stabilized solely by particles that adhere to the liquid–liquid interface, also known as Pickering HIPEs, have attracted a surge of interest. A variety of particles serving as stabilizer have been reported including silica,[4] titanium oxide[5] and organic microgel particles.[6] To obtain a stable Pickering HIPE, the wettability of particles is very important, which can also usually determine the type of emulsion to be water-in-oil or *vice versa*. Generally, relatively hydrophobic particles prefer to stabilize water-in-oil (w/o) emulsions whilst hydrophilic particles tend to stabilize oil-in-water (o/w) emulsions.[7]

Solidification of the continuous phase of a HIPE in order to prepare a porous monolith can be done through polymerization, the product then is referred to as a poly(HIPE).[2] We pioneered the fabrication of particle-stabilized poly(HIPE)s using polymer microgels, hereby employing sedimentation as a tool to concentrate an originally medium internal phase Pickering emulsion.[8] Bismarck and co-workers[9] reported on the successful preparation of hybrid poly(HIPE)s stabilized by titania and silica nanoparticles with internal phase volumes of up to 90%. In our previous study we stated that it was essential that the polymer colloids used as stabilizer were cross-linked to prevent disintegration *via* swelling once assembled at a liquid–liquid interface in which the organic phase was a solvent for the polymer, as this ultimately resulted in a loss of Pickering stabilization.[8] Zhang and Chen[10] showed that non-crosslinked polymer particles could be used in the preparation of poly(HIPE)s if upon exposure to the organic phase the swollen and disentangled individual polymer chains acted as an amphiphilic polymeric stabilizer. An interesting development was recently reported by Ngai and coworkers[11] who employed poly(methacrylic acid)-based microgel particles to prepare a HIPE without liquid-like flow behavior, in other words a colloidal gel based HIPE. Relatively large amounts of microgel particles are required (up to 5 wt%) in order to establish the fractal-like gel structure.

Here we report a facile strategy to produce strong HIPE-gels, more specifically HIPE-organogels. The approach involves the use of waterborne polymer colloids which are loaded with multiple hydrogen bond (MHB) arrays, in our case 2-ureido-4[1*H*] pyrimidinone (UPy) which can undergo very strong and highly directional self-complementary quadruple hydrogen bond interactions through dimerization, as first shown by Sijbesma, Meijer *et al.*[12] These were introduced during the synthesis of the polymer latex by emulsion polymerization using a functional comonomer (see ESI† for synthesis and Fig. 1). The latex particles are triggered to adhere to the oil–water interface upon addition of salt, which

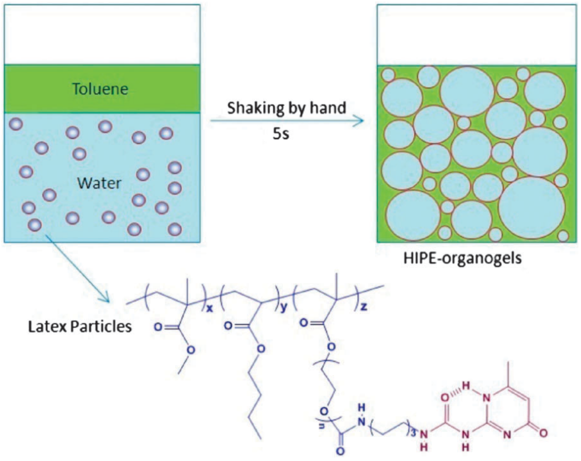

Fig. 1 Schematic of the method for preparation of HIPE-organogels.

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compresses their electrostatic double layer. Upon contact with the organic phase (which is by necessity a good solvent for the polymer) the particles can swell and the individual polymer chains can disentangle and diffuse further into the organic phase. The pendant UPy groups in the polymer chains create a physically crosslinked and self-supporting gel through self-complementary quadruple hydrogen bond interactions.

The polymer colloids functionalized with UPy moieties were prepared by soap-free emulsion polymerization, a well documented method for the synthesis of monodisperse polymeric nanoparticles. A 50 : 50 molar ratio (44 : 56 wt% ratio) of methyl methacrylate (MMA) and butyl acrylate (BA) was used as a monomer mixture with approximately 1.2 mol% (based on total monomer) of UPy functionalized methacrylate (ESI†).

Particles were fluorescently labelled using small quantities of Rhodamine B piperazine methacrylamide. This fluorescent monomer was made from the nucleophilic substitution reaction between Rhodamine B piperazine and methacryloyl chloride in 80% yield (Fig. 2). Full experimental details and characterisation are provided in the ESI.†

A reference latex which had carboxylic acid functionality was prepared using methacrylic acid (MAA, 4.6 mol%) as a functional monomer, instead of the UPy monomer. Monodisperse particle size distributions were obtained for both the UPy and the reference carboxylic acid functionalized latex particles (dispersity of 0.025 and 0.012, respectively) with *z*-average diameters of 223 nm and 235 nm, respectively, as measured by dynamic light scattering (ESI†, Fig. S1 and S2).

Our starting point for fabricating the HIPE-organogels is a 0.1 wt% waterborne dispersion of our polymer colloids (0.8 mL). To this we add 50 mg (1.05 mol dm^{-3}) of solid NaCl after which 0.2 mL of toluene was added. This amount of NaCl was required in order to compress the double layer sufficiently and trigger particle adhesion to the toluene–water interface (the dependency of the ζ potential of PMMA–PBA–PUPy particles on sodium chloride concentrations at pH = 7 is shown in Fig. S3, ESI†). At this salt concentration coagulation of the latex particles is relatively fast (the half-life time for fast coagulation is ~2 seconds according to the equation developed by Smoluchowski) so the subsequent emulsification step should be conducted directly after mixing. Next the mixture was shaken vigorously by hand for just 5 s. Alternatively the HIPE organogel can be easily made by placing on a vortex mixer (Fisherbrand, Whirlimixer) at 2800 rpm for 10 seconds (see ESI† for video). High internal phase emulsion self-standing organogels were formed immediately under these relatively low-shear conditions. Stable HIPE-organogels were made using particle weight fractions of 5% down to an impressive 0.1% with internal phase volumes of up to 85 vol%. An example of one of the HIPE-organogels in which the toluene continuous phase is tagged with hostasol dye is shown in Fig. 3a.

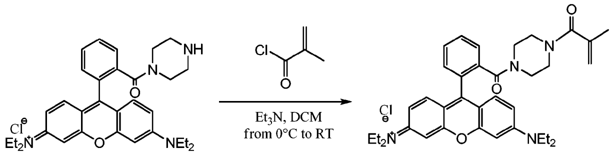

Fig. 2 Synthesis of Rhodamine B piperazine methacrylamide from Rhodamine B piperazine and methacryloyl chloride.

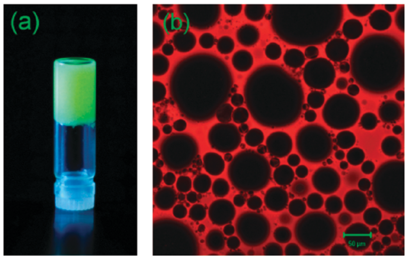

Fig. 3 (a) Photograph of an inverted vial containing a typical HIPE-organogel with aqueous dispersed phase volume of 80% (toluene containing a hostasol fluorescent dye as continuous phase) stabilized using UPy functionalized soft latex particles (0.1 wt%), (b) confocal image of the same fluorescently tagged HIPE-gel, scale bar: 50 μm.

Confocal laser scanning microscopy (CLSM) was used to investigate the porous microstructure of our HIPE gels. Fig. 3b confirms that water-in-oil HIPE gels were formed, with toluene (hostasol dye labelled) as the continuous organogel phase with droplets of water entrapped. The size of the water droplets varied from several to tens of micrometres. CLSM analysis of our rhodamine tagged polymer colloids indicates that the polymer chains and thus the supramolecular hydrogen bond reinforced gel network distributed themselves throughout the continuous toluene phase, proving that indeed successful phase transfer and disentanglement of the polymer chains have taken place. Note however that there is a logical enrichment at the w/o interface (Fig. 4a). Exposure of the HIPE gel to the open atmosphere for 30 min led to preferential evaporation of the toluene phase, hereby deforming the structure into a polyhedral morphology, more commonly observed in foams (Fig. 4b). The continuous cellular network is preserved and no fusion of neighbouring cells that contained water was observed. Prolonged drying periods throughout which the majority of both liquid phases evaporated led to relaxation of the polyhedral structure back into a more spherical porous morphology. Eventually upon drying some macroscopic buckling of the HIPE-gel monoliths was observed. The structure remained self-supporting.

Scanning electron microscopy analysis confirms the porous morphology of the HIPE organogel (Fig. S4, ESI†). No individual particles can be identified in HIPE gels after drying at room temperature, which confirms the theory that the particles (at least partially) film forms upon exposure to toluene. Increasing the concentration of the particle dispersion from 0.1 wt% up to 5 wt% showed no marked change in the average pore size and pore size distribution, presumably due to the low shear force employed limiting the droplet size (Fig. S5, ESI†).

The quadruple hydrogen bond network formed by UPy arrays reinforces the physical properties of the HIPE gel scaffolds and allows weight fractions down to 0.1% of colloidal particles in the aqueous phase to support the solid-like structures of the HIPE gel. To test the strength of the HIPE gel network reinforced by the UPy arrays, a HIPE organogel was made with enclosed water droplets containing 1 M NaCl and Rhodamine B as a dye. Submersion of this monolith into pure water created a high osmotic pressure difference between the dye labelled internal water phase and the outer water bulk phase.

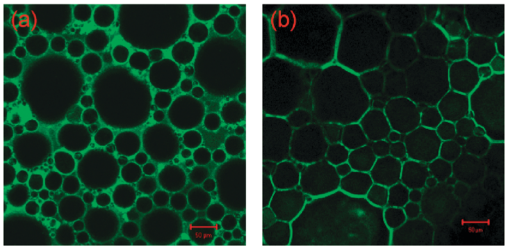

Fig. 4 Confocal images of (a) the HIPE gel and (b) the HIPE gel after 30 min of preparation, excited by laser with a wavelength of 480 nm for the rhodamine labeled UPy functionalized particles, both scale bars: 50 μm.

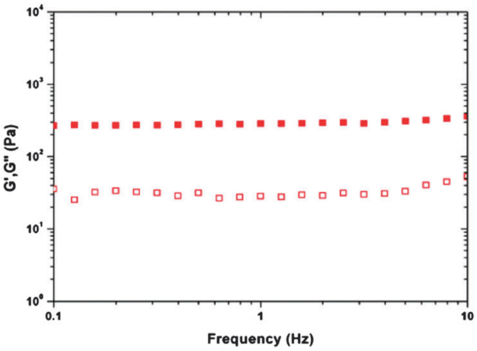

Fig. 5 Storage modulus G' (closed symbol) and loss modulus G'' (open symbol) of HIPE-organogels (0.1 wt%) as a function of frequency in the oscillatory frequency sweep.

No rupture of the closed cells of the organogel was observed, as this would lead to a rapid release of the dye into the continuous phase. Dye release was slow and occurred through diffusion, as confirmed by UV-Vis measurements of the continuous bulk water phase (Fig. S6, ESI†). This opens an opportunity to employ our organogels as potential controlled release vehicles, pressure sensors, and compartmentalized chemical reaction microenvironments.

We investigated the rheological properties of the HIPE-organogels. Fig. 5 shows the dependence of the storage and loss moduli of our HIPE-organogels (0.1 wt% of particles used) on the frequency in the oscillatory frequency sweep. Throughout the entire measured frequency range, the storage modulus (G') is considerably higher than the loss modulus (G''), which indicates that stable gels were formed. This is also consistent with the observation of Fig. 3a that the gels cannot flow even after inverting the vial.

To shine a light on the role and the reinforcement of the UPy groups we compared the rheological properties of HIPEs formed by PMMA–PBA–PMAA latex particles which have carboxylic acid providing double hydrogen bonding interactions. Upon loading 0.1 wt% of these particles, no HIPE-organogel can be prepared as the system can undergo flow easily. Only upon increasing the particle concentration by a factor of 10 up to 1 wt%, and also noting that the molar amount of carboxylic acid groups is fivefold with respect to UPy, can a HIPE-organogel be formed exhibiting comparable rheological performance (Fig. S7, ESI†).

In conclusion, HIPE gels were prepared by simple hand-shaking of a water–toluene mixture, the former containing small quantities (down to 0.1 wt%) of UPy functionalized (1.2 mol%) PMMA-*co*-PBA latex particles. Up to 85 vol% of water droplets could be dispersed into a continuous organic gel phase composed of toluene and unravelled polymer chains, originating from the polymer latex particles. The gel was physically reinforced through quadruple hydrogen bond interaction of the UPy moieties. The HIPE-gels were able to withstand a large osmotic pressure gradient, meaning that individual cells (water droplets) were kept intact and thus compartmentalized. Upon removal of all volatiles self-supporting cellular monoliths were obtained. We believe that our approach to the fabrication of the HIPE gels opens routes for potential applications in medical injectable gels, pressure sensors, and other interesting multiphase soft matter materials.

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