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

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

Herein, we report 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 the 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 changing the pH. SPS with a 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 the HIPEs.

Phase inversion of the oil-in-water emulsions occurred to form water-in-oil HIPEs by increasing the salt concentration in the aqueous phase. Two phase inversion points from oil-in-water emulsions to water-in-oil HIPEs were observed at pH 1 and 13. Moreover, synergistic effects between the salt concentration and pH changes occurred upon the inversion of the emulsion type. The organic phase can be a variety of organic solvents, including toluene, xylene, chloroform, dichloroethane, dichloromethane and anisole, as well as monomers such as styrene, butyl acrylate, methyl methacrylate and ethylene glycol dimethacrylate. Poly(HIPEs) were successfully prepared by the polymerization of monomers as the continuous phase in the ionomer-stabilized HIPEs.

Introduction

High internal phase emulsions (HIPEs) are emulsions with a total volume fraction of the internal/dispersed phase over 74%, and they can act as end products in a variety of areas, such as the 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 a 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) have been reported for numerous applications, including tissue scaffolds,4 catalysis,5 hydrogen storage6 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 the surfactant is also needed to avoid phase inversion at a high dispersed phase ratio.9 In addition to surfactants, solid particles with sizes from a few nanometres to micrometres are also used to stabilize emulsions; these are known as Pickering emulsions. However, it is not easy to prepare HIPEs with solid particles, as phase inversion tends to occur as the internal phase increases, although 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.11–16 Ngai et al. first developed a new strategy to prepare HIPEs by the phase inversion of microgel particle stabilized oil-in-water emulsions.12 However, a large number of microgel particles (5 wt% of oil phase) are required to obtain HIPEs. Very recently, HIPEs have been obtained by the 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 Until now, the preparation of HIPEs by phase inversion is still rare, and the phase inversion of oil-in-water emulsions to form water-in-oil HIPEs with low stabilizer concentrations is highly desirable, since most monomers used for poly(HIPEs) are oleophilic.5,17 We recently studied the preparation of HIPEs from polymer organogels based on block ionomer sulfonated polystyrene-block-poly(ethylene-ran-butylen)-block-polystyrene (SSEBS).14,18,19

In this paper, we report that water-in-oil HIPEs have been obtained by the 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 the HIPEs. The ionomer is sulfonated polystyrene (SPS), and the inversion is driven by salt concentration and/or pH changes. The continuous phase in the HIPE organogels can not only be organic solvents, Poly(HIPEs) were successfully prepared by the polymerization of monomers as the continuous phase in the ionomer-stabilized HIPEs.
This is the published version:

Zhang, Tao, Xu, Zhinguang, Cai, Zengxiao and Guo, Qipeng 2015, Phase inversion of ionomer-stabilized emulsions to form high internal phase emulsions (HIPEs), *Physical chemistry chemical physics*, vol. 17, no. 24, pp. 16033-16039.

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

**Experimental**

**Materials**

Polystyrene (PS) with an average molecular weight $M_w$ of 192,000 and a melt index of 6.0–9.0 g 10 min$^{-1}$ was used for the preparation of the 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 being passed 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 were used directly. Deionized water was used throughout the experiments.

Preparation of SPSs

The SPSs were prepared by the sulfonation of polystyrene according to the method reported in our previous paper, with a few modifications.\(^1\) In brief, 20 g of polystyrene was dissolved in 200 mL of dichloroethane, and the required amount of freshly prepared acetyl sulfonate was added at 50 °C. After reacting for 3 hours, the reaction mixtures were dropped into hot water. The water-insoluble SPSs were obtained by first evaporating the solvents and then washing with cold deionized water to remove acid. Water-soluble SPS was obtained by first evaporating the solvents and then dialysing against deionized water to remove acid. The sulfonation degrees of the SPSs were determined by titration of their THF solutions (for water-insoluble SPSs) or aqueous solution (for water-soluble SPSs) with a standard sodium hydroxide methanol solution (0.1 N, standardized with p-toluene sulfonic acid solution) using phenolphthalein as the indicator. The sulfonation degree of the 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, the SPSs were dissolved in THF to obtain 10 w/v% SPS solutions; the water-soluble SPS was used directly in aqueous solutions. Aqueous phases with different pH values were obtained by adding HCl solution or NaOH (1 M) solution to water and then measuring the pH with a pH meter (SevenEasy, Mettler-Toledo GmbH, Switzerland). Typically, emulsions were obtained by mixing as-prepared SPS solution in THF, 1 mL of organic solvent or monomers, and 4 mL of aqueous solutions with different pH values or salt concentrations for about 2 minutes with a vortex mixer. For the water-soluble SPSs, their aqueous solutions with different pH values and salt concentrations were used directly by mixing them 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 to evaporate in a fume hood to remove solvent and then dried under vacuum at 40 °C before measurement. The water-soluble SPS was first dried and then ground well with KBr powder to press a KBr disk for FTIR measurement. The spectra were collected in the wavenumber range of 600–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

Rheological measurements

Rheological experiments were carried out on a TA DHR 3 rheometer with a cone-plate geometry at 25 °C. A cone with a diameter of 40 mm and a tilt angle of 21° was used, and the gap width was set to 500 μm. A solvent trap was used to minimize the effect of evaporation. The HIPE organogels newly prepared 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 3000 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 values and salt concentrations were also studied for comparison.

Confocal laser scanning microscopy (CLSM)

Confocal imaging was performed on a laser scanning confocal microscope (Leica SP5, Leica Microsystems CMS GmbH, Germany). Emulsions and HIPEs prepared from aqueous solutions with different pH values and salt concentrations were transferred onto a glass slide and observed immediately. A laser with wavelength of 405 nm was used to excite pyrene in the organic phase.

Optical microscopy

The morphology of the ionomer-stabilized oil-in-water emulsions was examined using a Nikon Eclipse-80i optical microscope under polarized light. The emulsions were dropped on glass slides and observed directly.

Zeta potential

The zeta potentials of SPS3 at different NaCl concentrations were characterized using a Zetasizer Nano ZS analyzer. The concentration of the SPS3 aqueous solution was 0.2 mg mL$^{-1}$ with NaCl concentrations ranging from 0 to 1 M.

Preparation of poly(HIPEs)

HIPE organogels with monomers as the continuous phase were polymerised at 70 °C for 10 hours to obtain poly(HIPEs).
Results and discussion

The ionomer SPSs were prepared via the sulfonation of polystyrene, and the obtained SPSs were studied with FTIR spectroscopy. From the results in Fig. 1(a), it can be seen that some new absorption peaks appeared at 580, 1008, 1132 and 1180 cm\(^{-1}\); these peaks can be ascribed to the angle deformation vibration of \(\tilde{S}O\tilde{O}\tilde{S}\), the ring vibration of the \(p\)-substituted benzene ring, the vibration of hydrated sulfonate acid and the antisymmetric stretching of \(\tilde{S}O\tilde{O}\tilde{S}\), respectively.\(^{20}\) Moreover, it can be observed from Fig. 1(b) that a broad band (circled) centred at 3470 cm\(^{-1}\) clarifies as the sulfonation degree increases, and the absorption band is ascribed to the free and hydrogen bonded hydroxyl groups between the sulfonic acid groups, which verifies the sulfonation of polystyrene.\(^{21}\)

Polystyrene is hydrophobic, and after sulfonation, the \(-\text{SO}_3\text{H}\) groups are hydrophilic. Thus, SPSs are amphiphilic, and their solubility is dependent on their degrees of sulfonation. The three SPSs listed in Table 1 are denoted as SPS1, SPS2 and SPS3. \(^{5.9\%}\) and \(^{11.6\%}\) of the styrene groups of SPS1 and SPS2 were grafted with \(-\text{SO}_3\text{H}\) groups, respectively. These SPSs are soluble in THF and toluene but not in water. SPS3, which has a sulfonation degree of \(30.5\%\), can be totally dissolved in water.

SPSs are amphiphilic and can serve as surfactants. In our experiments, both the water soluble and insoluble SPSs were successfully used to stabilize oil-in-water emulsions, and the 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 efficiencies for stabilizing emulsions.

The efficiency of the SPSs was studied by stabilizing HIPEs formed from toluene and aqueous solution (20/80) with a pH of 7 and an NaCl concentration of 0.5 M in the aqueous phase. SPS2, with a sulfonation degree of \(11.6\%\), showed the highest efficiency; as little as \(0.2\) (w/v)% of the organic phase was enough for the formation of HIPEs without liquid-like flow behaviour. This concentration is much lower than that of the PS-co-PMAA microgel particles.\(^{12}\) When the sulfonation degree was decreased to \(5.9\%\) (SPS1), the efficiency decreased and the ionomer concentration increased to \(1.0\) (w/v)% of the organic phase. Water-soluble SPS3 required the highest concentration to stabilize HIPEs, at \(3.8\) (w/v)% of the aqueous phase. In this work, SPS3 was used for the study of structural changes with pH changes and salt concentration, and water-insoluble SPS2, which had the highest efficiency, was used for the investigation of the phase inversion between the emulsion types.

Emulsions were obtained by shearing a mixture of SPS2 solution in toluene (0.2%, w/v) and water at a fixed ratio of 20/80 (toluene/water). The appearances and conductivities of the ionomer-stabilized emulsions are shown in Fig. 2(a). It is noted that emulsions exhibiting low viscosity are formed at zero 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 a white top layer and a translucent bottom layer, after a few minutes. The separation is totally reversible, and the separated layers turn into emulsions again with a very gentle shake. It is believed that the separation results from the density

![Fig. 1 FTIR spectra of polystyrene, SPS1, SPS2 and SPS3 in the ranges of (a) 1400–800 cm\(^{-1}\) and (b) 3700–3000 cm\(^{-1}\).](image)

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

<table>
<thead>
<tr>
<th>Sulfonation degree (%)</th>
<th>Solubility</th>
<th>Concentration to stabilize HIPEs (w/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS1 5.9</td>
<td>Water-insoluble</td>
<td>1.0% of organic phase</td>
</tr>
<tr>
<td>SPS2 11.6</td>
<td>Water-insoluble</td>
<td>0.2% of organic phase</td>
</tr>
<tr>
<td>SPS3 30.5</td>
<td>Water-soluble</td>
<td>3.8% of aqueous phase</td>
</tr>
</tbody>
</table>

![Fig. 2 (a) Images 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 0.5 M NaCl obtained by fixing the toluene/water ratio at 20/80, the pH at 7 and the SPS2 concentration at 0.2 (w/v)% of the oil phase.](image)
difference between water and toluene, which was verified by the fact 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 the oil phase.

The formation of oil-in-water emulsions was observed under a polarized optical microscope, as shown in Fig. 2(b), and the sizes of the disperse phases varied from several to tens of micrometres, which fits in the size range of the emulsions. Control experiments show that no emulsions were formed without SPS2, and thus it is believed that SPS2 acts as a stabilizer/emulsifier.

Surprisingly, after the addition of NaCl to these pre-formed emulsions and mechanical shear, the viscosities of these emulsions increased obviously and their conductivities dropped to about 0.5 M, which indicates that phase inversion occurred with 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 Fig. 2(a), it can be observed that with a slight increase of the NaCl concentration to over 0.15 M, highly viscous water-in-oil HIPEs were formed and the conductivity dropped dramatically. When the NaCl concentration was further increased to 0.25 M and over, although the conductivities of these HIPEs remained at around 0.5 M, these water-in-oil HIPEs exhibited no liquid-like flow behaviour, indicating the formation of HIPE organogels. The confocal image in Fig. 2(c) confirmed the formation of HIPEs, and the newly formed HIPEs with water droplets range in size from several to a little over 100 nm, 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; however, their stabilizer concentration was quite high, at 5% of the continuous phase.\(^{12}\)

To study the effect of NaCl on the ionomer solutions, the zeta potentials of water soluble ionomer SPS3 solutions with different NaCl concentrations were measured, and the dependency of the zeta potentials of the SPS3 solutions on NaCl concentration at pH = 7 is shown in Fig. 3. Fig. 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 ionomers on the water–toluene interface.\(^{22}\)

SPSs may form nanoparticles in water and solvents,\(^{23}\) which stabilizes HIPEs. It is noted that all polymer HIPE stabilizers, including microgels,\(^{11,12,22,24}\) CCS polymers\(^{15,16}\) and bulk polymer organogels,\(^{14}\) have cross-linked structures, either due to chemical or strong physical interactions. SPs, as novel HIPE stabilizers, can be totally dissolved in water or organic solvents depending on the degree of sulfonation, showing that non-cross-linked ionomers can also serve as HIPE stabilizers.

The formation of three-dimensional networks at high salt concentrations was confirmed by rheological measurements. Typical results for the dynamic strain measurements of HIPE organogels with 0.5 M NaCl are presented in Fig. 4(a), and the extent of the linear viscoelastic regime is as high as 50%. The results for the dynamic frequency measurements are shown in Fig. 4(b). All the elastic moduli (\(G^\prime\)) are higher than the corresponding viscous moduli (\(G^\prime\prime\)) with salt concentrations in the aqueous phase of 0.3, 0.5 and 0.7 M, indicating the formation of three-dimensional networks. These moduli do not change greatly with increasing salt concentration in the aqueous phase, showing that the salt concentration does not have an obvious effect on the strengths of these HIPE organogels, although salt is critical for their formation.

Inversion of the emulsion type by tuning pH values has been reported,\(^{25}\) and pH induced inversion to prepare HIPEs has also been demonstrated with microgel particles or CCS as stabilizers.\(^{12,16}\) SPSs contain ionizable –SO\(_3\)H groups; thus, they can be affected by pH values. The appearances and conductivities of ionomer-stabilized emulsions at pH values from 1 to 14 are shown in Fig. 5(a). Surprisingly, two inversion points from pH 1 to 14 can be seen, 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 in the pH range from 1.5 to 13, while these emulsions turned into water-in-oil type HIPEs at pH values below 1.5 or over 13, which is confirmed by the high viscosities and low conductivities of the emulsions. The formation of water-in-oil HIPEs at low and
High pH has been confirmed by confocal microscopy, as shown in Fig. 5(b) and (d), respectively. Meanwhile, the formation of oil-in-water emulsions at moderate pH values was verified by polarized optical microscopy, as shown in Fig. 5(c).

SPSs can stabilize HIPEs at high concentrations of HCl or NaOH. Although their concentrations are quite high, this effect cannot be well-explained by the salt effect as no HIPEs form at an NaCl concentration of 0.1 M. The formation of HIPEs may be caused by pH-induced structural changes of SPSs, as it is known that in an acidic environment the –SO₃H groups may form hydrogen bonds between each other,²⁶ in basic solution, all the –SO₃H groups will deprotonate to form –SO₃⁻ ions, which will interact through dipole–dipole interactions.

The water-in-oil HIPEs at pH 1, 13 and 13.5 can be strong enough to form gels, and the formation of these gels was verified by dynamic frequency measurements. As shown in Fig. 6, HIPE organogel at pH 13.5 exhibits the highest strength, while HIPE organogel at pH 13 is the weakest. These results are in agreement with those from direct observation by the tube-inversion method. The G¹ and G¹¹ 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 for a long time.

The 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 that these HIPE organogels remain in the thermodynamic equilibrium state once prepared.

A synergetic interaction between NaCl and pH in the phase inversion of emulsion types was found in the ionomer-stabilized emulsion. For example, when the NaCl concentration was increased 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 a synergetic effect between the salt concentration and the pH. To further demonstrate the synergetic effect, an approximate diagram has been drawn in Fig. 7 based on the tube-inversion method. From the results, it can be seen that the pH values at which phase inversion occurs increase or decrease with increasing NaCl concentration from 0 to 0.15 M.

Experimental results showed that the organic phase can consist of hydrophobic organic solvents, including toluene, xylene, chloroform, dichloroethane, dichloromethane, and 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 inverted into water-in-oil HIPEs by tuning the pH and salt concentration of the aqueous phase.

To demonstrate the ability to prepare poly(HIPEs) from the ionomer-stabilized HIPEs, monomers with cross-linkers and initiators were used as the 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 Fig. 8(a). As the HIPE organogels form, mouldable organogels with different shapes can be obtained. Moreover, SPSs stabilized HIPEs for the preparation of poly(HIPEs) are obviously cost-effective in comparison with those stabilized by surfactants and gels. Fig. 8(b) shows that almost all the cells are closed, implying that these poly(HIPEs) have potential as thermal insulation and soundproof materials.

Interconnected cells have previously been 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 interactions between the \(-\text{SO}_3\text{H}\) groups of SPS,\(^{26}\) and the HIPEs are stabilized by these SPS particles. The 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 the SEM image in Fig. 8(c) that deformed particles are attached on the walls of the poly(HIPEs), indicating that the SPS2 formed particles do stabilize HIPEs.

### Conclusions

In summary, the phase inversion of SPS-stabilized oil-in-water emulsions to water-in-oil HIPEs has been achieved by tuning the 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 over the entire pH range, and a synergetic effect between pH and salt concentration has been found on the inversion of the emulsion type. Phase inversion occurs with a variety of hydrophobic solvents and commonly used monomers as organic phases, which facilitates a new route to the preparation of poly(HIPEs).

### Acknowledgements

T.Z. was supported by a Deakin University Postgraduate Research Scholarship (DUPRS).

### Notes and references


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

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

**Fig. 8** (a) An image, (b) and (c) SEM images of typical poly(HIPEs) from SPS2 stabilized HIPEs with styrene as the continuous phase.