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Synthesis of Star Polymeric Ionic Liquids and Use as the Stabilizers for High Internal Phase Emulsions*

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Abstract A series of well-defined core cross-linked star (CCS) polymeric ionic liquids (PILs) were synthesized *via* a three-step approach. First, the styrenic imidazole-based CCS polymer (S-PVBnIm) was prepared by the RAFT-mediated heterogeneous polymerization in a water/ethanol solution, followed by the quaternization of S-PVBnIm with bromoalkanes and anion exchange. The CCS polymers were characterized by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The obtained CCS polymers were used as the effective emulsifiers for oil-in-water high internal phase emulsions (HIPEs). Multiple oils with different polarity including *n*-dodecane, undecanol, toluene and octanol were emulsified using 0.5 wt% S-PVBnIm aqueous solution under the acidic condition to form HIPEs with long-term stabilities. The excellent emulsification properties of CCS PILs were demonstrated by HIPE formation for a variety of oils. The properties of HIPEs in terms of emulsion type and oil droplet size were characterized by the confocal laser scanning microscopy (CLSM). The intriguing capability of CCS PILs to stabilize HIPEs of various oils holds great potentials for the practical applications.

Keywords Star polymers; Poly(ionic liquids); Emulsions

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INTRODUCTION

High internal phase emulsions (HIPEs) are commonly defined as the concentrated emulsions containing an internal phase with a volume above 74%[1, 2]. They are important for a wide range of applications in food, cosmetic, pharmaceutical, and petroleum industries. HIPEs have also been used as the templates to prepare porous materials (polyHIPEs)[3] *via* the polymerization of the continuous phase containing monomers and cross-linkers, and then removal of the internal phase of HIPEs[4–6]. PolyHIPEs are the replica of the emulsion structures at the gel point of polymerization and the pore structures of polyHIPEs are predominantly determined by the emulsion template. The emulsifiers used in emulsions determine the droplet size as well as the emulsion stability during the polymerization and the properties of the resulting polyHIPE. Therefore, the efficient stabilizers for HIPEs are highly demanding in the burgeoning soft materials field.

Surfactants and particles are two important classes of emulsifiers for HIPEs. Typically, HIPEs are stabilized by large amounts of the surfactant (5%–50%)[4, 5] to ensure the stability of emulsion when the continuous phase is polymerized. However, significant efforts are needed to remove the surfactants from the resulting polyHIPEs.

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To address such a problem, the colloidal particles, known as the Pickering emulsions, have attracted much interest for the stabilization of HIPEs because of their irreversible adsorption at the interface of emulsions[7–9]. For example, Akartuna *et al*.[10] reported the preparation of macroporous ceramics from the Pickering HIPEs stabilized by the inorganic particles. In their system, about 35 vol% particles were needed to stabilize the emulsions with internal phase fractions of only 72%–78%. Bismark *et al*.[11, 12] reported the use of silica and titania particles at a concentration of 2 wt% to form stable HIPEs with an internal phase volume of 90%. Although various inorganic particles have been used to stabilize HIPEs, most of them required subsequent chemical treatment or surface modification to tune the wettability. In the preparation of polyHIPEs by the reactions of continuous phase, additional considerations of the employed chemistry are needed to avoid the collapse of the emulsion structures.

The organic particles have also been studied as the stabilizers for emulsions. Ngai *et al*. reported that the flexible microgels are excellent candidates for the HIPEs stabilization. The Pickering hexane-in-water (o/w) HIPEs with the volume fractions as high as 90% were stabilized by soft poly(*N*-isopropyl-*co*-methacrylic acid) microgel particles at the concentrations as low as 0.05 wt%[13]. They also prepared HIPEs by a phase inversion method using ionizable poly(styrene-*co*-methacrylic acid) microgels as the particulate emulsifiers[14]. Compared to the purely inorganic particles, the organic particles are relatively designable and can be modified with stimuli-responsive properties, potentially enabling a more diverse range of HIPE emulsifiers to be developed.

Star polymers represent an important class of polymer architectures and have been used in a wide range of fields[15–28]. The core cross-linked star (CCS) polymers have a large number of arms connected to a highly cross-linked central core, which have been synthesized *via* either the core-first or the arm-first methods[15, 16]. The synthesis of CCS polymers *via* the RAFT-mediated arm-first method has been carried out predominantly in the solution polymerization, which typically suffers long reaction time, relatively low yields or high dispersity. Recently, several strategies have been developed to resolve these problems associated with the RAFT solution synthesis of CCS polymers. Boyer and co-workers employed the cross-linkers of low solubility in organic solvents to provide the CCS polymers with low dispersity[29]. Qiao and co-workers improved the livingness of photo-controlled RAFT polymerization to synthesize well-defined CCS polymers in high yields[30]. Recently, we developed a new method for the synthesis of CCS polymers *via* the RAFT-mediated heterogeneous polymerization including both the emulsion and dispersion polymerization[31–36], and explored their properties as the effective interfacial stabilizers for HIPEs[37–40].

Ionic liquids (ILs) consist of cation/anion pairs with melting points below the boiling point of water (100 °C)[41]. The polymeric ionic liquids (PILs) have repeat units that are ionic liquids themselves. PILs combining the unique properties of ILs and the processability of polymers have been found the applications in various fields[42]. Especially, PILs have been investigated as the interfacial stabilizers and some of them show ion-responsive properties[42], which are discussed in this study. We hypothesize that if the arms of CCS polymers are made of PILs, the CCS PILs would have a combination of nanosize (high adsorption energy at interface), arm flexibility (optimal configuration at interface), and a high degree of structural diversity (tunable wettability). These projected properties of CCS PILs point to a new generation of effective interfacial stabilizers for the emulsions. Herein, we report the synthesis of a series of well-defined styrenic imidazolium-based CCS PILs, and their characterization and the use as the emulsifiers are also discussed.

EXPERIMENTAL

Materials

2,2′-Azobis(2-methylpropionamidine) dihydrochloride (V-50, 97%) and styrene (99%) were purchased from Sigma-Aldrich. 4-Vinylbenzyl chloride (VBCl, 90%) was purchased from J&K Scientific. Imidazole (99%), acetone (> 99.5%), *N*,*N*-dimethylformamide (DMF, > 99.5%), 2,2′-azobis(2-methylpropionitrile) (AIBN, CP), hydrogen chloride (36%–38%), sodium hydroxide (96%), anhydrous sodium sulfate (AR), sodium bicarbonate (99.5%), dichloromethane (99.5%), divinylbenzene (DVB; mixture of *o*-, *m*-, *p*- isomers; 50% ethyl vinyl benzene and diethylbenzene content), anhydrous diethyl ether (> 99.7%) were purchased from Sinopharm

Chemical Reagent Co., Ltd. Bromoethane (99%), *n*-butylbromide (99%), 1-bromooctane (98%), bromoacetonitrile (97%), sodium fluoroborate ($NaBF_4$, 99%), sodium hexafluorophosphate ($NaPF_6$, 99%) and lithium bis(trifluoromethanesulphonyl) imide (LiTFSI, 99%) were purchased from Aladdin Reagent.

Characterization

NMR spectra were collected on a Bruker AV 500 MHz spectrometer in dimethyl sulphoxide (DMSO) and the chemical shifts were reported using the solvent residue as the reference. Fourier transform infrared (FTIR) spectra were collected at room temperature on a Nicolet AVATAR370 FT-IR spectrometer. Gel permeation chromatography (GPC) was performed on a Waters Alliance e2695 GPC system, equipped with a Styragel guard column, a Waters Styragel HR3 (molecular weight range $5.0 \times 10^2 - 3.0 \times 10^4$ g/mol), a Waters Styragel HR4 (molecular weight range $5.0 \times 10^3 - 6.0 \times 10^5$ g/mol), and a Waters Styragel HR5 (molecular weight range $5.0 \times 10^4 - 4.0 \times 10^6$ g/mol), equipped with a 2414 refractive index (RI) detector using DMF (HPLC grade, containing 1 mg/mL LiBr) as the eluent at a flow rate of 0.8 mL/min. The temperature of the columns was set at 65 °C and the temperature of the refractometer was set at 45 °C. Analysis of the molecular weight and the dispersity was performed using Empower 2 software against PMMA standards (molecular weight range $2.4 \times 10^2 - 1.0 \times 10^6$ g/mol). Dynamic light scattering (DLS) was performed on a Malvern ZS90 at a detection angle of 90°. Z-average radius and polydispersity were automatically analyzed in the cumulant mode using the Malvern software. The concentration of the samples was 0.5 wt%. Thermal stabilities of PIL CCS polymers were measured by thermal gravimetric analysis (TGA, TA Instrument, Q500) at a heating rate of 10 K/min under N_2 over a temperature range of 25–600 °C. Glass transition temperatures (T_g) were measured on a differential scanning calorimeter (DSC) (TA Instrument, Q2000) under N_2. The samples were initially heated to 200 °C for 10 min to remove the thermal history. T_g was determined from the second heating cycle (−30 °C to 300 °C) at a heating ramp of 5 K/min. Interfacial tensions were measured at 25 °C on a Dataphysics OCA20 *via* drop shape analysis using the pendent drop method. A drop of water or CCS polymer aqueous solution (0.5 wt%) was slowly formed into dodecane *via* a needle, and the shape of the drop was analyzed using software. Confocal laser scanning microscopy (CLSM) was performed on an Olympus F1000 microscope using the 488 nm laser to excite the samples stained with Nile red in the oil phase. The samples were directly placed on the cover slides and the x/y layers were scanned. The photographs of emulsions were taken with a digital camera (FinePix JV100).

Synthesis of VBnIm Monomer

VBnIm was prepared according to the procedures described in the literature[43]. ^{1}H-NMR (500 MHz, DMSO, δ): 7.77 (1H, s, N—C<u>H</u>—N), 7.45 (2H, d, Ph), 7.23 (2H, d, Ph), 7.18 (H, s, N—C<u>H</u>=C<u>H</u>—N), 6.94 (H, s, N—C<u>H</u>=C<u>H</u>—N), 6.71 (1H, m, C<u>H</u>=C<u>H</u>), 5.82 (1H, d, C<u>H</u>=C<u>H</u>), 5.25 (1H, d, C<u>H</u>=C<u>H</u>), 5.18 (1H, s, Ph—C<u>H</u>—N).

Synthesis of PVBnIm Macro-CTA (L-PVBnIm)

PVBnIm macromolecular chain transfer agent (macro-CTA) was synthesized by the RAFT polymerization of VBnIm in DMF using a chain transfer agent (CTA) 2-ethylsulfanylthiocarbonylsulfanyl-propionic acid methyl ester at 70 °C. The concentration of VBnIm was 0.5 g/mL, and the molar ratio of CTA/VBIm/AIBN was controlled at 1:100:0.2. CTA (94.5%, 0.338 g, 1.4 mmol) and VBnIm (26.2 g, 140 mmol) were dissolved in 52.4 mL of DMF. The solution was degassed with nitrogen at 0 °C for 40 min and then immersed into an oil bath at 70 °C. After the temperature was stabilized, a degassed solution of AIBN (46.7 mg, 0.28 mmol) in dioxane was injected *via* a microsyringe. The polymerization was conducted for 24 h and was stopped when the monomer conversion reached 79% as determined by ^{1}H-NMR. The solution was diluted and the polymer was precipitated in ethyl ether. The polymer was collected by centrifugation and purified by the precipitation of the dichloromethane solution of the polymer in ethyl ether twice. After drying under vacuum, 18.74 g yellow solid was obtained, yield 89%. $M_{n,th}$ = 14.8 kg/mol, M_n = 14.8 kg/mol (GPC), $Đ$ = 1.07 (GPC). ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 7.67 (1H, s, N—C<u>H</u>—N), 7.00 (2H, d, Ph), 6.75 (2H, d, Ph), 6.34 (2H, d, N—C<u>H</u>=C<u>H</u>—N),

5.03 (2H, s, Ph—C<u>H</u>—N), 1.69–0.96 (backbone —C<u>H</u>$_2$—C<u>H</u>—).

Synthesis of PVBnIm CCS Polymer (S-PVBnIm)

S-PVBnIm was synthesized *via* the RAFT-mediated dispersion polymerization in a water/ethanol solution. The concentration of L-PVBnIm (macro-CTA) was 0.05 g/mL, and the molar ratio of L-PVBnIm/styrene/DVB/V-50 was controlled at 1:5:5:0.2. L-PVBnIm (7.27 g, 0.49 mmol) was dissolved in a water/ethanol solution (1:1, *V*:*V*, 145.2 mL), to which were added styrene (0.256 g, 2.45 mmol) and DVB (0.64 g, 2.45 mmol). After the mixture was degassed with N_2 in an ice/water bath for 40 min, it was immersed into an oil bath at 70 °C. After the temperature was stabilized, a predegassed V-50 solution (200 μL, 26.7 mg, 0.1 mmol) was injected *via* a microsyringe. The polymerization was allowed to continue for 5 h under the protection of N_2. The CCS polymer was synthesized in a 95% yield, which was purified by repeated ultrafiltration of its aqueous solution using Amicon Ultra-15 filtration tubes (MWCO 30 kg/mol) at a speed of 6000 r/min. RI-GPC: M_n = 96.6 kg/mol, $Đ$ = 1.10. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 8.03 (1H, s, N—C<u>H</u>—N), 7.21 (2H, d, Ph), 7.02 (2H, d, Ph), 6.37 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.11 (2H, s, Ph—C<u>H</u>—N), 2.08–0.98 (backbone —C<u>H</u>$_2$—C<u>H</u>—).

Synthesis of Cationic CCS Polymers by the Quaternization of S-PVBnIm

A general protocol for the synthesis of cationic CCS polymers was as follows: 0.06 mmol of S-PVBnIm, 7.2 mmol of *n*-alkyl bromide or bromoacetonitrile and 5 mL of methanol were added into a 10 mL reactor. The mixture was stirred at 80 °C for 48 h. After cooling down, the reaction mixture was added dropwise into 100 mL of ethyl ether. The precipitate was filtered and dried under vacuum to a constant weight.

CCS poly(3-ethyl-1-(vinylbenzyl)imidazolium) bromide (S-PVBnEtImBr), ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 9.92 (1H, s, N—C<u>H</u>—N), 7.91 (2H, d, Ph), 7.36 (2H, d, Ph), 6.37 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.55 (2H, s, Ph—C<u>H</u>—N), 4.23 (CH$_3$—C<u>H</u>$_2$—N), 2.01–0.59 (backbone —C<u>H</u>$_2$—C<u>H</u>— and CH$_3$—CH$_2$—N).

CCS poly(3-butyl-1-(vinylbenzyl)imidazolium) bromide (S-PVBnBuImBr), ^{1}H-NMR (DMSO-d$_6$, δ): 10.22 (1H, s, N—C<u>H</u>—N), 7.92 (2H, d, Ph), 7.33 (2H, d, Ph), 6.33 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.56 (2H, s, Ph—C<u>H</u>—N), 4.20 (CH$_3$(CH$_2$)$_2$—C<u>H</u>$_2$—N), 1.98–0.49 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—(CH$_2$)$_3$—N).

CCS poly(3-octyl-1-(vinylbenzyl)imidazolium) bromide (S-PVBnOcImBr), ^{1}H-NMR (DMSO-d$_6$, δ): 9.99 (1H, s, N—C<u>H</u>—N), 7.93 (2H, d, Ph), 7.34 (2H, d, Ph), 6.34 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.53 (2H, s, Ph—C<u>H</u>—N), 4.21 (CH$_3$(CH$_2$)$_6$—C<u>H</u>$_2$—N), 1.98–0.50 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—(C<u>H</u>$_2$)$_6$—N).

CCS poly(3-acetonitrile-1-(vinylbenzyl) imidazolium) bromide (S-PVBnAceImBr), ^{1}H-NMR (DMSO-d$_6$, δ): 10.11 (1H, s, N—C<u>H</u>—N), 8.07 (2H, d, Ph), 7.30 (2H, d, Ph), 6.39 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.91 (2H, s, Ph—C<u>H</u>—N), 5.59 (—C<u>H</u>$_2$—CN), 1.99–0.59 (backbone —C<u>H</u>$_2$—C<u>H</u>—).

Synthesis of PIL CCS Polymers by Anion Exchange

The anion exchange reactions for S-PVBnEtImBr were performed to replace the Br^- with other anions including BF_4^-, PF_6^- and $TFSI^-$. The salt (2.97 g $NaBF_4$, 4.49 g $NaPF_6$, 7.76 g LiTFSI) was dissolved in deionized water and the solution was added dropwise into a 0.5 g of S-PVBnEtImBr aqueous solution with an anion molar ratio of Br^-/(BF_4^- or PF_6^- or $TFSI^-$) at 1/10. The reaction mixture was stirred overnight, followed by filtration and washing with water three times. The end-point of exchange reactions was determined by showing no AgBr precipitation after the washing step (silver nitrate test). The resulting CCS PILs were dried in a vacuum oven for at least 24 h. The abbreviation of CCS PILs is designated according to the new anions: S-PVBnEtImBF$_4$, S-PVBnEtImPF$_6$ and S-PVBnEtImTFSI. Due to the low solubility of S-PVBnOcImBr in water, the anion exchange was conducted in DMF. S-PVBnOcImBr (0.21 g) and LiN(CF$_3$SO$_2$)$_2$ (0.25 g) were dissolved in 2.1 mL of DMF and stirred for 48 h at room temperature. Then, the reaction solution was added dropwise into 30 mL of water for affording a viscous solid, which was then dissolved in THF. The precipitation was conducted by adding methanol/water (1/1, *V*/*V*) mixture into THF solution. The precipitation was repeated as described above and the final precipitate was dried under vacuum.

S-PVBnEtImBF$_4$, ^{1}H-NMR (DMSO-d$_6$, δ): 9.16 (1H, s, N—C<u>H</u>—N), 7.72 (2H, d, Ph), 7.49 (2H, d, Ph), 7.11 and 6.43 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.22 (2H, s, Ph—C<u>H</u>—N), 4.16 (CH$_3$—C<u>H</u>$_2$—N), 1.99–0.80 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—CH$_2$—N).

S-PVBnEtImPF$_6$, ^{1}H-NMR (DMSO-d$_6$, δ): 9.16 (1H, s, N—C<u>H</u>—N), 7.72 (2H, d, Ph), 7.49 (2H, d, Ph), 7.04 and 6.43 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.22 (2H, s, Ph—C<u>H</u>—N), 4.16 (CH$_3$—C<u>H</u>$_2$—N), 1.99–0.53 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—CH$_2$—N).

S-PVBnEtImTFSI, ^{1}H-NMR (DMSO-d$_6$, δ): 9.20 (1H, s, N—C<u>H</u>—N), 7.76 (2H, d, Ph), 7.42 (2H, d, Ph), 6.96 and 6.39 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.18 (2H, s, Ph—C<u>H</u>—N), 4.16 (CH$_3$—C<u>H</u>$_2$—N), 1.99–0.53 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—CH$_2$—N).

S-PVBnOcImTFSI, ^{1}H-NMR (DMSO-d$_6$, δ): 9.27 (1H, s, N—C<u>H</u>—N), 7.76 (2H, d, Ph), 7.49 (2H, d, Ph), 6.96 and 6.32 (2H, d, N—C<u>H</u>=C<u>H</u>—N), 5.22 (2H, s, Ph—C<u>H</u>—N), 4.12 (CH$_3$—C<u>H</u>$_2$—N), 1.99–0.53 (backbone —C<u>H</u>$_2$—C<u>H</u>— and C<u>H</u>$_3$—(C<u>H</u>$_2$)$_6$—N).

Preparation of HIPEs

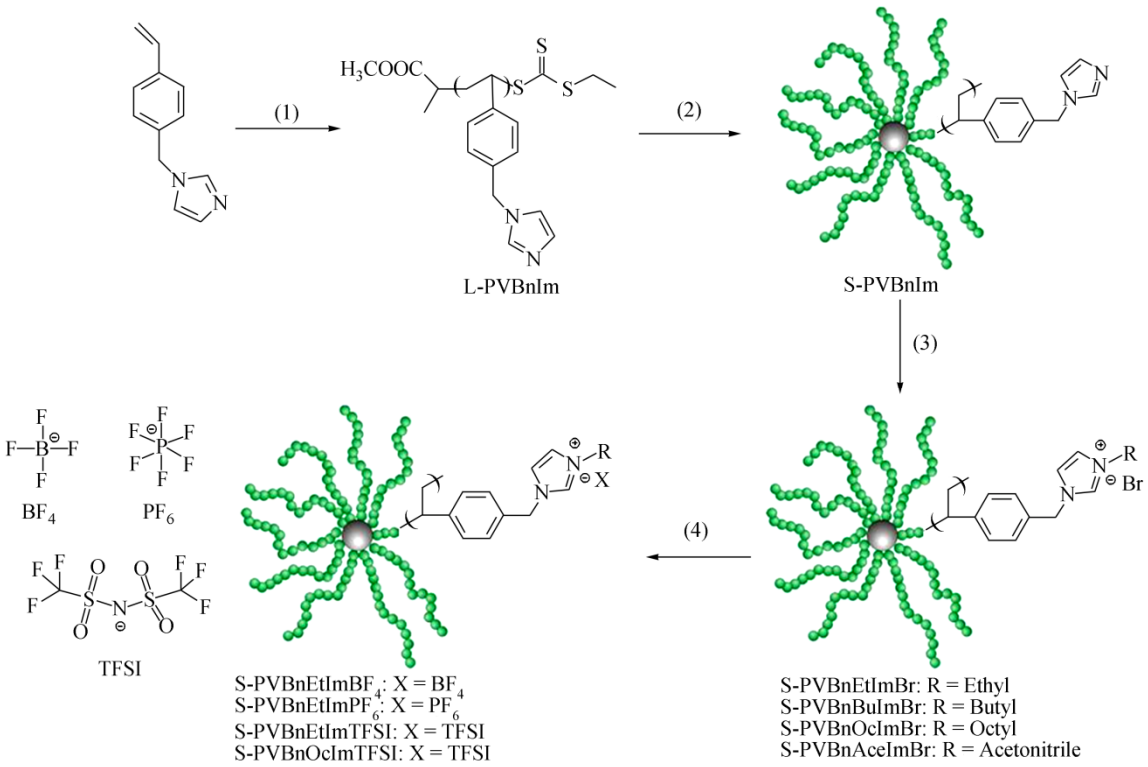
The total volume of all the prepared emulsions was 1.5 mL and the oil phase volume fraction (V_{oil}) was 80%. The oils include *n*-dodecane, undecanol, toluene, octanol and chloroform. An aqueous solution of the CCS polymers was mixed with one of the oils, and the mixture was homogenized using a Polytron PT 1200E homogenizer (7 mm head), operating first at the 1/4 position of the scale for 30 s and then at the maximum speed of 25000 r/min for 30 s. The emulsion type was identified by CLSM with the emulsions stained by Nile red in the oil phase.

RESULTS AND DISCUSSION

The synthesis of CCS PILs involved four steps as outlined in Scheme 1. In the first step, the RAFT polymerization of VBnIm in DMF was stopped at 79% monomer conversion and thus provided linear PVBnIm (L-PVBnIm) with M_n of 14.8 kg/mol and $Đ$ of 1.07. L-PVBnIm was used as the macro-CTA for the second step synthesis of CCS polymer (S-PVBnIm) *via* the dispersion polymerization in the ethanol/water solution (1/1, *V*/*V*) by using styrene as the spacing monomer and DVB as the cross-linker. The formation of S-PVBnIm was monitored by GPC, which showed a gradual reduction of L-PVBnIm and evolution of high molecular weight species as a function of polymerization time, and the monomer conversion reached 95% after 1.5 h (Fig. 1a). No apparent change of GPC traces was observed for the reactions over 2 h (see kinetic plot in Fig. S2), suggesting that the polymerization was completed within 1.5 h. In order to obtain S-PVBnIm with high purity, the as-synthesized crude product was purified by ultrafiltration. From Fig. 1(b), we can see that the well-defined S-PVBnIm with M_n of 96.6 kg/mol and $Đ$ of 1.10 was obtained after ultrafiltration. This purified S-PVBnIm was used for the subsequent synthesis to ensure the achievement of the well-defined CCS PILs. The purified S-PVBnIm was characterized by ^{1}H-NMR (Fig. 2a). As expected, it was similar to that of L-PVBnIm. The core of S-PVBnIm was highly cross-linked and thus the protons in the core were not detectable by ^{1}H-NMR measurement.

The quaternization reactions of S-PVBnIm were conducted with excess amounts of *n*-alkyl bromide (n = 2, 4 and 8) or bromoacetonitrile to ensure the quantitative conversion of the imidazole units to the imidazolium units. In comparison with the ^{1}H-NMR spectrum of S-PVBnIm, the ^{1}H-NMR spectra (Fig. 2a) of *n*-alkylated cationic CCS polymers, namely S-PVBnEtImBr, S-PVBnBuImBr, and S-PVBnOcImBr showed a new resonance (g) at δ = 4.25, corresponding to the methylene group resulted from alkylation. Both the benzylic protons and the protons on the imidazolium rings showed notable shifts to the downfield position, in comparison with those on the imidazole ring due to the aromatization upon quaternization. Most importantly, the integration ratio of g/c was unity, suggesting the quantitative conversion of quaternization. The successful quaternization was also confirmed by the FTIR analysis (Fig. 2b). Before quaternization, the neutral imidazole ring in

S-PVBnIm showed two absorption peaks at 1080 cm^{-1} (C—N—C and C—H in-plane bending) and 1520 cm^{-1} (C=C and C=N stretching). After quaternization, the cationic imidazolium rings in S-PVBn(alkyl)ImBr showed new absorption peaks at 1150 cm^{-1} (C—N—C in-plane bending) and 1560 cm^{-1} (C=C and C=N stretching), respectively.



Scheme 1 Synthesis of CCS PILs: (1) DMF, 0.4 g/mL, AIBN, 70 °C, 30 h; (2) ethanol/water (*V*/*V* = 1/1), 0.05 g/mL, styrene, DVB, V-50, 70 °C, 5 h; (3) methanol, 0.2 g/mL, *n*-alkyl bromide or bromoacetonitrile, 70 °C, 48 h; (4) water or DMF, $NaBF_4$ or $NaPF_6$ or LiTFSI, room temperature, 48 h

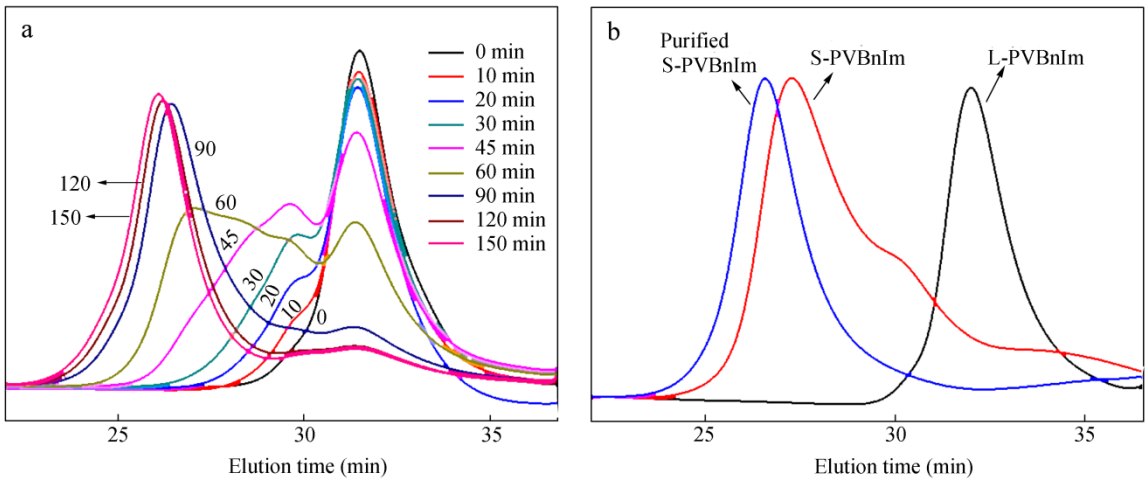


Fig. 1 (a) GPC traces as a function of polymerization time; (b) GPC traces of L-PVBnIm macro-CTA, as-synthesized S-PVBnIm and purified S-PVBnIm

CCS PILs were finally obtained *via* anion exchange of bromide in the corresponding cationic CCS polymers with three hydrophobic anions including BF_4^-, PF_6^-, and $TFSI^-$. The presence of different anions is expected to affect the thermal stability, glass transition temperature and amphiphilicity of CCS PILs. Upon the anion exchange, all the proton resonances of imidazolium rings shifted to the upfield (Fig. 3a), compared to those with bromide as the anion (Fig. 2a). For example, proton *f* was located at $\delta = 10.11$ in S-PVBnEtImBr, but it shifted to $\delta = 9.16$–9.27 in S-PVBnEtImBF_4, S-PVBnEtImPF_6, and S-PVBnEtImTFSI. The FTIR results (Fig. 3b) also confirmed structures of the anion-exchanged CCS PILs by showing the characteristic peaks of the corresponding anions (*i.e.* $TFSI^-$ 1340, 1200 cm^{-1}; PF_6^- 833 cm^{-1}; BF_4^- 1050 cm^{-1})[44–46].

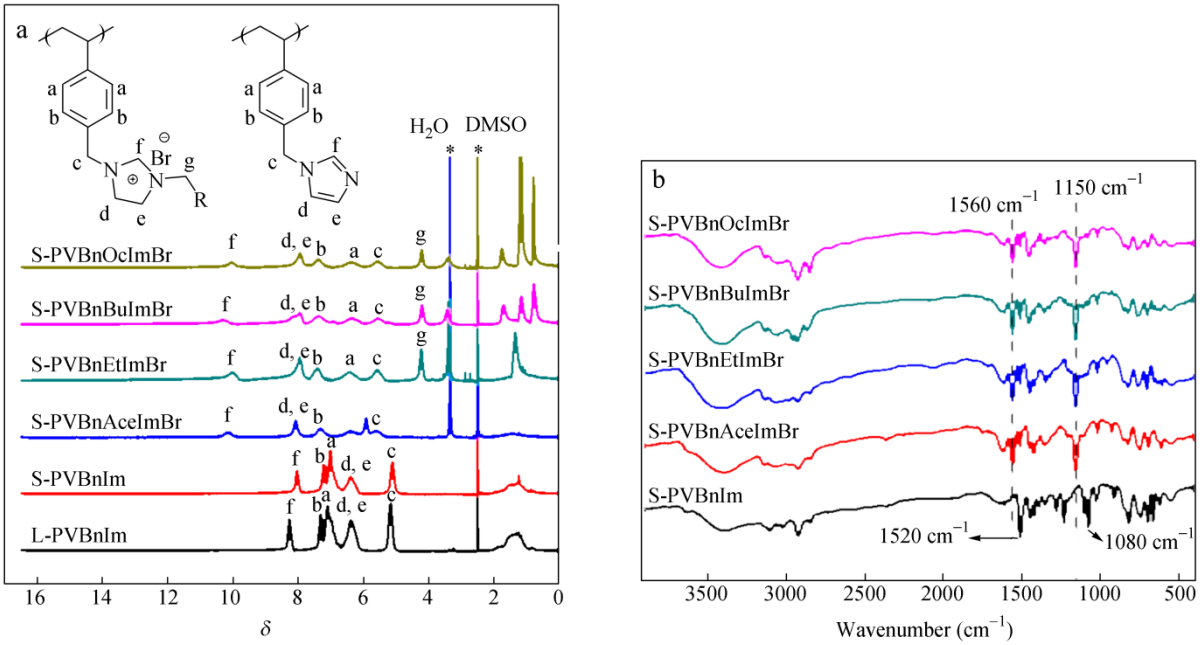


Fig. 2 (a) ^{1}H-NMR spectra of L-PVBnIm, S-PVBnIm and quaternized CCS polymers in DMSO-d_6; (b) FTIR spectra of S-PVBnIm and the quaternized CCS polymers

TGA profiles showed that the thermal stabilities of CCS PILs were very sensitive to different anions[47]. The CCS polymers bearing Br^-, S-PVBn(alkyl)ImBr (alkyl = Et, Bu, Oc), have the similar weight loss patterns (Fig. 4a). The first stage of weight loss (5%–10%) below 100 °C for S-PVBn(alkyl)ImBr was attributed to the loss of some residual water, due to the high hygroscopicity of these polyelectrolytes[48]. A sharp weight loss (35%–51%) appeared from 213 °C to 358 °C because of the nucleophilic substitution of alkylimidazole by Br^-[48, 49]. Finally, the third stage of weight loss (28%–30%) occurred starting from 409 °C, which was attributed to degradation of the polystyrene backbone. Figure 4(b) shows the different patterns of weight loss when Br^- was replaced by the less coordinating anions (*i.e.* BF_4^-, PF_6^-, $TFSI^-$). No weight loss corresponding to residual water was observed below 100 °C for the relatively high hydrophobicity of the CCS PILs. Moreover, the weight loss of CCS PILs with BF_4^- and $TFSI^-$ as anions did not take place until heating to 364 °C, suggesting the enhanced thermal stabilities of these CCS PILs[50, 51]. The occurrence of only one step of decomposition for S-PVBnEtBF_4 was somewhat different from the two steps of decomposition of the similar linear polymer[48]. However, S-PVBnEtImPF_6 displayed a two-step decomposition profile similar to the literature report on a linear polymer[48]. The onset of decomposition for S-PVBnEtImPF_6 occurred at 245 °C, ascribing to an anion-mediated decomposition mechanism and the second decomposition was due to the decomposition of polymer backbone[48].

T_g of the CCS PILs was highly dependent on the chain length of the alkyl groups and the type of anions. Because the CCS PILs were better plasticized by longer alkyl chains, T_g decreased from 161 °C for S-PVBnEtImBr bearing an ethyl group to 116 °C for S-PVBnOcImBr with an octyl group. For S-PVBnOcImBr,

T_g tremendously reduced to 8 °C after Br^- was replaced by $TFSI^-$ (Fig. 5a). To further investigate the effect of anions on T_g of CCS PILs, ethylimidazolium-based CCS PILs with different anions were also characterized by DSC (Fig. 5b). It was observed that T_g decreased in the order of $Br^- > PF_6^- > BF_4^- > TFSI^-$, in agreement with the literature data on the ionic liquids[52, 53].

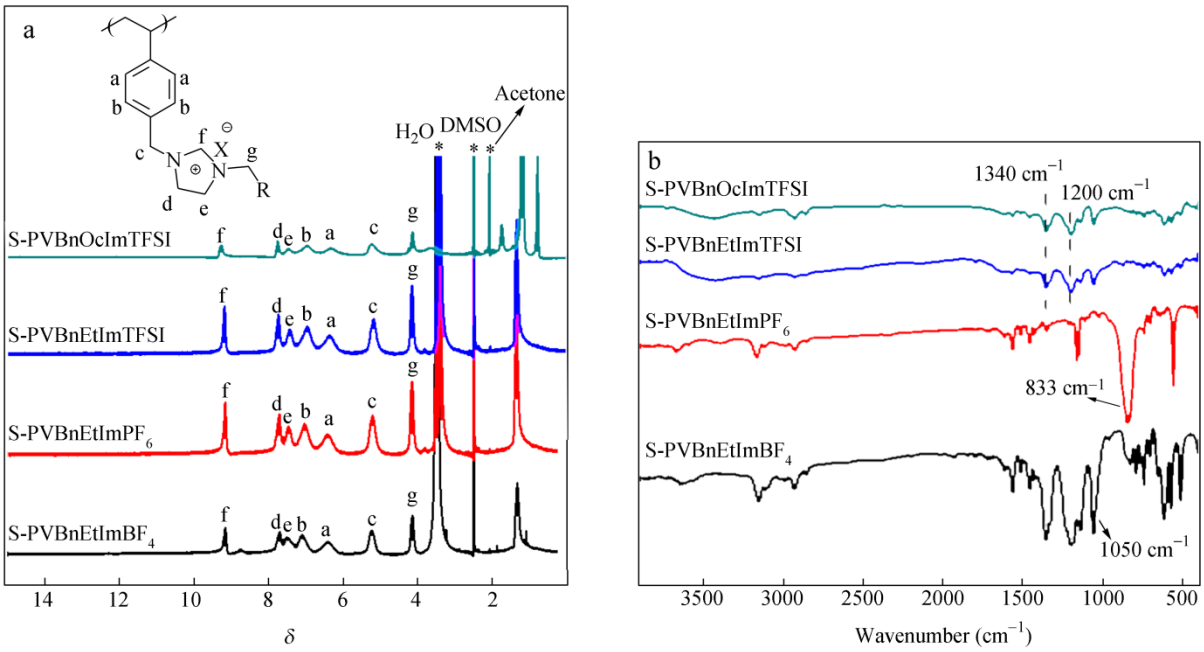


Fig. 3 (a) ^{1}H-NMR spectra of the PIL CCS polymers in DMSO-d_6; (b) FTIR spectra of the PIL CCS polymers

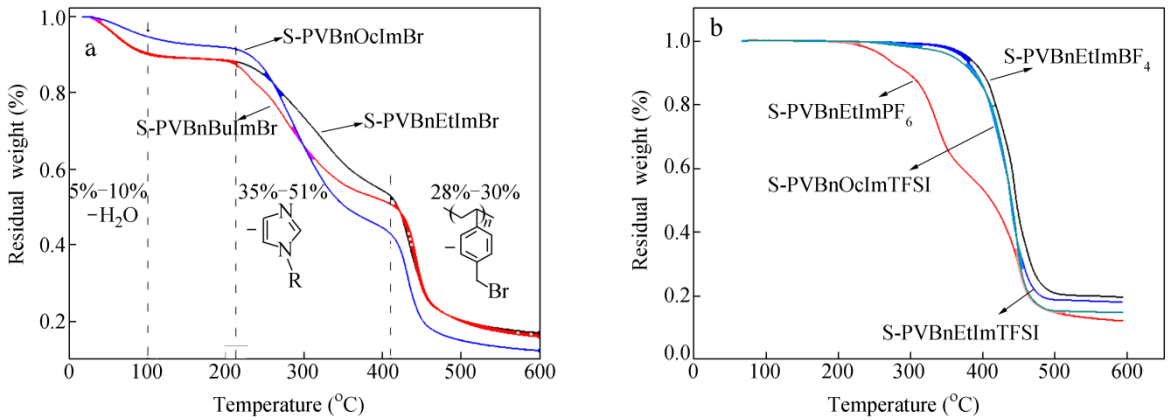


Fig. 4 TGA profiles of the CCS polymers

The imidazole units in S-PVBnIm can be protonated and thus can be dissolved in acidic aqueous solutions. Interestingly, S-PVBnIm in aqueous solutions with different pH values exhibited excellent emulsification properties for a range of oils with varying polarities (*e.g.* dodecane, undecanol, toluene, octanol and chloroform), leading to the formation of HIPEs. As shown by the inverted vials containing emulsions (Fig. 6A), stable and gelled HIPEs containing 80 vol% of dodecane and 20 vol% of S-PVBnIm aqueous solution (0.5 wt%) were formed at pH ⩽ 4.6. At pH above 4.6, S-PVBnIm became insoluble and thus could not be employed as an emulsifier in this case. CLSM revealed that the emulsions were of oil-in-water type comprising of droplets around 33 μm. When octanol (80 vol%) was used as the oil phase, stable HIPEs were formed as pH below 1.0

(Fig. 6B). The emulsions containing octanol were also of oil-in-water type with the droplets of ~13 μm as revealed by CLSM analysis. For toluene and chloroform with relatively higher polarity, the acidity of the solution necessary for HIPE formation was 2 mol/L HCl. In such a condition, it ensures a much higher degree of protonation (the imidazole units in the inner space of CCS polymers may be more difficult to be protonated) to reach a suitable wettability for the interface of octanol/water. HIPEs were stable and could be inverted under the acidic condition (Fig. S3). However, it should be emphasized that S-PVBnIm may not be suitable as the emulsifiers at high acidity, which is in direct contrast to the final PIL CCS polymers that are excellent emulsifiers on their own. At the pH 0.5, water-in-oil-in-water type of emulsions appeared and the size of the droplets reduced markedly from 50 μm to 20 μm. The emulsion evolution with increasing pH suggests that the degree of protonation of the imidazole units in S-PVBnIm primarily determines the solubility/location of S-PVBnIm in octanol, water, or the interface. Highly protonated S-PVBnIm predominantly dissolves in the aqueous solution and favors the formation of oil-in-water HIPEs, while at least a portion of less protonated S-PVBnIm may partition into the octanol phase, leading to the formation of multiple emulsions.

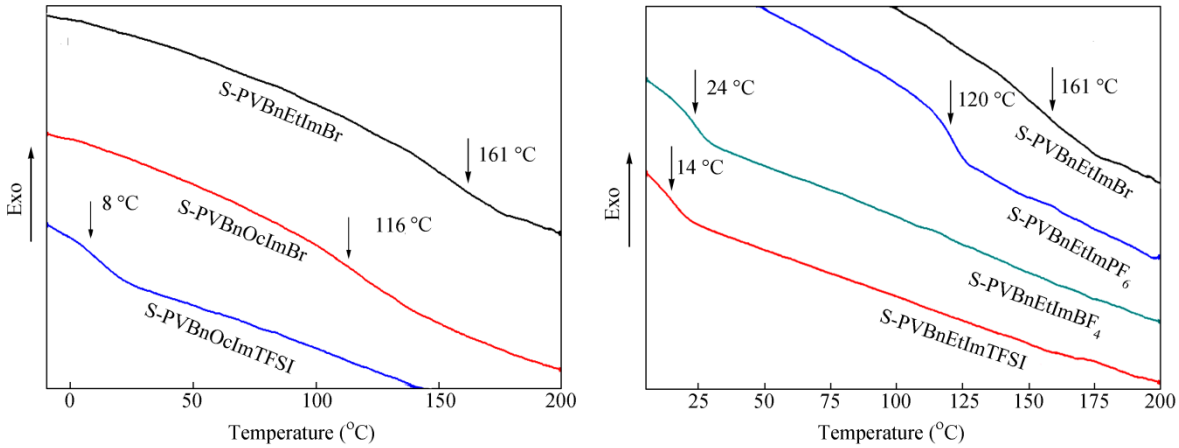


Fig. 5 DSC curves of the CCS polymers

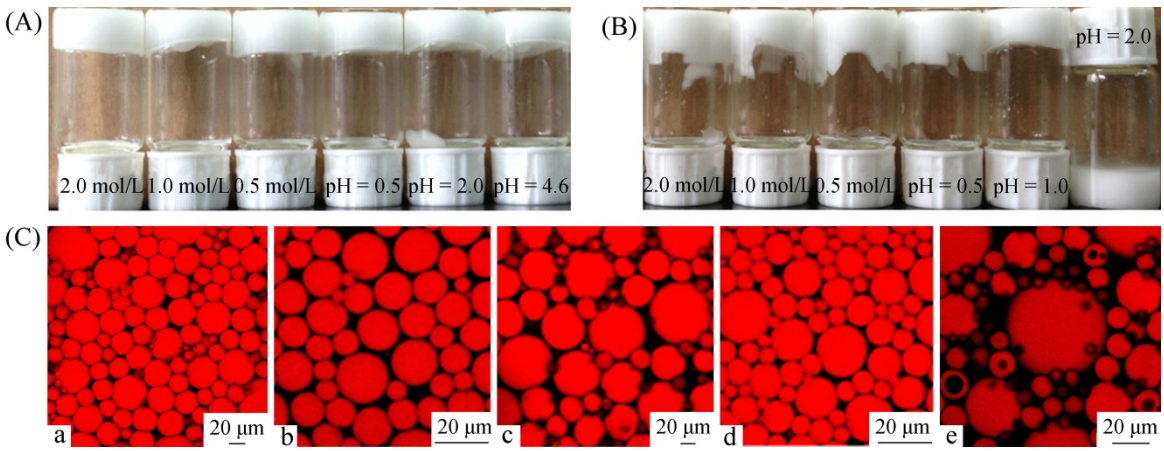


Fig. 6 Photographs of HIPEs stabilized by 0.5 wt% S-PVBnIm at different acidicity for dodecane (80 vol%) (A) and octanol (80 vol%) (B); (C) CLSM images of HIPEs (80 vol%, 0.5 wt% S-PVBnIm, pH = 0.5) with the oil being dodecane (a), undecanol (b), toluene (c), octanol (d) and chloroform (e)

After the quaternization of S-PVBnIm with bromoalkanes, the water-soluble imidazolium-containing CCS polymers, S-PVBnEtImBr and S-PVBnBuImBr, were also studied as the stabilizers in emulsions (Fig. 7).

S-PVBnIm, S-PVBnEtImBr and S-PVBnBuImBr could be used directly in water due to their excellent water solubility expect S-PVBnOcImBr with insolubility in water. S-PVBnEtImBr could emulsify dodecane, undecanol and toluene to form oil-in-water HIPEs with 80 vol% of oil, but could only emulsify octanol and chloroform to form water-in-oil-in-water multiple emulsions with 50 vol% of oil due to the relatively high polarity of octanol and chloroform. When S-PVBnBuImBr was used as the emulsifier, oil-in-water HIPEs containing 80 vol% of dodecane, undecanol, and toluene could be reliably formed, HIPEs with dodecane and undecanol were gelled emulsions as tested by invertedvial method while HIPE with toluene was a viscous fluidic emulsion. The emulsification of octanol using S-PVBnBuImBr only resulted in the formation of ordinary oil-in-water emulsions with 50 vol% of octanol, and further increase in the octanol volume fraction led to emulsion inversion, *i.e.*, the formation of water-in-oil emulsions. These results again suggest that S-PVBn(alkyl)ImBr with a shorter alkyl group and better water-solubility favors the formation of oil-in-water HIPEs, especially for the oils with relatively high polarity.

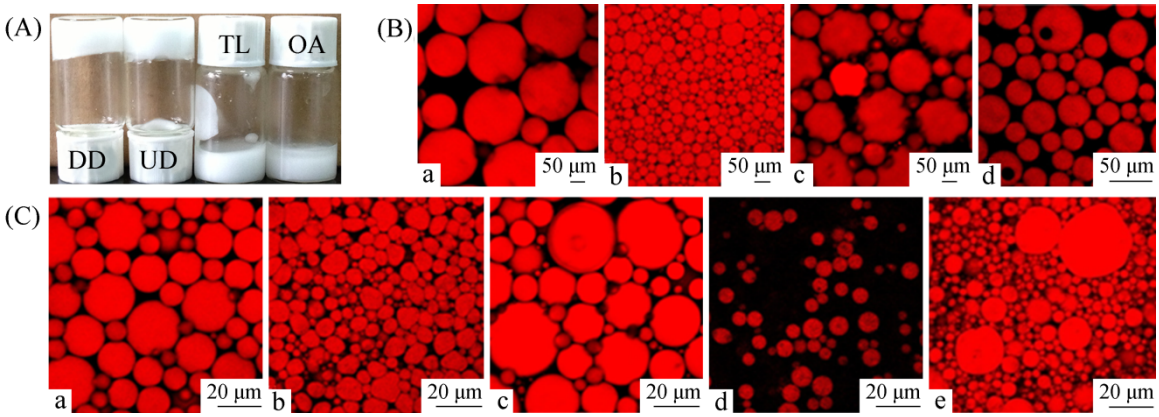


Fig. 7 (A) Photograph of HIPEs (80 vol% of dodecane (DD), undecanol (UD), toluene (TL) and octanol (OA)) stabilized by 0.5 wt% of S-PVBnBuImBr; (B) CLSM images of emulsions stabilized by 0.5 wt% of S-PVBnBuImBr; (C) CLSM images of emulsions stabilized by S-PVBnEtImBr with the oil being dodecane (80 vol%) (a), undecanol (80 vol%) (b), toluene (80 vol%) (c), octanol (50 vol%) (d) and chloroform (50 vol%) (e), respectively

For CCS PILs, only S-PVBnEtImBF$_4$ was readily soluble in water at the temperatures higher than 32 °C due to the presence of an upper critical solution temperature (UCST) for such polyelectrolytes bearing BF_4^- as the anion[54, 55]. The 0.5 wt% aqueous solution of S-PVBnEtImBF$_4$ was transparent at 40 °C, and it became translucent at 30 °C, and turned completely turbid at 25 °C (Fig. 8a). These solubility changes as a function of

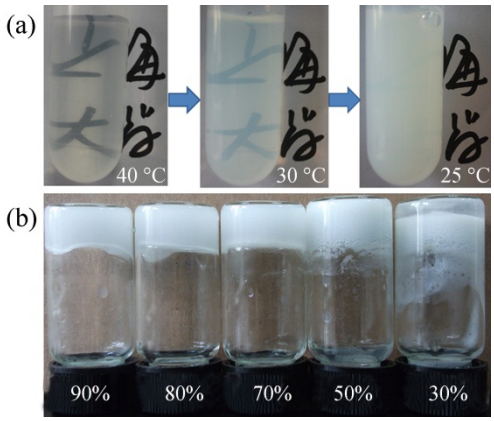


Fig. 8 (a) Appearance of a 0.5 wt% S-PVBnEtImBF$_4$ solution at different temperatures; (b) Photograph of the emulsions at room temperature containing different fractions of dodecane and 0.5 wt% S-PVBnEtImBF$_4$ solution

temperature are consistent with UCST thermal transitions. Because S-PVBnEtImBF$_4$ was completely dissolved in water at 40 °C with a D_h of 30 nm (a reasonable size for such CCS polymers), the emulsification of dodecane was first conducted at 40 °C and then naturally cooled to room temperature. Interestingly, gelled emulsions with a broad range of oil fractions (30 vol%–90 vol%) were effectively formed (Fig. 8b). While these gelled emulsions fully deserve further detailed investigations, we reasoned that the gelation of emulsions is presumably due to the UCST properties of S-PVBnEtImBF$_4$. Upon cooling below its UCST, intra-/inter- star association occurs, leading to the network-like structures between the oil droplets. The interesting emulsification and gelation properties for emulsions suggest that CCS PIL may serve as the effective and responsive stabilizers for emulsions.

CONCLUSIONS

Well-defined S-PVBnIm, S-PVBn(alkyl)ImBr and S-PVBn(alkyl)ImX (X = BF_4^-, PF_6^-, $TFSI^-$) CCS polymers were synthesized, producing a rich library of the pH-responsive and cationic CCS polymers whose thermal and emulsification properties could be modulated by a large degree of structural variations. S-PVBnIm are effective emulsifiers for the formation of HIPEs under the acidic conditions, while S-PVBn(alkyl)ImBr can be used under neutral conditions for the formation of HIPEs and their emulsification properties are dependent on the length of alkyl groups (Et versus Bu). Finally, S-PVBnEtImBF$_4$, the only water-soluble CCS PIL above its UCST, shows interesting gelation of emulsions containing a broad range of dodecane fractions (from low to high internal phase emulsions) due to the physical association of CCS polymers at room temperature. This library of the CCS polymers greatly expands the polymer materials as the effective emulsifiers and is also expected to find applications in the heterogeneous catalysis[56].

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REFERENCES

1 Cameron, N.R. and Sherrington, D.C., Adv. Polym. Sci., 1996, 126: 163
2 Chen, Y., Ballard, N., Gayet, F. and Bon, S.A.F., Chem. Commun., 2012, 48: 1117
3 Zhang, H. and Cooper, A.I., Soft Matter, 2005, 1(2): 107
4 Williams, J.M., Langmuir, 1991, 7(7): 1370
5 Barbetta, A. and Cameron, N.R., Macromolecules, 2004, 37(9): 3202
6 Cameron, N.R. and Barbettaa, A., J. Mater. Chem., 2000, 10(11): 2466
7 Fujii, S., Cai, Y., Weaver, J.V.M. and Armes, S.P., J. Am. Chem. Soc., 2005, 127(20): 7304
8 Dupin, D., Armes, S.P., Connan, C., Reeve, P. and Baxter, S.M., Langmuir, 2007, 23(13): 6903
9 Morse, A.J., Dupin, D., Thompson, K.L., Armes, S.P., Ouzineb, K., Mills, P. and Swart, R., Langmuir, 2012, 28(32): 11733
10 Akartuna, I., Studart, A.R., Tervoort, E. and Gauckler, L.J., Adv. Mater., 2008, 20(24): 4714
11 Menner, A., Ikem, V., Salgueiro, M., Shafferb, M.S.P. and Bismarck, A., Chem. Commun., 2007, 41: 4274
12 Ikem, V.O., Menner, A. and Bismarck, A., Angew. Chem. Int. Ed., 2008, 47(43): 8277
13 Li, Z., Ming, T., Wang, J. and Ngai, T., Angew. Chem., 2009, 48(45): 8490
14 Sun, G., Li, Z. and Ngai, T., Angew. Chem., 2010, 49(12): 2163
15 Gao, H., Macromol. Rapid Commun., 2012, 33(9): 722
16 Blencowe, A., Tan, J., Goh, T. and Qiao, G.G., Polymer, 2009, 50(1): 5
17 Zhang, M., Liu, H., Shao, W., Ye, C. and Zhao, Y., Macromolecules, 2012, 45(23): 9312
18 Ito, S., Goseki, R., Senda, S. and Hirao, A., Macromolecules, 2012, 45(12): 4997
19 Fukae, K., Terashima, T. and Sawamoto, M., Macromolecules, 2012, 45(8): 3377

20 Zhang, H., He, J., Zhang, C., Ju, Z., Li, J. and Yang, Y., Macromolecules, 2012, 45(2): 828
21 Dong, Z., Liu, X., Liu, H. and Li, Y., Macromolecules, 2010, 43(19): 7985
22 Jiang, X., Chen, Y. and Xi, F., Macromolecules, 2010, 43(17): 7056
23 Hu, M., Shen, Y., Zhang, L. and Qiu, L., Biomacromolecules, 2016, 17(3): 1026
24 Li, Y., Yu, H., Qian, Y., Hu, J. and Liu, S., Adv. Mater., 2014, 26(39): 6734
25 Liu, T., Zhang, Y. and Liu, S., Chinese J. Polym. Sci., 2013, 31(6): 924
26 Cao, W., Zhou, J., Wang, Y. and Zhu, L., Biomacromolecules, 2010, 11(12): 3680
27 Kim, S.J., Ramsey, D.M., Boyer, C., Davis, T.P. and McAlpine, S.R., ACS Med. Chem. Lett., 2013, 4(10): 915
28 Ren, J.M., Fu, Q., Blencowe, A. and Qiao, G.G., ACS Macro Lett., 2012, 1(6): 681
29 Ferreira, J., Syrett, J., Whittaker, M., Haddleton, D., Davis, T.P. and Boyer, C., Polym. Chem., 2011, 2(8): 1671
30 McKenzie, T.G., Wong, E.H.H., Fu, Q., Sulistio, A., Dunstan, D.E. and Qiao, G.G., ACS Macro Lett., 2015, 4(9): 1012
31 Qiu, Q., Liu, G. and An, Z., Chem. Commun., 2011, 47(47): 12685
32 Zhang, C., Miao, M., Cao, X. and An, Z., Polym. Chem., 2012, 3(9): 2656
33 Shi, X., Zhou, W., Qiu, Q. and An, Z., Chem. Commun., 2012, 48(59): 7389
34 Shi, X., Miao, M. and An, Z., Polym. Chem., 2013, 4(6): 1950
35 Cao, X., Zhang, C., Wu, S. and An, Z., Polym. Chem., 2014, 5(14): 4277
36 Hou, L., Chen, Q., An, Z. and Wu, P., Soft Matter, 2016, 12(8): 2473
37 Chen, Q., Cao, X., Liu, H., Zhou, W., Qin, L. and An, Z., Polym. Chem., 2013, 4(15): 4092
38 Chen, Q., Cao, X., Xu, Y. and An, Z., Macromol. Rapid Commun., 2013, 34(19): 1507
39 Chen, Q., Xu, Y., Cao, X., Qin, L. and An, Z., Polym. Chem., 2014, 5(1): 175
40 Chen, Q., Deng, X. and An, Z., Macromol. Rapid Commun., 2014, 35(12): 1148
41 Lu, J.M., Yan, F. and Texter, J., Prog. Polym. Sci., 2009, 34(5): 431
42 Mecerreyes, D., Prog. Polym. Sci., 2011, 36(12): 1629
43 Green, M.D., Choi, J.H., Winey, K.I. and Long, T.E., Macromolecules, 2012, 45(11): 4749
44 Seki, T., Grunwaldt, J.D. and Baiker, A., J. Phys. Chem. B, 2009, 113(1): 114
45 Holomb, R., Martinelli, A., Albinsson, I., Lassègues, J.C., Johansson, P. and Jacobsson, P., J. Raman Spectrosc., 2008, 39(7): 793
46 Ye, Y. and Elabd, Y.A., Polymer, 2011, 52(5): 1309
47 Jovanovski, V., Marcilla, R. and Mecerreyes, D., Macromol. Rapid Commun., 2010, 31(18): 1646
48 Weber, R.L., Ye, Y., Banik, S.M., Elabd, Y.A., Hickner, M.A. and Mahanthappa, M.K., J. Polym. Sci., Part B: Polym. Phys., 2011, 49(18): 1287
49 Chowdhury, A.T. and Thynell, S.T., Thermochim. Acta, 2006, 443(2): 159
50 Kroon, M.C., Buijs, W., Peters, C.J. and Witkamp, G.J., Thermochim. Acta, 2007, 465(1-2): 40
51 Ohtani, H.I.S. and Kumai, M., Anal. Sci., 2008, 24(10): 1335
52 McEwen, A.B., Ngo, H.L., LeCompte, K. and Goldman, J.L., J. Electrochem. Soc., 1999, 146(5): 1687
53 Fredlake, C.P., Crosthwaite, J.M., Hert, D.G., Aki, S.N.V.K. and Brennecke, J.F., J. Chem. Eng. Data, 2004, 49(4): 954
54 Liu, C., Wang, S., Zhou, H., Gao, C. and Zhang, W., J. Polym. Sci., Part A: Polym. Chem., 2016, 54(7): 945
55 Cao, X. and An, Z., Macromol. Rapid Commun., 2015, 36(23): 2107
56 Ren, J.M., Mckenzie, T.G., Fu, Q., Wong, E.H.H., Xu, J., An, Z., Shanmugam, S., Davis, T.P., Boyer, C. and Qiao, G.G, Chem. Rev., 2016, 116(12): 6743