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ARTICLE

Phase inversion of ionomer-stabilized emulsions to form high internal phase emulsions (HIPEs)

Tao Zhang, Zhiguang Xu, Zengxiao Cai and Qipeng Guo*

We report here the phase inversion of ionomer-stabilized emulsions to form high internal phase emulsions (HIPEs) induced by salt concentration and pH changes. The ionomers are sulfonated polystyrenes (SPSs) with different sulfonation degrees. The emulsion types were determined by conductivity measurements, confocal microscopy and optical microscopy, and the formation of HIPE organogels was verified by tube-inversion method and rheological measurements. SPSs with high sulfonation degrees (water-soluble) and low sulfonation degrees (water-insoluble) can stabilize oil-in-water emulsions; these emulsions were transformed into water-in-oil HIPEs by varying salt concentrations and/or pH change. SPS with sulfonation degree of 11.6% is the most efficient and as low as 0.2 (w/v) % of the organic phase is enough to stabilize HIPEs. Phase inversion of oil-in-water emulsions occurred to form water-in-oil HIPEs by increasing salt concentration in aqueous phase. Two phase inversion points from oil-in-water emulsions to water-in-oil HIPEs were observed at pH 1 and 13. Moreover, synergetic effects between salt concentration and pH changes occurred upon the inversion of emulsion type. The organic phase can be a variety of organic solvents including toluene, xylene, chloroform, dichloroethane, dichloromethane, anisole and monomers such as styrene, butyl acrylate, methyl methacrylate and ethylene glycol dimethacrylate. Poly(HIPEs) were successfully prepared by the polymerization of monomer as the continuous phase in the ionomer-stabilized HIPEs.

Introduction

High internal phase emulsions (HIPEs) are emulsions with the total volume fraction of the internal/dispersed phase over 74%, and they can act as end products in a variety of areas, such as cosmetic, food, petroleum and pharmaceutical industries.[1] HIPEs usually exhibit high viscosity due to the low volume fraction of the continuous phase, and thus they are also called gel emulsions.[2] If polymerizable continuous phase is used, HIPEs can be applied as templates to prepare macro-porous materials[3] which are known as poly(HIPEs). Poly(HIPEs) are reported for numerous applications, including tissue scaffolds,[4] catalyst,[5] hydrogen storage[6] and oil-water separation.[7] Surfactants are commonly used to stabilize HIPEs, but as much as 5 – 50 (w/v) % of the continuous phase is required to prepare stable HIPEs.[8] Moreover, careful selection of surfactants is also needed to avoid phase inversion at high dispersed phase ratio.[9] Besides surfactants, solid particles with a few nanometres to micrometres are also used to stabilize emulsions and they are known as Pickering emulsions. However, it is not easy to prepare HIPEs with solid particles, as phase inversion tends to occur with the increase of the internal phase though some particles have been successfully used to stabilize HIPEs.[10]

Over the past few years, various organic gels and particles have been successfully used to stabilize HIPEs.[11-13, 14, 15, 16] Ngai et al. first developed a new strategy to prepare HIPEs by phase inversion of microgel particle stabilized oil-in-water emulsions.[12] However, a large amount of microgel particles (5 wt % of oil phase) are required to obtain HIPEs. Very recently, HIPEs have been obtained by phase inversion of core cross-linked star (CCS) polymer stabilized water–in-oil emulsions where the stabilizer concentration is as low as 0.5 wt %.[15, 16] Till now, the preparation of HIPEs by phase inversion is still rare, and phase inversion of oil-in-water emulsions to form water-in-oil HIPEs with low stabilizer concentration is highly required since most monomers used for poly(HIPEs) are oleophilic.[3, 17] We recently studied the preparation of HIPEs from polymer organogels based on block ionomer sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS).[14, 18, 19]

In this paper, we report that water-in-oil HIPEs were obtained by phase inversion of oil-in-water emulsions with an ionomer as the stabilizer, where only 0.2 (w/v) % of the continuous phase is required to stabilize HIPEs. The ionomer is sulfonated polystyrene (SPS) and the inversion is driven by salt concentration and/or pH changes. As the continuous phase in the HIPE organogels can not only be organic solvents such as toluene, xylene, chloroform, dichloroethane,

*Polymers Research Group, Institute for Frontier Materials, Deakin University, Locked Bag 20000, Geelong, Victoria 3220, Australia. E-mail: qguo@deakin.edu.au; Fax: +61 3 5227 1103; Tel: +61 3 5227 2802

dichloromethane, anisole but also be commonly used monomers and cross-linkers including styrene, butyl acrylate, methyl methacrylate and ethylene glycol dimethacrylate. Therefore, the ionomer-stabilized HIPEs facilitate the preparation of poly(HIPEs).

Experimental

Materials. Polystyrene (PS) with an average molecular weight M_w of 192,000 and melt index of 6.0-9.0 g ·10 min^{-1} was used for the preparation of SPSs. Ethylene glycol dimethacrylate and 2,2'-azobis(2-methylpropionitrile) (AIBN) solution (0.2 M in toluene) were used as received. Monomers including butyl acrylate, styrene and methyl methacrylate were purified by passing through a neutral aluminium oxide column before use. All the chemicals mentioned above were purchased from Sigma-Aldrich. The other reagents and solvents were analytical grade and used directly. Deionized water was used throughout the experiments.

Preparation of SPSs. SPSs were prepared by sulfonation of polystyrene according to the method reported in our previous paper with a few modifications.[19] In brief, 20 g of polystyrene was dissolved into 200mL of dichloroethane, and then required amount of freshly prepared acetyl sulfonate was added at 50 °C. After reaction for 3 hours, the reaction mixtures are dropped into hot water. For water-insoluble SPSs, they were obtained by evaporating solvents first and then washing with cold deionized water to remove acids. Water-soluble SPS was obtained by evaporating solvents first and then dialysing against deionized water to remove acids. The sulfonation degrees of SPSs were determined by titration of their THF solutions (for water-insoluble SPSs) or aqueous solution (for water-soluble SPS) with standard sodium hydroxide methanol solution (0.1 N, standardized by *p*-toluene sulfonic acid solution) using phenolphthalein as the indicator. The sulfonation degree of SPSs was calculated as follows: Sulfonation degree = moles of sulfonic acid / moles of styrene ×100%.

Preparation of emulsions or high internal phase emulsions (HIPEs). For water-insoluble SPSs, they were dissolved into THF to obtain 10 w/v % of SPS solution, and water-soluble SPSs were used directly in aqueous solutions. Aqueous phase with different pH values was obtained by adding HCl solution or NaOH (1 M) solution into water and then pH was measured with a pH meter (SevenEasy, Mettler-Toledo GmbH, Switzerland). Typically, emulsions were obtained by mixing as-prepared SPS solution in THF, 1mL of organic solvents or monomers, and 4 mL of aqueous solutions with different pH or salt concentrations for about 2 minutes with a vortex mixer. For water-soluble SPSs, their aqueous solutions with different pH and salt concentrations were used directly by mixing with organic solvents or monomers.

Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer. THF solutions of polystyrene and water-insoluble SPSs were dropped onto the KBr disks. The disks were left evaporating in fume hood to remove solvent and then dried under vacuum at 40 °C before measurement. The water-soluble SPS was dried first and then grounded well with KBr powder to press KBr disk for FTIR measurement. The spectra were collected in the wavenumber range 600–4000 cm^{-1} with a resolution of 4 cm^{-1}.

Rheological measurements. Rheological experiments were carried out on a TA DHR 3 rheometer a with cone-plate geometry at 25 °C. A cone with a diameter of 40 mm and a tilt angle of 2° was used, and gap width was set to be 500 um. A solvent trap was used to minimize the effect of evaporation. The newly prepared HIPE organogels at different salt concentrations and pH values were used. Dynamic strain sweeps were carried out at 1 and 10 rad s[-1] from 0.3 to 300%. Dynamic frequency sweeps with an angular frequency from 0.3 to 300 rad s[-1] were performed at a strain of 1 %.

Conductivity measurements. The conductivity measurements were carried out on a SevenEasy conductivity meter (Mettler-Toledo GmbH, Switzerland) at room temperature. Each sample was measured 5 times and the conductivity was the average value of the 5 results. The conductivities of water at different pH and salt concentrations were also studied for comparison.

Confocal laser scanning microscopy (CLSM). Confocal imaging was taken on a laser scanning confocal microscope (Leica SP5, Leica Microsystems CMS GmbH, Germany). Emulsions and HIPEs prepared from aqueous solutions with different pH and salt concentrations were 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. The morphology of ionomer-stabilized oil-in-water emulsions was examined using a Nikon eclipse-80i optical microscope under polarized light. These emulsions were dropped on glass slides and observed directly.

Zeta potential. The zeta potentials of SPS 3 at different NaCl concentrations were characterized by the Zetasizer Nano ZS. The concentration of the SPS 3 aqueous solution was 0.2 mg·mL^{-1} with NaCl concentrations ranged from 0 to 1M.

Preparation of poly(HIPEs). HIPE organogels with monomers as the continuous phase were polymerised at 70°C for 10 hours to obtain poly(HIPEs). 2,2'-Azobis(2-methylpropionitrile) solution 0.2 M in toluene from Aldrich was used as initiator.

Results and discussion

The ionomers SPSs were prepared via sulfonation of polystyrene and the obtained SPSs were studied with FTIR

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spectroscopy. From the results in Figure 1(a), it can be seen that some new absorption peaks appeared at 580, 1008, 1132 and 1180 cm^{-1} and these peaks can be ascribed to the angle deformation vibration of S=O=S, ring vibration of *p*-substituted benzene ring, vibration of hydrated sulfonate acid and antisymmetric stretching of S=O=S, respectively.[20] Moreover, it can be observed from Figure 1(b) that a broad band (circled) centred at 3470 cm^{-1} becomes clear with the increase of sulfonation degrees, and the absorption band is ascribed to the free and hydrogen bonded hydroxyl groups between sulfonic acid groups, which verifies the sulfonation of polystyrene.[21]
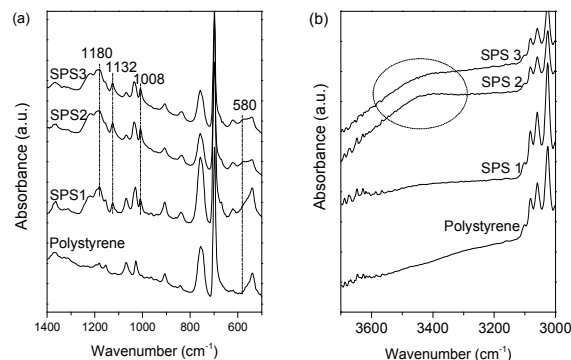
Figure 1 FTIR spectra of polystyrene, SPS1, SPS2 and SPS3 in the range of (a) 1400–800 cm^{-1} and (b) 3700–3000 cm^{-1}.

Polystyrene is hydrophobic, and after sulfonation, the −SO$_3$H groups are hydrophilic. Thus SPSs are amphiphilic, and their solubility are dependent on sulfonation degrees. Three SPSs listed in Table 1 are denoted as SPS1, SPS2 and SPS3. There are 5.9% and 11.6% of styrene groups of SPS1 and SPS2 were grafted with with −SO$_3$H groups, respectively. They are dissoluble in THF and toluene but not in water. SPS3 with a sulfonation degree of 30.5% can be totally dissolved into water.

SPSs are amphiphilic and able to serve as surfactants. In experiments, both the water soluble and insoluble SPSs were successfully used to stabilize oil-in-water emulsions, and phase inversion of these SPS-stabilized emulsions to form water-in-oil HIPEs was observed by tuning the salt concentration and pH value of the aqueous phase. However, these SPSs showed different efficiency to stabilize emulsions.

Table 1 Three SPSs with different sulfonation degrees and concentrations required to stabilize HIPEs

	Sulfonation degree	Solubility	Concentration to stabilize HIPEs (w/v)
SPS1	5.9%	Water-insoluble	1.0% of organic phase
SPS2	11.6%	Water-insoluble	0.2% of organic phase
SPS3	30.5%	Water-soluble	3.8% of aqueous phase

The efficiency of SPSs was studied by stabilizing HIPEs formed from toluene and aqueous solution (20/80) with pH at 7 and NaCl concentration at 0.5 M in aqueous phase. SPS2 with sulfonation degree of 11.6% showed highest efficiency, where as low as 0.2 (w/v) % of organic phase is enough for the formation of HIPEs without liquid-like flow behaviour. The concentration is much less than the PS-*co*-PMAA microgel particles.[12] With the decreasing of sulfonation degree to 5.9% (SPS1), the efficiency decreased and the ionomer concentration increase to 1.0 (w/v) % of organic phase. The highest concentration is required for water-soluble SPS3 to stabilize HIPEs, at 3.8 (w/v) % aqueous phase. In this work, SPS3 was used for the study of structural changes with pH changes and salt concentration, and water-insoluble SPS2 with highest efficiency was used for the investigation of phase inversion between emulsion types.

Emulsions were obtained by shearing the mixture of SPS2 solution in toluene (0.2%, w/v) and water at a fixed ratio of 20/80 (toluene/water). The appearance and conductivity of ionomer-stabilized emulsions are shown in Figure 2(a). It is noted that emulsions exhibiting low viscosity are formed with no or low NaCl concentration and that conductivity measurements confirmed the formation of oil-in-water emulsions. These emulsions tend to separate into two distinctive layers with the white top layer and the translucence

bottom layer after a few minutes. The separation is totally reversible, and the separated layers turned into emulsions again with very gentle shake. It is believed that the separation is resulted from the density difference between water and toluene, which was verified by facts that no separation was observed even after a few hours when toluene was replaced by a mixture of toluene and dichloroethane (170/100, v/v, density about 1 g cm^{-3}) as oil phase.
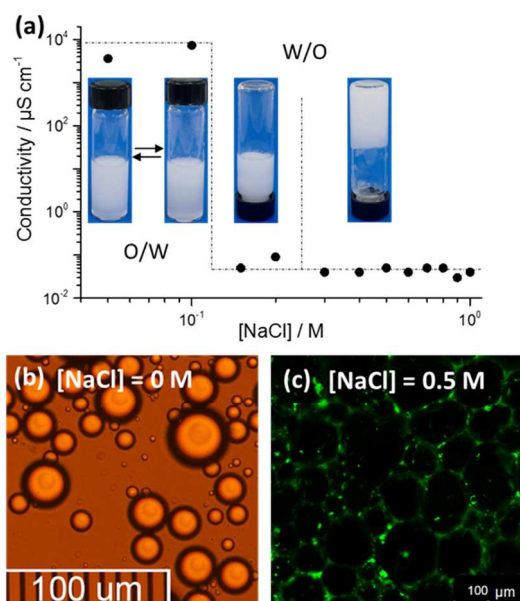
Figure 2. (a) Photos and conductivities of emulsions formed at different NaCl concentrations; (b) polarized optical micrograph of emulsions with 0 M NaCl; (c) confocal image of HIPE with 0.5M NaCl by fixing toluene/water ratio at 20/80, pH at 7 and SPS2 concentration at 0.2 (w/v) % of oil phase.

The formation of oil-in-water emulsions was observed under polarized optical microscope as shown in Figure 2(b), and the sizes of the disperse phase vary from several to tens of micrometres, which fills in the size range of emulsions. Control experiments shows that no emulsions were formed without SPS2, and thus it is believed that SPS2 acts as stabilizers/emulsifiers.

Surprisingly, after addition of NaCl into these pre-formed emulsions and mechanical shear, viscosities of these emulsions increase obviously and conductivities dropped to about 0 μS cm^{-1}, which indicates phase inversion occurred to these emulsions. To investigate the inversion thoroughly, aqueous NaCl solutions with different NaCl concentrations were used instead of adding NaCl to the pre-formed oil-in-water emulsions. From Figure 1(a), it can be observed that with slightly increase of NaCl concentration to over 0.15 M, highly viscous water-in-oil HIPEs were formed and the conductivity dropped dramatically. Further increasing NaCl concentration to 0.25 M and over, although the conductivities of these HIPEs maintains around 0.5 μS cm^{-1}, these water-in-oil HIPEs exhibit no liquid-like flow behaviour, indicating the formation of HIPE organogels. Confocal image in Figure 2(c) confirmed the formation of HIPEs, and the newly formed HIPEs with water droplets range from several to a little over 100 μm dispersed in the continuous organic phase (pyrene labelled). It is noted that Ngai *et al.* reported the salt induced phase inversion of water-in-oil emulsions to form HIPE hydrogels by microgel particles, but the stabilizer concentration is quite high at 5% of the continuous phase.[12]

To study the NaCl effect on the ionomer solutions, zeta potentials of water soluble ionomer SPS3 solution with different NaCl concentrations were measured, and the dependency of the zeta potential of SPS3 solutions on NaCl concentrations at pH = 7 was shown in Figure 3. Figure 3 shows that the zeta potential increased with salt concentration, indicating that the addition of salt suppresses the double layers and facilitates the adhesion of ionomer on the water-toluene interface.[22]
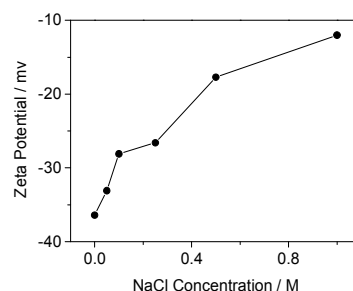

Figure 3. Zeta potential of SPS3 as a function of NaCl concentrations at pH 7.

SPS may form nanoparticles in water and solvents,[23] which stabilizes HIPEs. It is noted that all the polymer HIPE stabilizers including microgels,[11, 12, 22, 24] CCS polymer[15, 16] and bulk polymer organogels[14] have cross-linked structures either from chemical or strong physical interactions. SPSs as a novel HIPE stabilizer can be totally dissolved into water or organic solvents depending on sulfonation degrees, showing that non-cross-linked ionomers can also serve as HIPE stabilizer.

The formation of three-dimensional networks at high salt concentrations was confirmed by rheological measurements. Typical results for dynamic strain measurements of HIPE organogels with 0.5 M NaCl are presented in Figure 4(a), and the extent of the linear viscoelastic regime is as high as 50%. The results for dynamic frequency measurements are shown in Figure 4(b). All the elastic moduli (G') are higher than the corresponding viscous moduli (G") with salt concentrations in aqueous phase at 0.3, 0.5 and 0.7 M, indicating the formation of three-dimensional networks. These moduli do not change greatly with the increase of salt concentrations in the aqueous phase, showing that salt concentration does not affect the strengths of these HIPE organogels obviously though salt is critical for their formation.
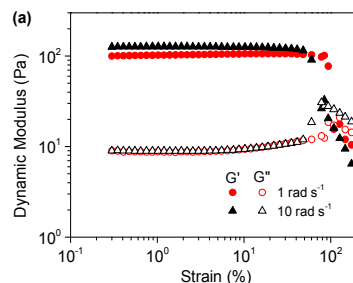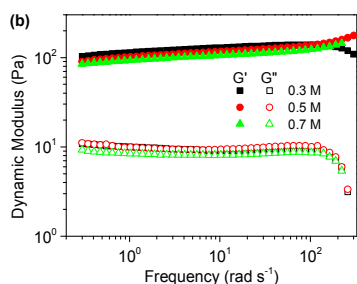
Figure 4. Dynamic moduli G' and G" for (a) HIPE organogel with NaCl concentration at 0.5 M as a function of strain (b) HIPE organogels formed with NaCl concentrations at 0.3, 0.5 and 0.7 M as a function of oscillatory shear frequency.

The inversion of emulsion type has been reported by tuning pH values,[25] and pH induced inversion to prepare HIPEs has also been presented with microgel particles or CCS as stabilizer.[12, 16] SPSs contain ionisable –SO$_3$H groups and they can be affected by pH values. The appearances and conductivity of ionomer-stabilized emulsions at pH from 1 to 14 are shown in Figure 5(a). Surprisingly, there exhibit two inversion points from pH 1 to 14 in comparison with one inversion point in microgel particles and CCS stabilized emulsions.[12, 16]Oil-in-water type emulsions were formed with high conductivities at pH range from 1.5 to 13, while these emulsions turned into water-in-oil type HIPEs with pH below 1.5 or over 13, which are confirmed by the high viscosities and low conductivities of emulsions. The formation of water-in-oil HIPEs at low and high pH has been confirmed by confocal microscopy shown in Figure 5(b) and (d), respectively. While the formation of oil-in-water emulsions at moderate pH values is verified by polarized optical microscopy, as shown in Figure 5(c).
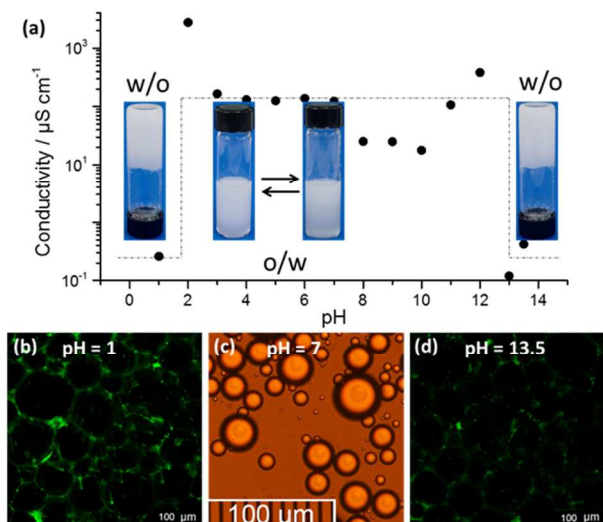

Figure 5. (a) Photos and conductivities of emulsions formed at different pH, (b) confocal image of HIPE at pH = 1, (b) polarized optical micrograph of emulsion at pH = 7 and (d) confocal image of HIPE at pH = 13.5 by fixing toluene/water ratio at

20/80, NaCl concentration at 0 M and SPS2 concentration at 0.2 (w/v) % of oil phase.

SPSs are able to stabilize HIPEs at high concentration of HCl or NaOH. Although their concentrations are quite high, they cannot be well-explained by the salt effect as no HIPEs form at NaCl concentration at 0.1 M. The formation of HIPEs may be caused by the pH induced structures change of SPSs, as it is known that at acidic environment the –SO$_3$H groups may form hydrogen bonds between each other,[26] and in basic solution, all the –SO$_3$H groups will deprotonate to form –SO$_3^-$ which will interact through dipole-dipole interaction.
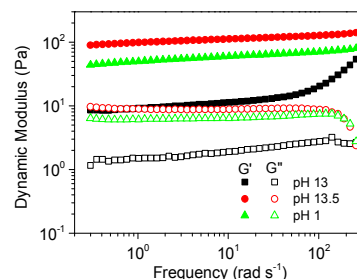

Figure 6. G' and G" of HIPE organogels formed with pH at 13, 13.5 and 1 as a function of oscillatory shear frequency.

The water-in-oil HIPEs at pH 1, 13 and 13.5 can be strong enough to form gels, and the formation of gels is verified by dynamic frequency measurements. As shown in Figure 6, HIPE organogel at pH 13.5 exhibits highest strength, while HIPE organogel at pH 13 is weakest. These results are agreeable with these from direct observation by tube-inversion method. The G' and G" of HIPE organogel at pH 13 show a slight rise with frequency, suggesting that there is a crossover in a certain experimentally inaccessible range. Therefore, the HIPE organogel may flow in a long time.

These HIPE organogels formed (with toluene as the continuous phase) at high salt concentration or high/low pH are quite stable. They were stored in closed vials at 0 °C for two months without any change in appearance, showing these HIPE organogels are always in the thermodynamic equilibrium state once prepared.

Synergetic interaction between NaCl and pH on the phase inversion of emulsion types was found in the ionomer-stabilized emulsion. For example, with the increase of NaCl concentration to 0.05 M, the inversion points changed from pH 13 to 12 and from pH 1 to 1.7, respectively, indicating the presence of synergetic effect between salt concentration and pH. To further demonstrate the synergetic effect, a diagram has been drawn approximately in Figure 7 based on the tube-inversion method. From the results, it can be seen that pH values at which phase inversion occurs increase or decrease with the increase of NaCl concentration from 0 to 0.15M.
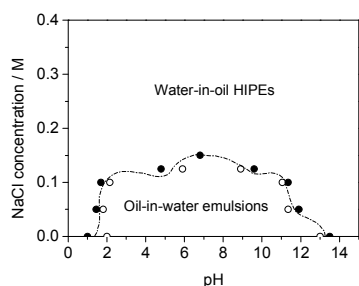
Figure 7. Synergetic effect between NaCl and pH on the inversion of emulsion type.

Experimental results showed that the organic phase can be hydrophobic organic solvents including toluene, xylene, chloroform, dichloroethane, dichloromethane, anisole, and commonly used monomers for poly(HIPEs) such as styrene, butyl acrylate, methyl methacrylate and ethylene glycol dimethacrylate. Moreover, all emulsions from these solvents or monomers can be inversed into water-in-oil HIPEs by tuning pH and salt concentration in aqueous phase.

Table 2 A typical recipe of HIPE organogels for the preparation of poly(HIPEs)

	Components	Amounts
Continuous phase	Styrene	19% of the total volume (v/v)
Organic phase	Ethylene glycol dimethacrylate	2.5% of the monomer (v/v)
	SPS2	0.2% of the monomer (w/v)
	AIBN	2.5 % of the monomer (v/v)
Disperse phase Aqueous phase	Aqueous NaCl solution (0.5M)	80% of the total volume

To demonstrate the ability to prepare poly(HIPEs) from the ionomer-stabilized HIPEs, monomers with cross-linkers and initiators were used as oil phase to prepare HIPEs. A typical recipe of polymerisable HIPE is presented in Table 2, and a photograph of the corresponding poly(HIPEs) sample obtained is shown in Figure 8(a). As the formation of HIPE organogels, mouldable organogels with different shapes can be obtained. Moreover, SPSs stabilized HIPEs for preparation of poly(HIPEs) is obviously cheap in comparison with those stabilized by surfactants and gels. Figure 8(b) shows that almost all the cells are closed, implying that these poly(HIPEs) have potential as a thermal insulation and soundproof material.

Interconnected cells were previously observed in poly(HIPEs).[27] In the present study, closed-cell structures have been observed in the poly(HIPEs) system. The formation of closed-cell structures may be explained by the formation of SPS particles via hydrogen bonding interaction between $-SO_3H$ groups of SPS,[26] and the HIPEs are stabilized by these SPS particles. As particles are usually strongly absorbed on the walls between the continuous phase and the dispersed aqueous phase,[28] leading to the formation of porous materials with closed-cell structures. It is noted from SEM in Figure 8(c) that deformed particles are attached on the walls of poly(HIPEs), indicating that the SPS2 formed particles to stabilize HIPEs.
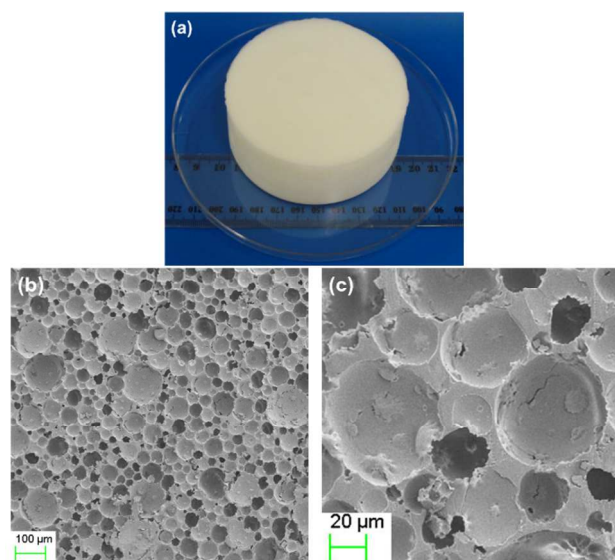
Conclusions

In summary, phase inversion of SPS-stabilized oil-in-water emulsions to water-in-oil HIPEs has been achieved by tuning salt concentration and/or pH. SPSs act as an efficient stabilizer for emulsions and HIPEs with a concentration as low as 0.2 (w/v) % of the oil phase. Two inversion points were first observed on the whole pH range, and synergetic effect between pH and salt concentration has been found on the inversion of emulsion type. Phase inversion occurs with a variety of hydrophobic solvents and commonly used monomers as organic phase, which facilitates a new route to preparation of poly(HIPEs).

Figure 8. (a) A photograph, (b) and (c) SEM images of a typical poly(HIPEs) from SPS2 stabilized HIPEs with styrene as continuous phase.

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