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COMMUNICATION

Hybrid high internal phase emulsion (HIPE) organogels with oil separation property

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Hybrid HIPE organogels were prepared from pre-formed hybrid organogels, which formed from a triblock ionomer and Fe₃O₄ nanoparticles via charge-driven assembly. Magnetic materials can be obtained from these hybrid HIPE organogels simply by removal of solvents, and these materials have been confirmed to be an excellent candidate for absorption of oil from water.

High internal phase emulsions (HIPEs) consist of continuous phase and internal/dispersed phase, with the total volume fraction of the internal phase exceeding 74%.^[1] HIPEs are usually highly viscous, and they are also known as gel emulsion.^[2] HIPEs can be solidified to prepare various materials with low density and porous structures through polymerization of the continuous phase, and they are also called poly(HIPEs).^[3] The poly(HIPEs) exhibit a variety of applications from tissue engineering,^[4] sensor,^[5] drug delivery^[6] to hydrogen storage.^[7] The route to prepare poly(HIPEs) usually includes three steps.^[8] First, a stable HIPE is prepared with a polymerizable continuous phase, and then polymerize the continuous phase to solidify the emulsion's microstructures. Finally, removal of the residue of continuous phase and dispersed phase to obtain porous materials with low density. To prepare HIPE, surfactants and solid particles are the most commonly used as stabilizer. However, surfactants show low efficiency, where as much as 5-50% (w/v) of the continuous phase is required to stabilize HIPEs.^[9] Solid particles stabilized HIPEs are known as Pickering emulsions.^[10] Phase inversion may occur in Pickering emulsion although some inorganic particles have been successfully used as stabilizer. As a result, it can be complicated to prepare hybrid materials from poly(HIPEs).

Recently, solidification of HIPEs has been achieved directly by applying gels as stabilizer,^[11, 12, 13] and they are also called as HIPE organogels or hydrogels according to the kinds of the continuous phase. Ngai and co-workers first reported HIPE hydrogels and organogels stabilized by ionisable polymer microgel particles, and porous materials have been obtained from the HIPE organogels.^[11] By introduction of inorganic particles into these gel particles stabilized HIPE gels, hybrid HIPE gels can be obtained, and these

gels can be used as template to prepare various porous inorganic materials.^[14] However, there is no report on the preparation of hybrid materials from these hybrid HIPE gels, which may result from the lack of strong interaction between the microgel particles and inorganic particles.

Herein we describe a new strategy to prepare hybrid HIPE organogels from hybrid organogels, which formed from a triblock ionomer, namely sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) and an inorganic nanoparticle, (3-aminopropyl)triethoxysilane modified Fe₃O₄ nanoparticles, by charge-induced assembly. Fe₃O₄ was chosen as inorganic component because of its magnetic responsiveness, which endows some advantages for separation by applying a magnetic field. In our previous study, we pioneered the fabrication of HIPE organogels from polymer organogels, which were from SSEBS and a series of hydrophilic polypropylenimine (PPI) dendrimers.^[13] By tuning the hydrophilicity and functional groups on Fe₃O₄ nanoparticles, strong interactions may occur between SSEBS and the inorganic nanoparticles. The sulfonated polystyrene blocks of SSEBS and modified Fe₃O₄ nanoparticles work together to stabilize water droplets in organic solvents. The middle EB blocks may connect different droplets to form three dimensional networks. When the volume fraction of water droplets in the networks exceeds 74%, hybrid HIPE organogels formed. After removal of solvents, these gels transform into a type of magnetic materials with low density, which are excellent candidate for oil absorption from water.

Hybrid organogels were obtained by mixing SSEBS solution and -NH₂ modified Fe₃O₄ nanoparticles dispersed in THF, and the formation of the organogels was in 10-30 seconds, which was confirmed by tube-inversion method (See ESI, Movie 1).^[15] The fast formation of these organogels is contributed to the strong interaction between SSEBS and the inorganic nanoparticles, and the interaction has been verified to be ionic interaction by FT-IR (See ESI, Fig. S2). It can be seen that there are peaks in the SAXS profiles of the hybrid organogels (See ESI, Fig. S3), which implies the microphase separation in these organogels. Thus the formation of these organogels is driven by charge-induced assembly.

A grey hybrid gel was obtained by mixing the pre-formed hybrid organogel, THF and aqueous salt solution, and the formation of the new gels was again confirmed by tube-inversion method.^[15] Control experiments indicate that the ionic interaction between SSEBS and $-NH_2$ modified Fe_3O_4 nanoparticles induces the formation of the new gels, since SSEBS, $-NH_2$ modified Fe_3O_4 , SSEBS/non-modified Fe_3O_4 nanoparticles or SEBS/ $-NH_2$ modified Fe_3O_4 nanoparticles cannot drive the formation of the gels under the same condition.

The structures of the newly-formed gels were studied by measuring their conductivity, and the conductivity of the gels was about $0 \mu S cm^{-1}$, which indicates that the two phase system formed with organic solvent as the continuous phase.^[13] So they are organogels. The volume fraction of the internal phase was over 74%, and thus hybrid high internal phase organogels was formed.

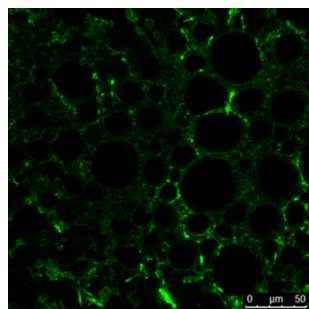


Fig. 1 Confocal image of hybrid HIPE organogels, excited by laser with a wavelength of 405 nm for the pyrene labelled organic phase, scale bar: 50 μm .

To verify the formation of high internal phase organogels, confocal microscopy was applied to these gels. The confocal image of the gel in Fig. 1 confirmed the formation of water-in-oil organogels, with toluene (pyrene labelled) as the continuous organogel phase with water droplets entrapped. The size of water droplets varied from several to tens of micrometres, which was in the size range of emulsions, and thus hybrid HIPE organogels formed.

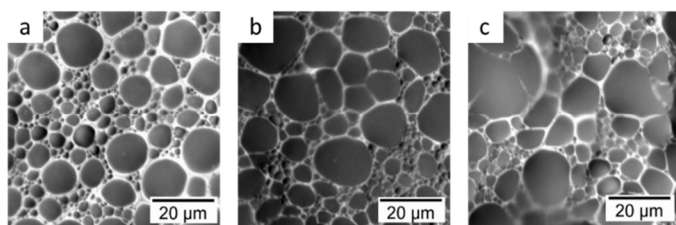


Fig. 2 Optical micrographs (Mag. $\times 100$) of the hybrid HIPE organogels with (a) 80%, (b) 84% and (c) 88% of internal phase.

The morphologies of the hybrid HIPE organogels were further observed by optical microscopy, and the photos are shown in Fig. 2. It can be seen that the sizes of the dispersed phase are from a few to tens of micrometres, and this result is same as that from confocal microscopy. Few water droplets deformed in the hybrid HIPE organogels with 80% of internal phase, and the deformed droplets increase gradually with the increase of internal phase. Most of the spheres deformed when the internal phase is up to 88%. With the increase the internal phases from 80% to 88%, the sizes of water droplets also increase. It seems that some deformed water droplets

emerged into a bigger one in the organogel with 88% of internal phase.

In the preparation of the hybrid HIPE organogels, aqueous NaCl solution was added to the mixture step by step. It was noticed that with the increase of water, the mixtures transferred from fluid to solid. The gels flow very slowly in an inversed vial with 75% internal phase, and no flow was observed for a few hours with increasing the internal phase to 88%. The effects of water content on the strength of the hybrid HIPE organogels were studied quantitatively by rheological measurements. From the results for dynamic frequency measurements in Fig. 3, It is observed that the all the elastic modulus G' is higher than the corresponding viscous modulus G'' , indicating the formation of three dimensional networks. Both the G' and G'' increase with the increase of dispersed water phase in the hybrid HIPE organogels, which is the typical property of HIPEs.

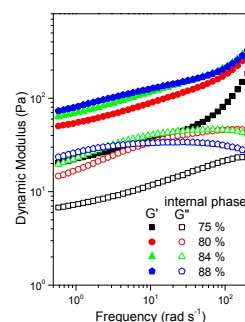


Fig. 3 G' and G'' of HIPE organogels with volume fractions of internal phase at 75, 80, 84 and 88 % as a function of oscillatory shear frequency.

The amount of Fe_3O_4 on the mechanical properties of HIPE organogels was also studied, since it determines the magnetism of the organogels. It can be seen from Fig. 4(a) that increasing the amount of Fe_3O_4 nanoparticles in the gels does not affect the strengths of these organogels. This result means that a large amount of Fe_3O_4 nanoparticle can be loaded onto the hybrid HIPE organogels, and it will increase the magnetism of these organogels.

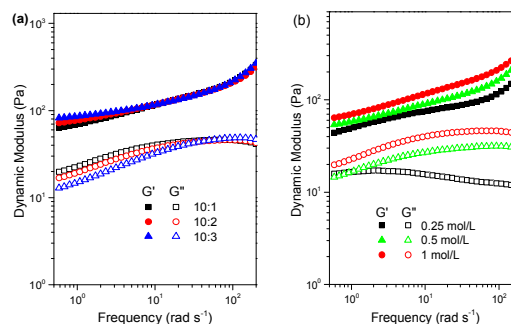


Fig. 4 G' and G'' of HIPE organogels with (a) different Fe_3O_4 nanoparticles at and (b) different salt concentrations.

The hybrid HIPE organogels are induced by ionic interaction between SSEBS and inorganic nanoparticles, and it is expected that electrolytes will affect the formation or strength of the hybrid HIPE organogels. Control experiments showed that the hybrid HIPE organogels cannot be obtained by using water instead of NaCl

aqueous solution, as water cannot disperse into oil phase which contains SSEBS and Fe_3O_4 . Other types of salt such as KCl and K_2SO_4 are tried, and they can be used in the situation.

The effect of salt concentration on the strength of these organogels was studied quantitatively by rheological measurements, and the results for dynamic frequency measurements are shown in Fig. 4(b). From the results, it is observed that the strength of these organogels increases with the salt concentration, which will be benefit for the application of the hybrid HIPE organogels in oil spill recovery in sea.

The hybrid HIPE organogels are quite stable, which was confirmed by an aging experiment. The experiment was conducted in closed vials. It was observed about 5% (v/v) of water was separated from the hybrid HIPE organogels in the first week, which indicates that these organogels are not always in the thermodynamic equilibrium state. Further observation of these organogels for two months, no further change was observed.

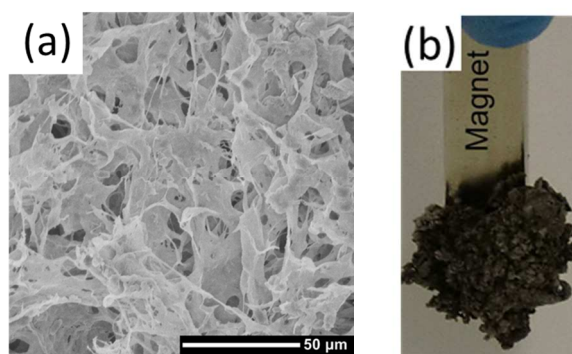


Fig. 5 (a) SEM micrograph (Mag. $\times 500$) of porous materials dried from HIPE organogel with 88% internal phase and (b) optical photo of porous material with a magnet.

After removal of the solvent from the hybrid HIPE organogels, porous materials with low density have been obtained. The porous structures have been observed by optical microscopy and scan electron microscopy (SEM). The optical micrograph and SEM micrograph are shown in Fig. S4 and Fig. 5(a), respectively. From these micrographs, it can be seen the size of porous structures vary from several to about 50 μm , which means the aggregation of dispersed internal phase occurred during the removal of solvents. The materials have a low density of 0.04 g cm^{-3} , which is consistent with the volume shrinkage during removal of solvents. The hybrid materials show magnetic properties, which have been confirmed by applying magnetic field with a magnet in Fig. 5(b) (See ESI, Movie 2).

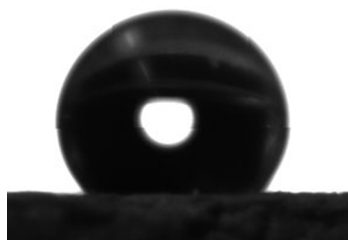


Fig. 6 Photograph of water droplet on surface of porous materials taken during contact measurements.

The surface property was examined with contact angle measurements, and a typical photo of water droplet on the surface of the porous material is shown in Fig. 6. The modified Fe_3O_4 nanoparticles and the sulfonated polystyrene blocks of SSEBS can be hydrophilic, but the middle EB block of SSEBS is hydrophobic. From the results of the contact angle measurements, it can be calculated that the average water contact angle of the porous material is 136° , indicating that the material is hydrophobic.

The magnetic porous materials were studied for the separation of oil and water, and results showed the materials absorbed oil from an oil water mixture in a few seconds (See ESI, Movie 3), which is quickest in the reported absorbers for the separation of oil and water. The magnetic materials exhibit various absorption capacity from 13 to 26 times to different kinds of oil from water, and the results are shown in Fig. 7. Furthermore, as the newly formed organogels still contains magnetic nanoparticles, they can be easily collected from water by applying the magnetic field (See ESI, Movie 4). The porous materials are from polymers with simple modification, and thus they are inexpensive in comparison with low molecular weight gelators.^[16] Moreover, unlike organogels from low molecular-weight gelators,^[17] there is no co-solvent used in the separation of oil and water, which can be cheap and environmental-friendly. Thus, we believe that the magnetic materials from hybrid HIPE organogels can be an excellent candidate for absorption of oil from water.

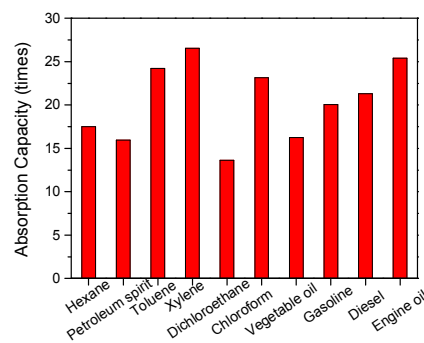


Fig. 7 Oil absorption capacity of hybrid materials from hybrid HIPE organogels.

In conclusion, we have presented hybrid HIPE organogels prepared from hybrid organogels, which are formed from a triblock ionomer SSEBS and -NH_2 functionalized Fe_3O_4 nanoparticles by charge-induced assembly. After removal of solvents, the hybrid HIPE organogels transformed into a magnetic porous material, which is believed to be an excellent candidate for separation of oil and water. The sulfonation degrees and block lengths can be easily tuned, and many kind of inorganic nanoparticles can be modified with -NH_2 groups, we believe this method can be a versatile route to prepared hybrid HIPE organogels and materials.

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Notes and references

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