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# *Electronic Supplementary Information (ESI)*

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

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## 1. Experimental section

***Materials.*** Triblock ionomer, namely sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS), was prepared by sulfonation of polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS, Mn = 11,800) according to the method described in our previous study.[1] The SEBS contains 28 % of polystyrene and after sulfonation, the SSEBS has 15.0 mol % of polystyrene on SEBS grafted with -$SO_3H$ groups by titration. $Fe_3O_4$ nanoparticles were prepared via co-precipitation method according to reference.[2] Deionized water was used in all experiments.

***Preparation of –NH$_2$ modified Fe$_3$O$_4$ nanoparticles.*** –$NH_2$ modified $Fe_3O_4$ nanoparticles were prepared by surface silanization of $Fe_3O_4$ nanoparticles. In details, 0.95 g of the $Fe_3O_4$ nanoparticles were dispersed into 20 mL of water, and 0.5 mL of (3-Aminopropyl)triethoxysilane in 2 mL of ethanol was added into the $Fe_3O_4$ nanoparticles solution at 25°C. After 24 hours, the surface modified $Fe_3O_4$ nanoparticles were separated and washed with deionized water for several times with the help of a magnet. Subsequently, –$NH_2$ modified $Fe_3O_4$ nanoparticles were re-dispersed into 20 mL of tetrahydrofuran (THF) for further use. The synthesis of the $Fe_3O_4$ nanoparticles was characterized by transmission electron microscopy (TEM), and from the result in Fig.S1, it is observed that the sizes of the nanoparticles vary from several to about 20 nm.

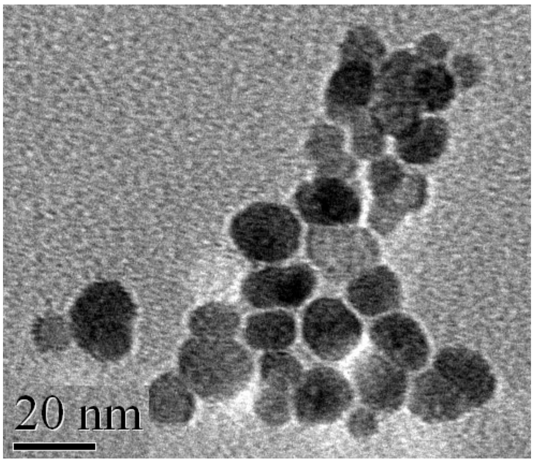

Fig.S1 TEM imagine of $Fe_3O_4$ nanoparticles.

***Preparation of pre-formed hybrid organogels.*** Hybrid organogels were obtained by mixing SSEBS solution and –$NH_2$ modified $Fe_3O_4$ nanoparticles. 5 % (w/v) SSEBS solution was obtained by dissolving SSEBS into mixed solvents of toluene and methanol (98/2, v/v). Hybrid organogels formed when SSEBS solution and dispersed $Fe_3O_4$ nanoparticles mixed at 10:1 (v/v).

***Preparation of hybrid HIPE organogels.*** HIPE organogels were prepared by shearing a mixture of aqueous salt solutions (4, 5, 6 or 7 mL) with different NaCl concentrations (0.5 or 1 mol $L^{-1}$), THF (1 mL), pre-formed hybrid organogels (1 mL) for about 2 minutes with a Vortex mixer at 3,400 rpm. The fraction of water phase in HIPE organogels was determined by control experiment described in our previous paper.[3] The volume fractions of water phase are 75%, 80%, 84% and 88% in corresponding to the addition of 4, 5, 6 and 7 mL of aqueous salt solution, respectively. THF is necessary in preparation of hybrid HIPE organogels from SSEBS/$Fe_3O_4$ organogels although it is believed the ionic domains are hydrophilic. Control experiment showed that a precipitate formed without addition of THF.

***Removal of solvents from the hybrid HIPE organogels.*** The hybrid HIPE organogels were poured into diethyl ether under mechanical stirring, and after collected from diethyl ether, the hybrid organogels were washed twice with water. Subsequently, the hybrid HIPE organogels were freeze drying for 48 hours.

***Rheological experiments.*** Rheological experiments were carried out on a TA DHR 3 rheometer with a cone-plate geometry at 25 °C. A cone with a tilt angle of $2^o$ and a diameter of 40 mm was used, and gap width was set to be 200 *u*m. A solvent trap was used to minimize the effect of evaporation. Frequency sweeps with an angular frequency from 0.5 to 600 rad $s^{-1}$ were performed at a strain of 1 %. For accuracy, the data from 0.5 to 200 rad $s^{-1}$ were used.

***Fourier-transform infrared (FTIR) spectroscopy.*** FTIR spectra were obtained with a Bruker Vertex 70 FTIR spectrometer. To prepare samples for FTIR, SSEBS solution, $Fe_3O_4$ dispersed solution and the newly formed mixtures of SSEBS solution and $–NH_2$ modified $Fe_3O_4$ dispersed solution were was dropped onto the KBr disk, respectively. The solvents were evaporated in fume hood first and then dried in vacuum oven at 40 $^oC$ for 2 hours prior to measurements. The spectra were recorded in the range of 600 – 4000 $cm^{-1}$ at a resolution of 4 $cm^{-1}$.

***Conductivity measurement.*** The conductivity of the hybrid HIPE organogels was determined on a SevenEasy conductivity meter (Mettler-Toledo GmbH, Switzerland) at 25 degrees. The conductivities of water and organic solvents were also studied for comparison, where water and organic solvents used were from the control experiment described above.

***Confocal microscopy.*** Confocal imaging was taken on a laser scanning confocal microscope (Leica SP5, Leica Microsystems CMS GmbH, Germany). Magnetic HIPE organogel with 80 % of dispersed water was transferred onto a glass slide and observed immediately. A laser with wavelength of 405 nm was used to excited pyrene in the organic phase.

***Optical microscopy.*** Optical imaging was taken on an optical microscope (Olympus BX51). Magnetic HIPE organogels with 80 %, 84 % and 88% of dispersed water phase were transferred onto a glass slide and observed at 100 times immediately. Porous material from HIPE organogel (88% of dispersed phase, SSEBS/$Fe_3O_4$ nanoparticles = 10/1, using 0.5 mol/L aqueous NaCl solution) was cut into pieces, and then put onto a glass slice for observation.

***Contact angle measurements.*** Contact angle measurements of the porous materials were carried out in a KSV CAM 101 contact angle instrument. Distilled water was used for the analyses on the samples, and the measurements were taken at room temperature. For accuracy, the water contact angle was calculated from 5 measurements which were obtained from different parts of the same sample.

***Small-angle X-ray scattering (SAXS).*** SAXS experiments were carried out at the Australian Synchrotron on the small/wide-angle X-ray scattering beamline, and the camera length used is 7 meters. The samples were put into a multiwall gel plate, and the background correction was done with the same solvent used.

***Scan Electron Microscopy (SEM).*** Surface morphologies were imaged with a NEOSCOPE JCM-5000 SEM. The samples used are same with these for optical microscopy, and the surfaces were coated with a thin gold layer. The images were taken under an accelerating voltage of 10 kV.

***Oil Absorption Evaluation.*** Oil absorption capacity experiments were carried out as follows. Typically, 20 mL of oil was dropped into 50 flasks with 20 mL of water in it, and then about 0.2 g of hybrid material was put into the flasks. It was observed the hybrid material absorbed oil very quickly, and after enough time to reach equilibrium, the hybrid materials were picked up with a tweezer or magnetic bar. They were weighed on a balance after laying on a filter paper to remove the excess oil. Oil absorption capacity was calculated as follows: absorption capacity = $\frac{w_2 - w_1}{w_1}$ , where $w_1$ and $w_2$ stand for the weight of hybrid materials before and after oil absorption.

## 2. Charge-driven assembly of hybrid organogels

***Ionic interaction.*** FTIR spectroscopy was applied to study the ionic interaction between SSEBS and -$NH_2$ modified $Fe_3O_4$ nanoparticles after evaporation of solvents. FTIR spectra in Fig. S2 shows with the increase of -$NH_2$ modified $Fe_3O_4$ nanoparticles in the mixtures, characteristic peaks of the protonated amine moieties can be observed at 1541 and 1560 $cm^{-1}$.[4] Moreover, the characteristic peak of $–SO_3H$ at 1538 $cm^{-1}$ transfer to 1533 $cm^{-1}$ which is the characteristic absorption peak of $–SO_3^-$ groups.[5] This is in accordance with the ionic interactions observed between sulfonic acid groups and amine moieties in our previous studies on blends of triblock ionomer SSEBS.[1, 6]

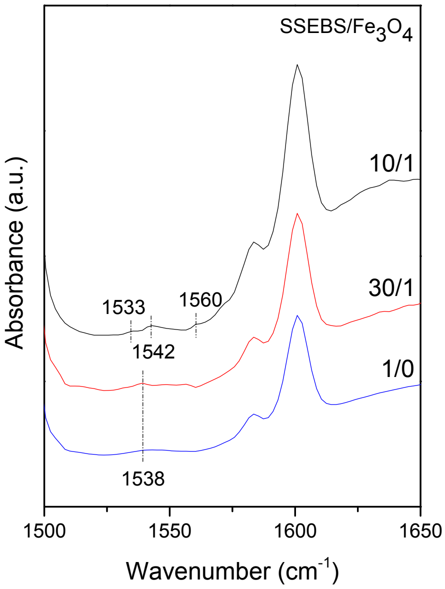

Fig. S2 FT-IR spectra of SSEBS, mixtures with SSEBS/-$NH_2$ modified $Fe_3O_4$ nanoparticles = 30/1 and 10/1 (v/v) in the range of 1500–1650 $cm^{-1}$.

***Microphase separation.*** Small angle X-ray scattering (SAXS) measurement was applied to elicit the morphology of SSEBS/$Fe_3O_4$ hybrid organogels, and their SAXS profiles are shown in Fig. S3. Our previous results have shown that there is no microphase separation in SSEBS solutions.[1] However, obvious peaks occurred in SAXS profiles for SSEBS/$Fe_3O_4$ hybrid organogels, implying the appearance of microphase separation in these organogels. The separation should result from charge-driven assembly.

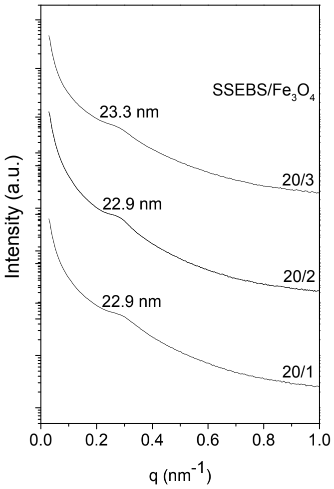

Fig. S3 SAXS profiles for SSEBS/Fe$_3$O$_4$ hybrid organogels with SSEBS/Fe$_3$O$_4$ = 20/3, 20/2 and 20/1.

## 3. Optical and SEM micrographs of porous materials

***Porous structures.*** The porous structures can be observed with optical microscopy and SEM microscopy. Fig. S4 (a) shows the sizes of the pores in about 20 to 120um, which is consistent with that from SEM. Fig. S4(b) and (c) show the pores are connect with each other, which may explain the rapid absorption of the materials.

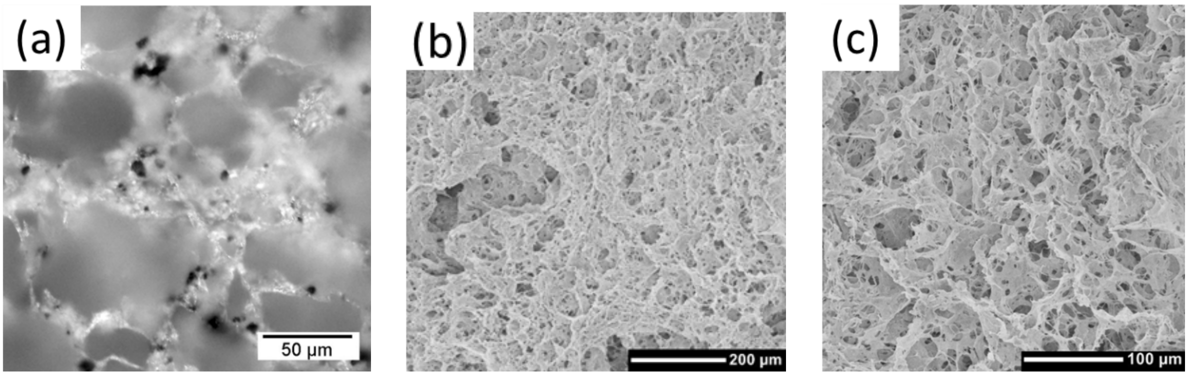

Fig. S4 optical micrograph (Mag. × 100) (a) and SEM micrographs (Mag. × 100) (b) and (Mag. × 200) (c) of porous materials.

## 4. Movies

Four short movies are available:

***Movie 1.*** Formation of hybrid organogels: Hybrid organogels formed when SSEBS solution and $-NH_2$ modified $Fe_3O_4$ nanoparticles mixed;

***Movie 2.*** Magnetism: After removal of solvents, the hybrid HIPE organogels can be collected by a magnet, showing their magnetism;

***Movie 3.*** Fast absorption of oil: The porous materials can absorb oil from oil/water mixture in a few seconds;

***Movie 4.*** Collection: After absorption of oil, the gels can be collected by applying magnetic field.

## 5. References

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