



Supporting Information

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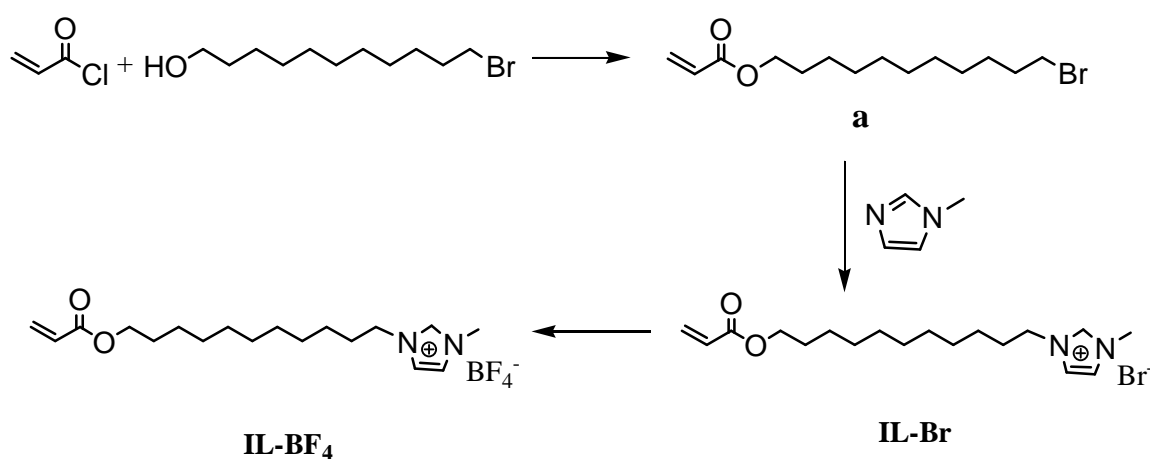
Supporting Information

Solvent-reversible poration in ionic liquid copolymers

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Chemicals. Acryloyl chloride (96%), 1-bromododecane (98%), 11-bromoundecanol (98%), triethylamine, 1-methylimidazole (99%), methyl methacrylate (MMA, 98%), 2,6-di-tert-butyl-4-methylphenol (98%), sodium tetrafluoroborate (98%), 2,2-azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), acetonitrile, diethyl ether, ethyl acetate were purchased from Aldrich Chemical Co. MMA was purified by passing through an inhibitor column (Aldrich) to remove the inhibitor. Distilled deionized water was used for all experiments.



Scheme. Synthesis of Ionic Liquid surfactants

Synthesis of 11-bromoundecylacrylate (a). 11-Bromoundecanol (10.00 g, 40 mmol) was dissolved in 40 ml of dry tetrahydrofuran (THF) in a two-necked round bottom flask. The flask was cooled in an ice-bath and triethylamine (5.13 mL, 40 mmol) in THF (40 mL) was added to the stirring solution. Acryloyl chloride (3.65 g, 40 mmol) dissolved in 40 ml of THF was added dropwise to the stirring solution over a period of 15 min under N₂ atmosphere. The mixture was further stirred for 2 days at room temperature and was filtered. The filtrate was washed with 2% sodium bicarbonate solution to remove any unreacted acid chloride and dried over anhydrous MgSO₄. The dried solution was filtered and the filtrate was passed through a short column of neutral alumina, using CH₂Cl₂ as the light yellow liquid (yield 10.58 g, 87%). ¹H NMR (400 MHz, CDCl₃): 6.37–6.36 (1H, m, CH₂=CH), 6.15–6.12 (1H, m, CH₂=CH), 5.81–5.79 (1H, m, CH₂=CH), 4.16–4.12 (2H, t, –OCOCH₂), 1.85–1.82 (2H, m, BrCH₂CH₂–), 1.66–1.64 (2H, m, –OCOCH₂CH₂), 1.42–1.27 (14H, m, –CH₂CH₂(CH₂)₇CH₂CH₂–).

Synthesis of 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (IL-Br). Under N₂ atmosphere, a mixture of 11-bromoundecylacrylate (6.08g, 20 mmol) and 1-methylimidazole (1.64g, 20 mmol) and a small amount of 2,6-di-tert-butyl-4-methylphenol (inhibitor) was stirred at 40 °C for 48 h, and yielded a viscous liquid. The viscous liquid was purified by the precipitation method with diethyl ether to obtain yellow viscous liquid 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide. The viscous liquid was dried under vacuum at room temperature as the white waxy solid (5.73g, 74 %). ¹H NMR (400 MHz, CDCl₃): 10.66 (1H, m, N–CH–N), 7.34–7.25 (2H, s, N–CH=CH–N), 6.36–6.35 (1H, m, CH₂=CH), 6.14–6.11 (1H, m, CH₂=CH), 5.81–5.79 (1H, m, CH₂=CH), 4.30–4.29 (2H, t, N–CH₂(CH₂)₁₀O–), 4.11 (3H, s, N–CH₃), 1.90–1.82 (2H, t, N–CH₂(CH₂)₁₀O–), 1.66–1.62 (2H, m, –OCOCH₂CH₂), 1.30–1.24 (14H, m, –

$\text{CH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{CH}_2-$). Elemental analysis: Calculated: $\text{C}_{18}\text{H}_{32}\text{BrN}_2\text{O}_2$, C: 55.67 %; H, 8.31 %; N, 7.21 %. Found: C: 55.22 %, H: 7.79 %, N: 7.35 %. mp: 37.2 °C.

Synthesis of 1-(2-acryloyloxyundecyl)-3-methylimidazolium tetrafluoroborate (IL- BF_4). IL-Br (7.74 g, 20 mmol) was dissolved in 50 mL of dry acetonitrile and stirred with NaBF_4 (2.75 g, 25 mol) at room temperature. After the mixture was stirred for 48 h under N_2 atmosphere, the sodium bromide precipitate was removed by filtration and the filtrate was concentrated. The concentrated filtrate was diluted with methylene chloride (300 mL) and filtered through a short column of silica gel. The Br^- concentration was checked qualitatively by the formation of AgCl after adding of silver nitrate (AgNO_3) into the decanted water. The resulting ionic liquid 1-(2-acryloyloxyundecyl)-3-methylimidazolium tetrafluoroborate was dried under vacuum for 24 h as the white waxy solid. (6.24g, 79% yield). ^1H NMR (400 MHz, CDCl_3): 8.78 (1H, m, N-CH-N), 7.34–7.25 (2H, s, N-CH=CH-N), 6.36–6.35 (1H, m, $\text{CH}_2=\text{CH}$), 6.14–6.11 (1H, m, $\text{CH}_2=\text{CH}$), 5.81–5.79 (1H, m, $\text{CH}_2=\text{CH}$), 4.15–4.10 (2H, t, N- $\text{CH}_2(\text{CH}_2)_{10}\text{O}-$), 3.99 (3H, s, N- CH_3), 1.85–1.84 (2H, t, N- $\text{CH}_2(\text{CH}_2)_{10}\text{O}-$), 1.66–1.62 (2H, m, $-\text{OCOCH}_2\text{CH}_2-$), 1.30–1.24 (14H, m, $-\text{CH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{CH}_2-$). Elemental Analysis: Calculated: $\text{C}_{18}\text{H}_{32}\text{BF}_4\text{N}_2\text{O}_2$, C: 54.70 %; H, 8.16 %; N, 7.09 %. Found: C: 54.22 %, H: 7.85 %, N: 7.35 %. mp: 31.8 °C.

Phase Diagram. The single-phase domains of IL- BF_4 /water/MMA microemulsions were determined visually on the basis of transparency and absence of phase separation in PTFE-lined, screw-capped culture tubes. These titrations were conducted at 24°C.

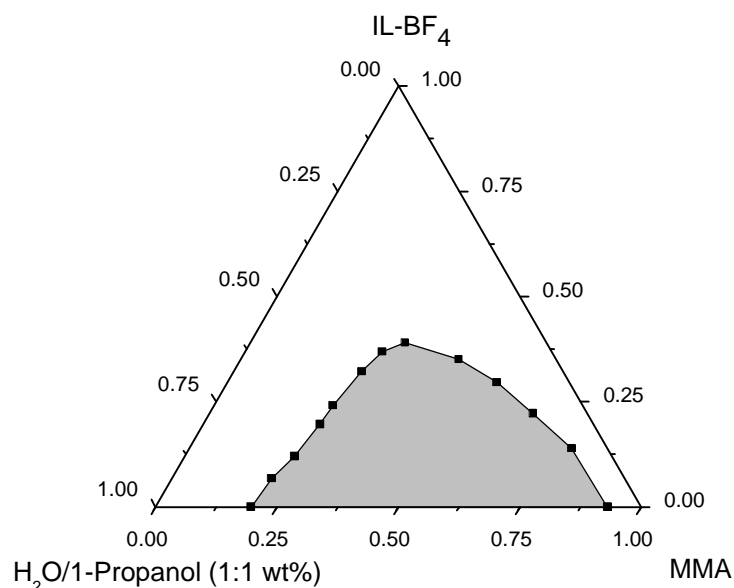


Figure S1. Phase diagram (weight fraction) of **IL-BF₄**/water/MMA systems at 24°C, shadowed area shows two-phase region.

Polymerization. Polymerization of microemulsions was carried out in capped NMR tubes (or in 20 ml screw-capped culture tubes) at 60°C in an oil bath for 6 hr. AIBN was used as initiator at 0.5% (w/w) relative to MMA and IL-BF₄. No special attempt was made to remove dissolved oxygen. Conversion of final product was checked by analyzing the gels produced with 2% and 10% EGDMA. Small sections of gel slabs were cyclically soaked in the aqueous propanol solution and drained (three cycles) to try to remove unreacted IL-BF₄. The slab was then weighed and placed in a vacuum oven at 105°C overnight to remove solvent and volatile monomer. The samples were then weighed again and the percent solids determined: 2% EGDMA – 32.2% (calc. 30.8%); 10% EGDMA – 36.7% (calc. 32.2). The apparently > 100% conversion suggests solvent loss from the gel slabs after draining and before weighing.

Surface Tension. Surface tension measurements were carried out using the pendant drop method in water on a Sigma 703 surface tensiometer at 24°C. The critical micelle concentration

(CMC) of **IL-BF₄** in water, determined by surface tension (pendant drop) measurements, is 0.9 mM at 24°C.

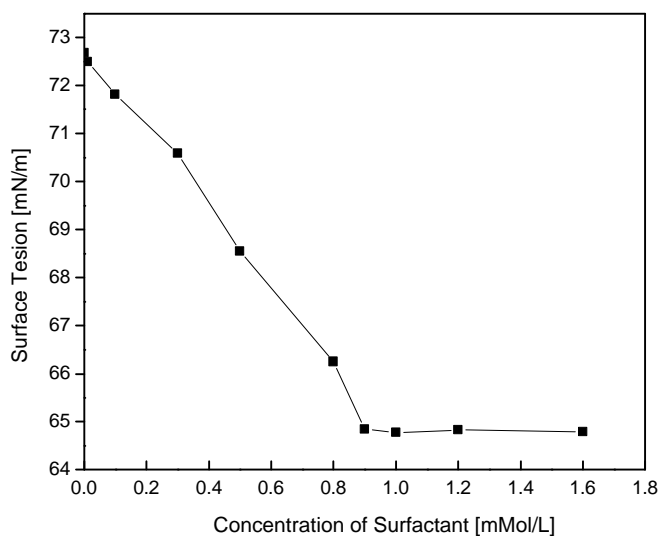


Figure S2. Surface tension versus concentration of **IL-BF₄** aqueous solutions at 24 °C.

Proton NMR. ¹H NMR spectra were recorded on a JEOL 400 MHz spectrometer. The samples were dissolved in CDCl₃.

SEM. Scanning electron microscopy (SEM) images were recorded on a Hitachi S3400 SEM and a Philips XL30 FEG SEM. All of the samples were freeze-fractured in liquid nitrogen to expose the fresh fracture surfaces.

DSC. Melting points were measured on a TA Instruments SDT 2960 Simultaneous Differential Scanning Calorimetry (DSC), with the heating scans of 10°C/min.

TGA. Thermal analysis of polymers was evaluated using a TA Instruments TGA Q500 thermogravimetric analyzer.

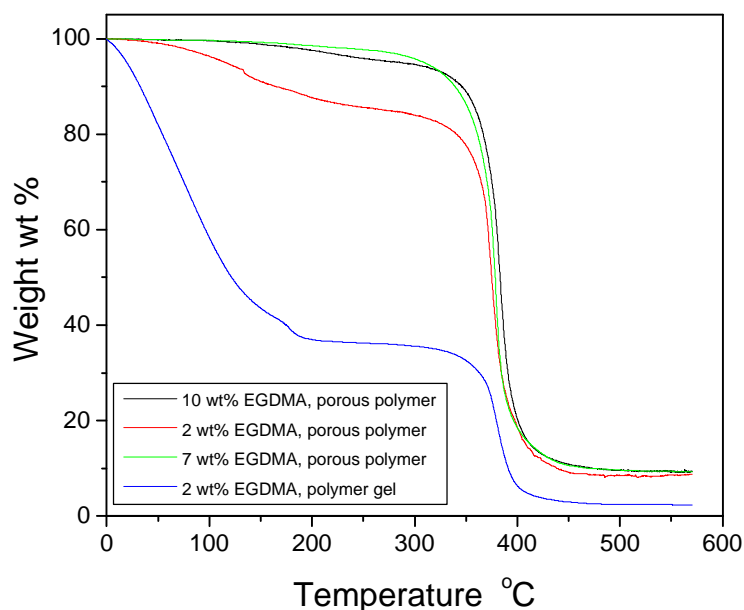


Figure S3. TGA thermal analysis of copoly(IL-BF₄/MMA) samples with different crosslinker (EGDMA) contents.

DMA. The DMA measurements of porous polymer rods (~3 mm diameter) were conducted with a TA Instruments (New Castle, Delaware, USA) DMA Q 800. Three-point bending tests were performed using a double cantilever clamp with 50 mN static force and 50 mN dynamic force applied at a frequency of 1.0 Hz. The samples were heated from -20°C to 100°C at a heating rate of 5.0°C/min. The sample chamber was purged with nitrogen at 20 mL/min throughout the test.

The storage modulus of the porous polymer ranges from about 54.5 MPa (2 wt % EGDMA) to 136.9 MPa (7 wt % EGDMA) and 236.6 MPa (10 wt% EGDMA) at 25 °C. Thermal analyses of the porous materials show that all the polymers have high decomposition

temperatures ranging from 405 °C to 415 °C, indicating excellent thermal properties and likely ignition resistance.

Swelling Ratio. To measure the equilibrium swelling ratio (ESR) of the porous polymers, vacuum dried samples were immersed in water/DMSO solution (1:4 v/v) to equilibrate at room temperature. The excess surface solvent was removed by touching the sample surface with a filter paper. The ESR value was calculated using the following equation:^[r1]

$$ESR = (W_s - W_d) / W_d$$

W_d is the dried sample weight, W_s is the weight of swollen sample.

For the purposes of drug delivery, the equilibrium swelling ratio (ESR) of the porous polymers has been characterized at room temperature. Porous polymer prepared with 1 wt% EGDMA shows an ESR value of 4.2, and decreases to 3.5 and 2.9 with the crosslinker content increased to 7 wt% and 10 wt%, respectively. These swelling results demonstrate that these materials can be effectively used for chemical and drug delivery.

Reference

[r1] S. Wang, P. Y. Chow, D. C. Tan, W. D. Zhang and Y. Y. Yang, *Adv. Mater.*, **2004**, *16*, 1790.