

Electronic supplementary information for:

High-Internal-Ionic Liquid-Phase Emulsions

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1. Experimental

Materials The IL [omim]PF₆ was synthesized following the procedures reported literature,¹ and its purity was confirmed by ¹H NMR. [bmim]PF₆ and [hmim]PF₆ were purchased from Centre of Green Chemistry and Catalysis, LICP, CAS (purity >99%). The Pluronic surfactants were purchased from BASF. Acrylamide and the crosslinker N,N'-methylenebisacrylamide at laboratory grade were obtained from Alfa Aesar, and potassium persulfate (A. R. grade) was supplied by Sinopharm Chemical Reagent Co., Ltd. The fluorescent dye Rhodamine B was provided by Wako Pure Chemical Industries, Ltd. as standard solution. Doubly distilled water was used throughout experiment.

Preparation of emulsions and stability determination The Pluronic surfactant was dissolved into water and IL [omim]PF₆ separately by a fixed concentration of 3 wt%, forming the aqueous and oleaginous solutions. The two solutions with the desired volume were placed in capped glass vessels with magnetic stirrer inside, and the mixture was vigorously stirred (1800 rpm) for 5 minutes. Then the emulsions were stored at a constant temperature (20.0 C) and the phase behaviour at different time was observed.

Confocal laser scanning microscopy The images of the emulsion were measured on an OLYMPUS FV1000-IX81 confocal laser scanning microscopy with magnification 1000 times. A 5.0 μL newly formed emulsion was trickled through microsyringe on a 0.7 mm thick coverslip and covered with another, and was monitored and captured by a digital CCD. For fluorescence microscope, Rhodamine B solution was injected into the emulsion (9 mM), and the emulsion was sufficiently stirred. Rhodamine B dye was excited by laser with wavelength 559 nm, and its emission was captured on the microscopy.

FTIR spectra The samples were prepared by two zinc sulfide (ZnS) windows (2.25 cm in diameter and 0.60 cm in thick), and the FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer. Each sample was recorded with 32 scans at an effective resolution of 2 cm^{-1} .

Polymerization The polymerization was performed in 20 mL glass vessels with screw cap and magnetic stirrer inside. For the polymerization of acrylamide, 0.400 g of the monomer acrylamide, 0.008 g of the crosslinker N,N'-methylenebisacrylamide and 0.008 g of the initiator potassium peroxydisulfate were dissolved in 1.0 mL of water and the mixture was stirred to form a homogeneous solution. The aqueous solution was mixed with 9.0 mL of [omim]PF₆ and 0.388 g of Pluronic surfactant by agitation. The emulsion was stirred at 70 °C for 0.5 h to initiate the polymerization, and then cooled down to room temperature and the stir was stopped. After reaction for 24 hrs, the product was washed by acetone for 10 times and dried at 120 °C for 2 hrs.

For the polymerization of styrene, the Pluronic/IL/water HIPE with IL volume fraction 0.90 was first prepared. A 3 mL amount of styrene/divinylbenzene (1:0.09 v/v) mixture was added into 10 mL of the HIPEs under stirring. After stirred for 30 min, the initiator potassium peroxydisulfate was added into the vessel ($[\text{K}_2\text{S}_2\text{O}_8] = 1.0\text{ mg/mL}$). The vessel was kept at 70 °C for 24 hrs under gentle stirring. After the sample was cooled down to room temperature, the product was washed by acetone for 10 times to remove the IL and surfactant, and dried at 120 °C for 2 hrs.

The morphologies of the products obtained above were characterized by scanning electron microscope (HITACHI S-480).

2. Results

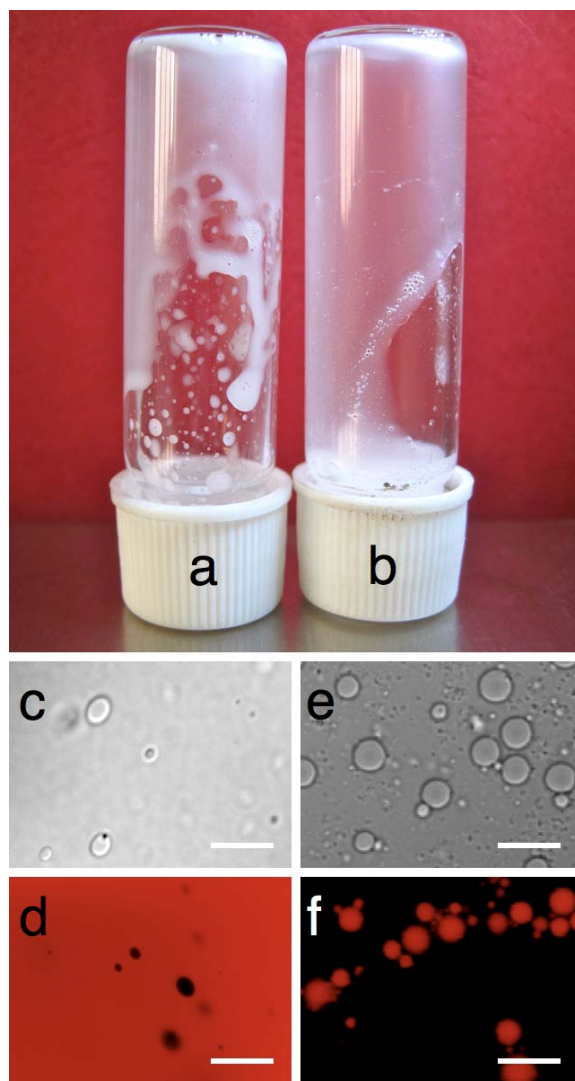


Fig. S1 Photographs and CLSM images of P105 normal emulsions with IL volume fractions of 0.96 (a, c, d) and 0.60 (b, e, f). Bar represents 10 μm in all CLSM images.

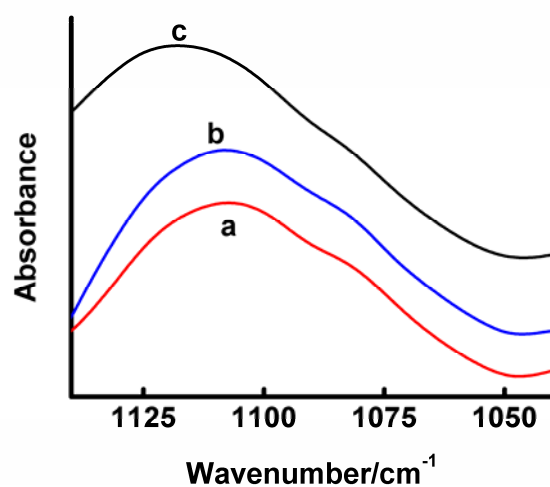


Fig. S2 C-O-C stretching vibration band on the FTIR spectra of the P105/[omim]PF₆/water emulsions with different IL volume fractions of 0.9 (a), 0.8 (b), and 0.7 (c).

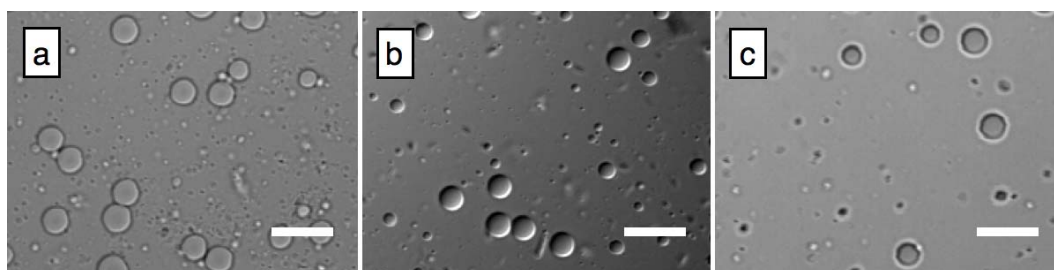


Fig. S3 CLSM images of P105/[omim]PF₆/water emulsions with IL volume fractions of 0.30 (a), 0.20 (b) and 0.10 (c). Bar represents 10 μm in all CLSM images.

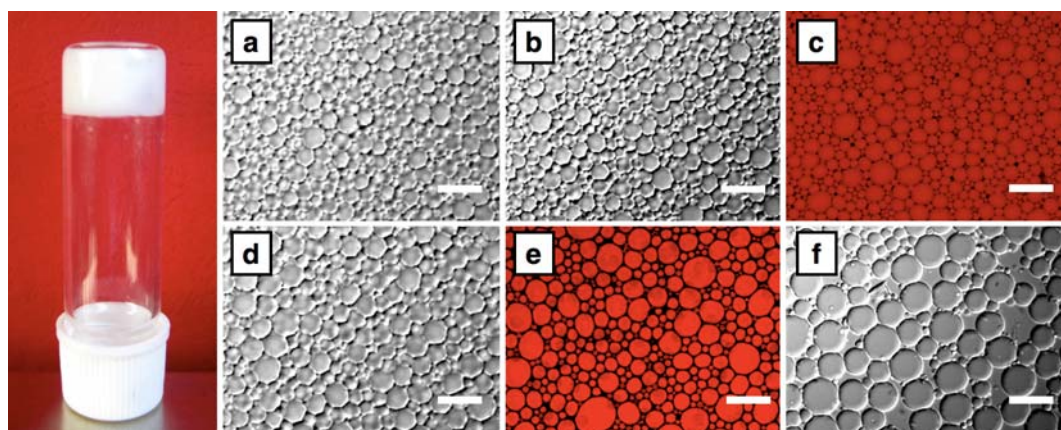


Fig. S4 Photograph and CLSM images of the HIPES prepared with P104 at IL volume fraction of 0.95 (a), 0.90 (b, c), 0.80 (d, e) and 0.70 (f). Photograph was taken on sample b, and images c and e were marked with Rhodamine B. Bar equals to 10 μm in all CLSM images.

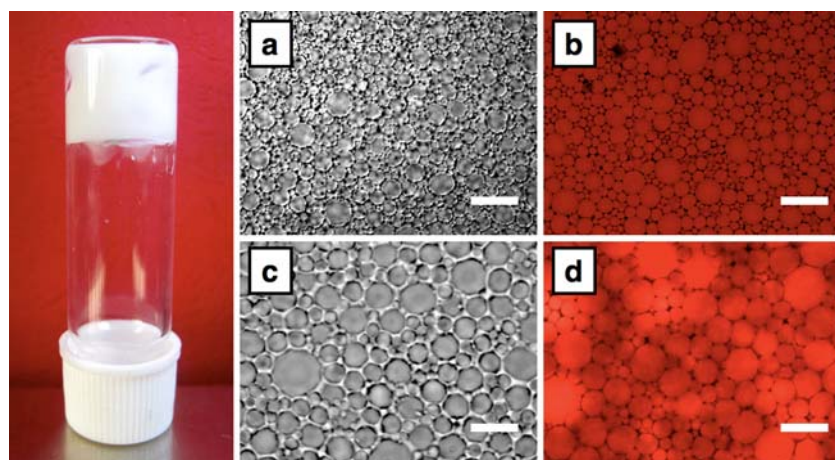


Fig. S5 Photograph and CLSM images of the HIPES prepared with P103 at IL volume fraction of 0.90 (a, b) and 0.80 (c, d). Photograph was taken on sample a, and images b and d were marked with Rhodamine B. Bar equals to 10 μm in all CLSM images.

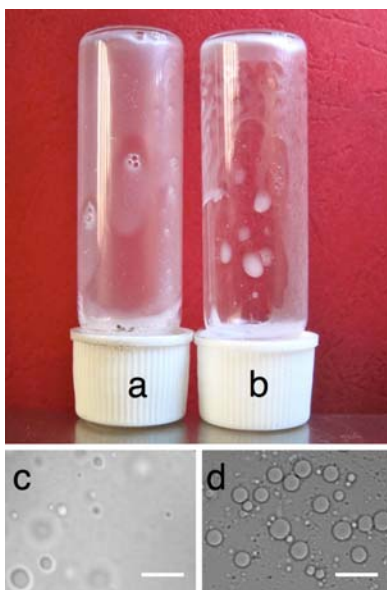


Fig. S6 Photographs and CLSM images of P104 normal emulsions with IL volume fractions of 0.96 (a, c) and 0.60 (b, d). Bar represents 10 μm in all CLSM images.

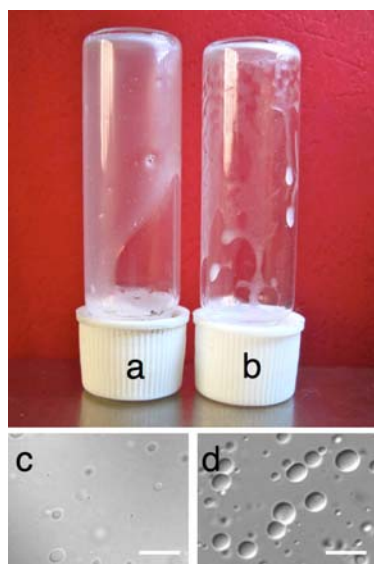


Fig. S7 Photographs and CLSM images of P103 normal emulsions with IL volume fractions of 0.95 (a, c) and 0.70 (b, d). Bar represents 10 μm in all CLSM images.

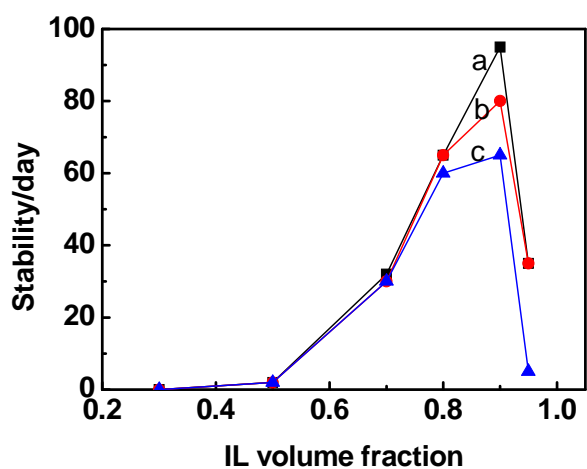


Fig. S8 The stability periods of Pluronic/[omim]PF₆/water emulsions with different IL volume fractions prepared by P105 (a), P104 (b) and P103 (c).

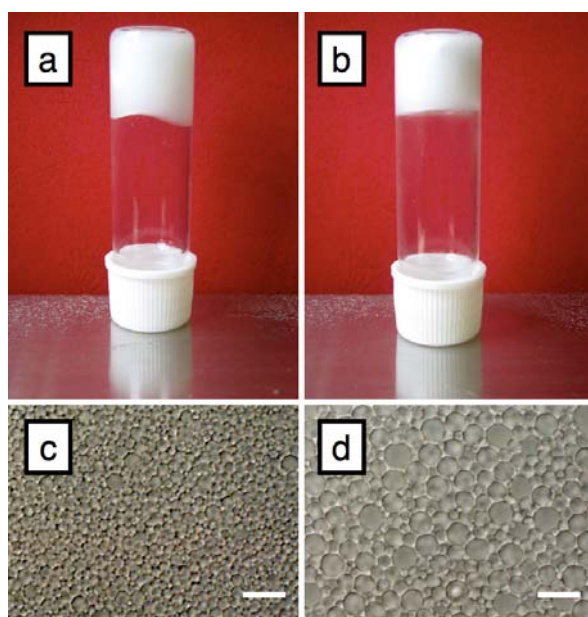


Fig. S9 Photographs and CLSM images of P105/[bmim]PF₆/water (a and c) and P105/[hmim]PF₆/water (b and d) HIPEs at IL volume fraction of 0.90. Bar represents 10 μ m in CLSM images. The droplet size decreases with the decreasing alky chain length of the IL.

Reference

1. A. B. Pereiro, J. L. Legido and A. Rodríguez, *J. Chem. Thermodynamics*, 2007, **39**, 1168.