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Isorefractive high internal phase emulsion organogels for light induced reactions

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1. Experimental section

Experimental

Materials. Sulfonated polystyrene (SPS) was obtained from the sulfonation of polystyrene (M_w, 192 000; melt index, 6.0-9.0 g/10 min) according to our previous paper and the sulfonation degree is 6.9 % based on titration method.[1] Butyl acrylate was passed through an aluminium oxide column to remove inhibitors prior to use. Ethylene glycol dimethacrylate, phosphotungstic acid ($H_3PW_{12}O_{40}$), photoinitiator (2-hydroxy-2-methylpropiophenone), $FeCl_3$ and citric acid were purchased from Sigma-Aldrich without further purification. The other solvents and reagents were analytical and used directly.

Preparation of HIPE organogels. The as-prepared SPS was dissolved into tetrahydrofuran (THF) to produce 10 w/v% SPS solution. HCl and NaOH were dissolved into distilled water to obtain acidic and basic aqueous solutions, respectively, and pH values of these aqueous solutions were measured with a SevenEasy pH meter (Mettler-Toledo GmbH, Switzerland). The aqueous solutions with different refractive indexes were prepared by mixing different weight fractions of glycerol and acidic, basic or NaCl aqueous solutions. The refractive index of the aqueous mixtures was measured with an Abbe refractometer. HIPE organogels were obtained typically by shearing a mixture of 20 μL of SPS solution, 1 mL of chloroform and 4 mL of aqueous solution on a vertex over 3400 r min^{-1}. The type of emulsions was checked by the conductivity measurements.[18] All the HIPE organogels were prepared with SPS concentration at 0.2 w/v% of the continuous phase and a volume fraction of the dispersed phase at 80 %.

Optical microscopy. The morphology of the HIPE organogels was observed under Nikon optical microscopy. HIPE organogels were sandwiched between a microscope slide and a cover glass for observation.

Rheological measurements. Rheological experiments were performed on a TA DHR 3 rheometer with a plate geometry of 40 mm at 25 °C. The gap was set at 500 μm, and a solvent trap was applied to minimize the evaporation of solvents. The as-prepared HIPE organogels were stored for at least 1 hour before measurements. Dynamic strain sweeps were conducted at 1 and 10 rad s^{-1} before dynamic frequency sweeps, and frequency measurements were carried out at a strain of 1 % with an angular frequency from 0.3 to 300 rad s^{-1}.

Light transmittance measurements. The transparency of HIPE organogels were recorded on a Varian Cary UV-visible spectrophotometer in a transmittance mode with the wavelength range of 200–800 nm. The glycerol aqueous solution with 0.5 M NaCl was used to check the baseline.

Light induced reactions. The light driven reactions were conducted in closed vials under UV or visible irradiation in an Electro-Lite ELC-500 UV curing chamber for different time.

Gel fraction measurement. Gel fractions of polyHIPE monoliths with different irradiation times were conducted with THF as solvent, and the monoliths were extracted for 24 h at the boiling temperature about 70 °C. The residual polyHIPEs were dried at 40 °C for 48h.

Scan electron microscopy (SEM). The morphology of polyHIPEs was observed under a NEOSCOPE JCM-5000 SEM. The as-prepared polyHIPEs was squeezed and washed for several times to remove water and glycerol, dried under vacuum, and then coated with a thin gold layer prior to observation. The images were taken with an accelerating voltage of 10 kV.

Fourier transform infrared (FTIR) spectroscopy. ATR-FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer. The spectra were collected at room temperature with a resolution of 4 cm^{-1}.

2. Formation of isorefractive HIPE organogels

SPS was chosen to stabilize HIPE organogels because it is an efficient and versatile stabilizer for both emulsions and HIPEs; It has been reported to stabilize a variety of organic solvents including xylene, toluene, dichloroethane, chloroform, anisole, dichloromethane and monomers such as butyl acrylate, styrene, ethylene glycol dimethacrylate and methyl methacrylate to form emulsions and HIPEs.[1] The appearance of HIPEs varies from opaque to translucent with different organic phases, and the variation is ascribed to the difference in refractive index between the continuous phase and the dispersed phase.

Isofractive/contrast-matched emulsions and HIPEs should be fabricated with carefully tuning the dispersed phase and the continuous phase. There are usually two methods to produce the contrast-matched dispersed phase and the continuous phase. One method is to choose contrast-matched immiscible liquids as the continuous phase and the dispersed phase,[2] but unfortunately these liquids are rare. Another method is to tune the refractive index of the continuous phase, the dispersed phase or both by mixing other solvents. The refractive index of mixture is calculated by Lorentz-Lorenz relation: [3]

$$\frac{n_L^2 - 1}{n_L^2 + 2} = \O_1 \frac{n_{D1}^2 - 1}{n_{D2}^2 + 2} + \O_2 \frac{n_{D2}^2 - 1}{n_{D2}^2 + 2} \tag{1}$$

where $n_L$represents the refractive index of the mixture; $\O_1$ and $\O_2$ stand for the volume fractions of the constituent parts, calculated from volume determinations from the mass and density, and n_{D1} and n_{D2} denote the refractive indexes of the constituent parts, respectively. In experiments, we chose the aqueous phase to tune its refractive index as it is less smelly and flammable. According to the Lorentz-Lorenz relation, a water-immiscible solvent with a high refractive index should be chosen to meet the requirement. Here, glycerol was selected as a model since it does not mix with a variety of organic solvents.

The emulsions changed from opaque to translucent with the addition of glycerol in the aqueous phase. When HCl, NaOH or NaCl was added to these emulsions, phase inversion occurred from oil-in-water emulsion to water-in-oil emulsions. NaCl, HCl or NaOH aqueous solution was used instead of pure water to form mixture with glycerol, and according to Lorentz-Lorenz relation, the refractive indexes of the mixtures changed with the changes of density of water. For accuracy, the refractive indexes of these aqueous mixtures were checked with refractometer.

All the organic solvents and monomers reported before[18] could form emulsions or HIPE organogels with glycerol in aqueous phase. However, only chloroform, butyl acrylate and methyl methacrylate could form isorefractive emulsion as others solvents and monomer (styrene) exhibit a high refractive index that out of the reach of the aqueous phase. With glycerol in the aqueous phase, SPS also shows a high efficiency, where 0.2 w/v% of the continuous phase is enough to stabilize HIPE organogels. Chloroform was chosen to study the properties of HIPE organogels as it is less smelly in comparison to butyl acrylate or methyl methacrylate.

The formulations of two typical isorefractive HIPE organogels are listed in Table S1 and Table S2, corresponding to the reacted and unreacted HIPEs.

Table S1 Formulation of a typical isorefractive HIPE organogels

	Components	Amounts
Continuous phase (Organic phase)	Chloroform	20% of the total volume (v/v)
	10% SPS in THF (w/v)	2% of chloroform (v/v)
Disperse phase (Aqueous phase)	Mixture from 20% of aqueous NaCl solution (0.5M) and 80% of glycerol (w/w)	80% of the total volume

HIPE organogels with 0 %, 46 %, 67 %, 80 % and 99 % of glycerol by weight in the aqueous phase in manuscript have a similar formulation except that the dispersed phases have 0 %, 46 %, 67 %, 80 % or 99 % of glycerol, respectively.

Table S2 Formulation of isorefractive HIPE organogels for preparation of poly(HIPEs)

	Components	Amounts
Continuous phase (Organic phase)	Butyl acrylate	19% of the total volume (v/v)
	Ethylene glycol dimethacrylate	2.5% of the monomer (v/v)
	10% SPS in THF (w/v)	2% of the monomer (w/v)
	Photo-initiator	2.5 % of the monomer (v/v)
Disperse phase (Aqueous phase)	Mixture from 38% of aqueous NaCl solution (0.5M) and 62% of glycerol (w/w)	80% of the total volume

The control non-transparent HIPE has a similar formulation except that the dispersed phase is aqueous NaCl solution (0.5M) without glycerol.

HIPE organogels were formed at a higher salt concentration (over 0.15 M) with a glycerol concentration below 70 v/v% of the aqueous phase; while a low salt concentration and even no salt is required for an aqueous phase with glycerol concentration over 70 v/v%. The diagram shown in Fig. S1 demonstrates the antagonistic and synergic effects between salt concentration and glycerol concentration. From the diagram, it can be seen that HIPE organogels could be formed over 80 v/v% of glycerol without the addition of salt in the aqueous phase. The range for the formation of HIPE organogels increases with the incorporation of glycerol into the aqueous phase, which endows SPS as a more versatile HIPE stabilizer. It requires partial wettability of the particles to stabilize water-in-oil (high internal phase) emulsion,[4] i.e. the spreading coefficient of water S(w/o) is negative and the adhesion energy of water E_{Adh}(w/o) is positive:

$$S(w/o) = -E_{Adh}(o/w) = \gamma_{p-o} - \gamma_{o-w} - \gamma_{s-w} < 0 \quad (2)$$

$$E_{Adh}(w/o) = -S(o/w) = \gamma_{p-o} + \gamma_{o-w} - \gamma_{s-w} > 0 \quad (3)$$

where γ_{p-o} γ_{p-w} and γ_{w-o} stand for interfacial energies of the following three interfaces: particle-oil, particle-water and water-oil, respectively. With the introduction of glycerol to the aqueous phase, the salt concentration was diluted and thus deceases the suppression of the double layers, rendering the adhesion of ionomers at the interface. While at the high concentration of glycerol, the hydrogen interaction between $-SO_3H$ groups of SPS and glycerol enhances the interaction between the SPS and the aqueous phase, decreasing the S(w/o) and increasing the E_{Adh}(w/o).

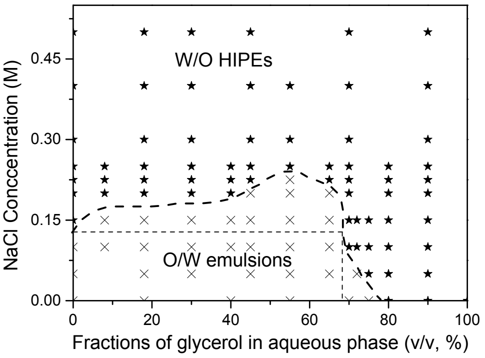

Fig. S1 The effects of NaCl concentration and glycerol concentration in the aqueous phase on the inversion of emulsion types.

The sizes and size distributions of emulsion droplets were studied with microscope, and 100 droplets from microscopy pictures of the emulsions were evaluated with the software ImageJ (downloaded from http://rsbweb.nih.gov/ij/). The results are shown in Fig. S2, these HIPE organogels with 0 %, 46 %, 67 % and 80 % of glycerol by weight in the aqueous phase have mean sizes of 81.0, 84.5, 74.9 and 79.1 *u*m, respectively.

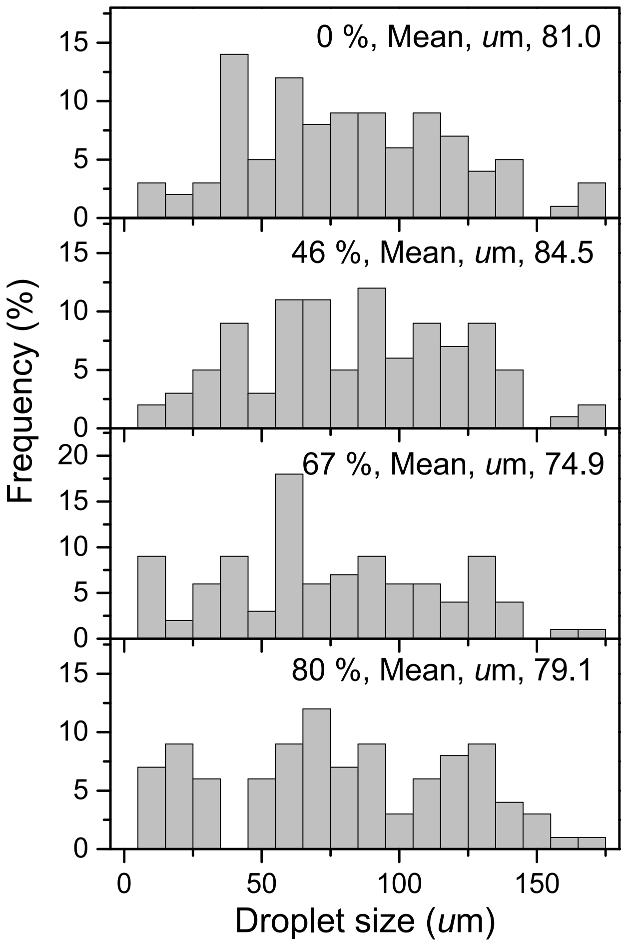

Fig. S2 Sizes and size distributions of emulsion droplets in HIPE organogels with 0 %, 46 %, 67 % and 80 % of glycerol by weight in the aqueous phase.

3. Light induced reactions within isorefractive HIPE organogels

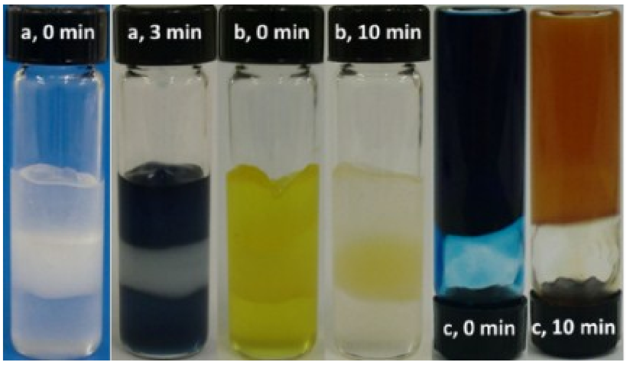

Fig. S3 Photographs of layered HIPE organogels containing (a) $H_3PW_{12}O_{40}$ and (b) citric acid/$FeCl_3$ as indicators irradiated by UV and visible light, respectively. The upper and low layers are isorefractive HIPE organogels and the middle layer is conventional opaque HIPE organogel. (c) Isorefractive HIPE organogels with methylene blue in the dispersed phase and 2-hydroxy-2-methylpropiophenone in the continuous phase before and after 10 minutes' UV exposure.

4. A comparison of polyHIPEs from transparent and conventional HIPE organogels

Photographs of polyHIPEs from light induced polymerization of transparent and conventional HIPE organogels are shown in Fig. S4. It can be seen that emulsion is totally polymerised in transparent HIPE organogels (Fig. S4a). While only a polymerized shell were obtained from light induced polymerization of the conventional HIPE organogels (Fig. S4c), leaving the HIPE organogel in the core (Fig. S4b).

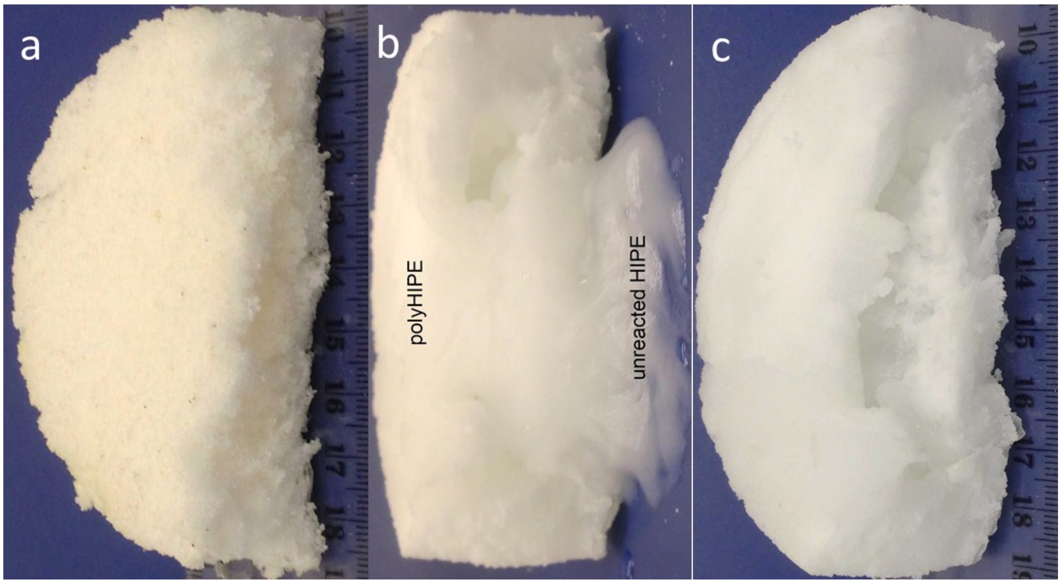

Fig. S4 Photographs of polyHIPEs (a) from a typical transparent HIPE organogel, (b) and (c) from a typical conventional HIPE organogel before and after removal of the unreacted HIPE organogel, respectively.

5. The changes in transparency of HIPE organogels during polymerization

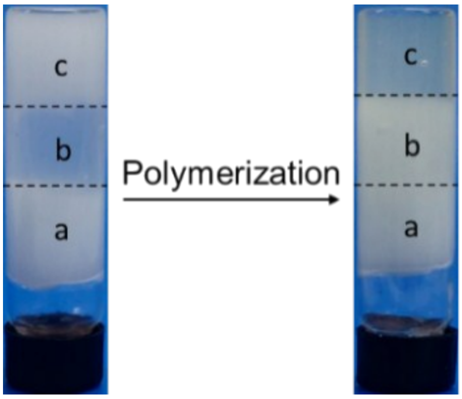

Fig. S5 Photographs of a layered HIPE organogels before and after polymerization with different dispersed aqueous phases: (a) water, (b) 62 wt% of glycerol in the aqueous phase and (c) glycerol.

The refractive index of the polymerizable phase changes with the conversion of monomers to polymers. Transparent polyHIPEs were successfully obtained by the pre-tuning the refractive index of the dispersed phase to match that of the polymers. A typical result is shown in Fig. S5, where photos of layered HIPE organogels are shown before and after polymerization. It can be seen that distinct boundaries were formed between HIPE organogels due to their high viscosity. These boundaries were well-preserved because light induced polymerization was conducted at room temperature and completed in a short time of few minutes. Furthermore, it can be observed from Fig. S5a that both conventional HIPE organogels and its corresponding polyHIPE are opaque as the refractive index of the dispersed phase is much lower than that of the continuous phase. In the middle layer, the parent HIPE organogel was transparent but the obtained polyHIPE became opaque due to the refractive index changes upon the polymerization of the monomers. A nearly transparent polyHIPE was achieved with pure glycerol as the dispersed phase, as the refractive index of glycerol is similar to that of poly(butyl acrylate) shown in Fig. S5c.

6. References

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