Supplementary Material (ESI) for Chemical Communications

Surfactant Ionic Liquid-Based Microemulsions for Polymerization

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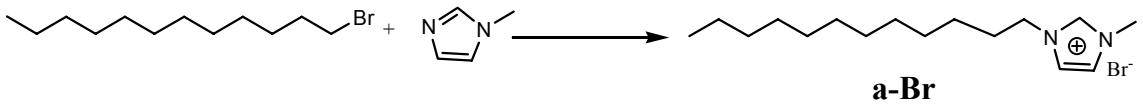
Synthesis of Surfactant ILs

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%), 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.

Methods. The single-phase domains of surfactant/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 24ºC. The partial phase diagram at 60°C was determined by titration with MMA containing a few parts per million of 2,6-di-tert-butyl-4-methylphenol in order to inhibit thermal polymerization. Polymerization of microemulsions was carried out in 20 ml screw-capped culture tubes at 60°C in an oil bath for 6 hr. AIBN (0.5 wt % of MMA) was added to the samples to induce free radical polymerization. No special attempt was made to remove dissolved oxygen. The synthesized polymer particles were purified by dialysis (Spectra/Por 7 dialysis membrane, molecular weight cut off 12000) against daily changes of water for at least 3 days to remove the surfactant and unreacted monomers.

Characterization. Surface tension measurements were carried out using the pendent drop method in water on a Sigma 703 surface tensiometer at 24°C. ^{1}H NMR spectra were recorded on a JEOL 400 MHz spectrometer. The samples were dissolved in $CDCl_3$. Melting points were measured on a SDT 2960 Simultaneous Differential Scanning Calorimetry (DSC), with the heating scans of 10°C/min. Fourier transform infrared (FTIR) spectra were taken using a Nicolet fourier transform spectrometer in the range of 4000–400 cm^{-1}. The samples were obtained by preparing KBr pellets. Transmission electron microscopy (TEM) images of the polymer latexes synthesized were recorded on a JEOL 3011. Scanning electron microscopy (SEM) images were recorded on a Hitachi S3400. All of the samples were freeze-fractured in liquid nitrogen to expose fresh fracture surfaces.



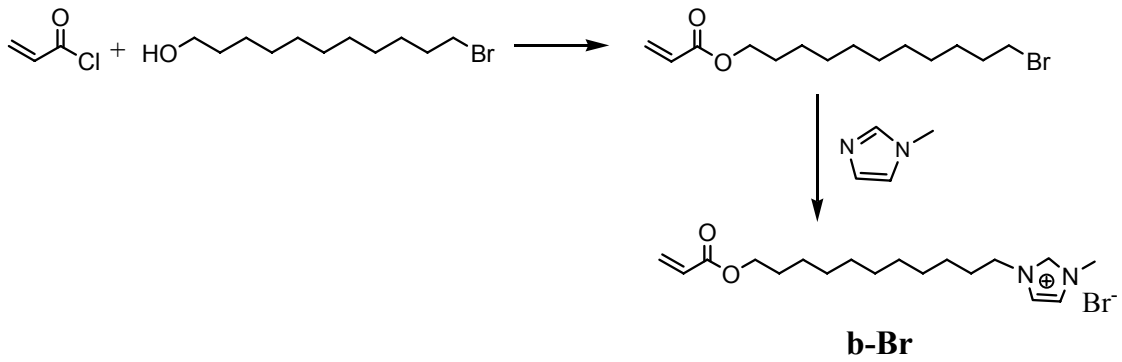
a-Br

Scheme S1 Synthesis of Ionic Liquid Surfactant **a-Br.**

Synthesis of 1-dodecyl-3-methylimidazolium bromide (a-Br)

A mixture of 1-Bromododecane (12.4g, 50 mmol) and 1-methylimidazole (4.11g, 50 mmol) was stirred at 75^{o}C for 24 h. The viscous liquid was washed with ethyl acetate several times and heated at 85ºC under vacuum for 24 h to produce waxy 1-dodecyl-3-methylimidazolium bromide (15.64g, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$): 10.61 (1H, m, N–CH–N), 7.25–7.34 (2H, s, N–CH=CH–N), 4.32–4.30 (2H, t, N–$CH_2(CH_2)_{10}CH_3$), 4.12 (3H, s, N–CH_3), 1.91–1.90 (2H, m, N–$CH_2(CH_2)_{10}CH_3$), 1.32–1.23 (18H, m, N–$CH_2(CH_2)_{10}CH_3$),

0.87–0.84 (3H, t, N–$CH_2(CH_2)_{10}CH_3$). Elemental analysis: Calculated $C_{16}H_{32}BrN_2$: C 57.28 %, H: 9.71 %, N: 8.43 %; Found: C: 56.62 %, H: 9.49 %, N: 8.35 %. mp: 39.7°C.



b-Br

Scheme S2 Synthesis of Ionic Liquid Surfactant **b-Br.**

Synthesis and characterization of b-Br

Synthesis of 11-bromoundecylacrylate

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 N_2 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 $MgSO_4$. The dried solution was filtered and the filtrate was passed through a short column of neutral alumina, using CH_2Cl_2 as the light yellow liquid (yield 10.58 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): 6.37– 6.36 (1H, m, CH_2=CH), 6.15–6.12 (1H, m, CH_2=CH), 5.81–5.79 (1H, m, CH_2=CH), 4.16–4.12 (2H, t, –$OCOCH_2$), 1.85–1.82 (2H, m, $BrCH_2CH_2$–), 1.66–1.64 (2H, m, –$OCOCH_2CH_2$), 1.42–1.27 (14H, m, –$CH_2CH_2(CH_2)_7CH_2CH_2$–).

Synthesis of 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (**b-Br**)

Under N_2 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^{o}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 %). ^{1}H NMR (400 MHz, $CDCl_3$): 10.66 (1H, m, N–CH–N), 7.34–7.25 (2H, s, N–CH=CH–N), 6.36–6.35 (1H, m, CH_2=CH), 6.14–6.11 (1H, m, CH_2=CH), 5.81–5.79 (1H, m, CH_2=CH), 4.30–4.29 (2H, t, N–$CH_2(CH_2)_{10}O$–), 4.11 (3H, s, N–CH_3), 1.90–1.82 (2H, t, N–$CH_2(CH_2)_{10}O$–), 1.66–1.62 (2H, m, –$OCOCH_2CH_2$), 1.30–1.24 (14H, m, –$CH_2CH_2(CH_2)_7CH_2CH_2$–). Elemental analysis: Calculated: $C_{18}H_{32}BrN_2O_2$, C: 55.67 %; H, 8.31 %; N, 7.21 %. Found: C: 55.22 %, H: 7.79 %, N: 7.35 %. mp: 37.2 °C.

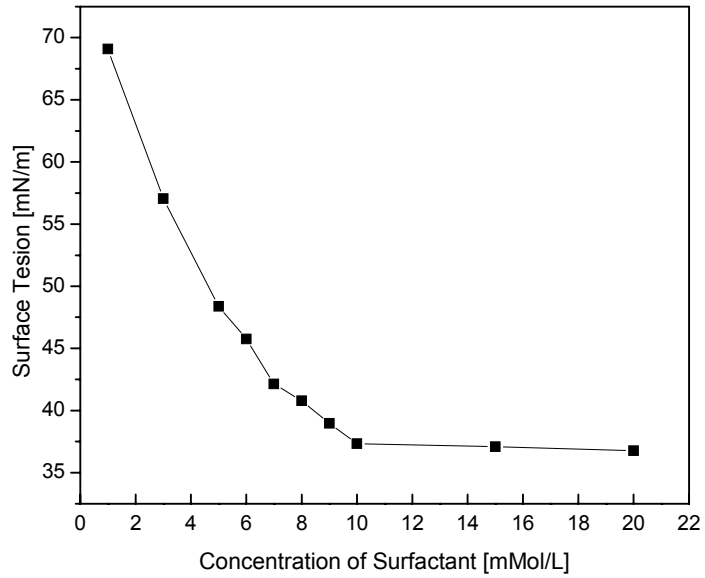


Figure S1 Surface tension versus concentration of **a-Br** aqueous solutions at 24°C.

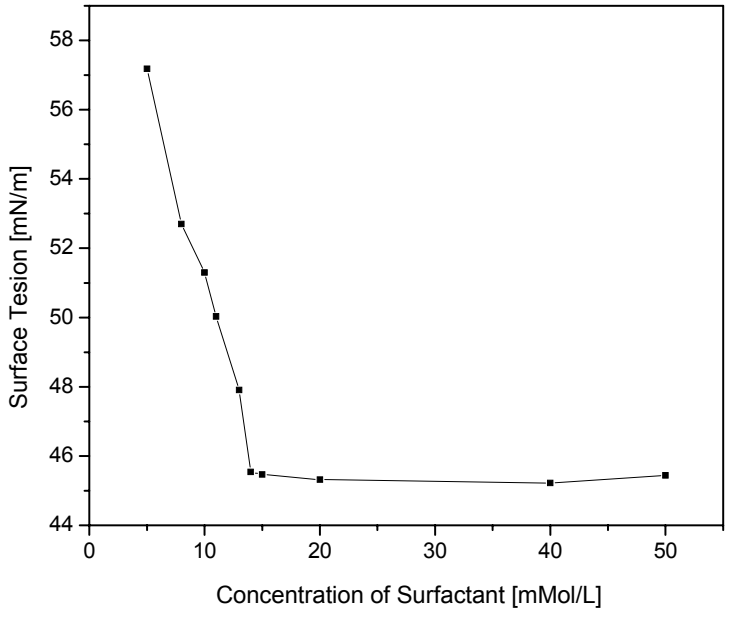


Figure S2 Surface tension versus concentration of **b-Br** aqueous solutions at 24°C.

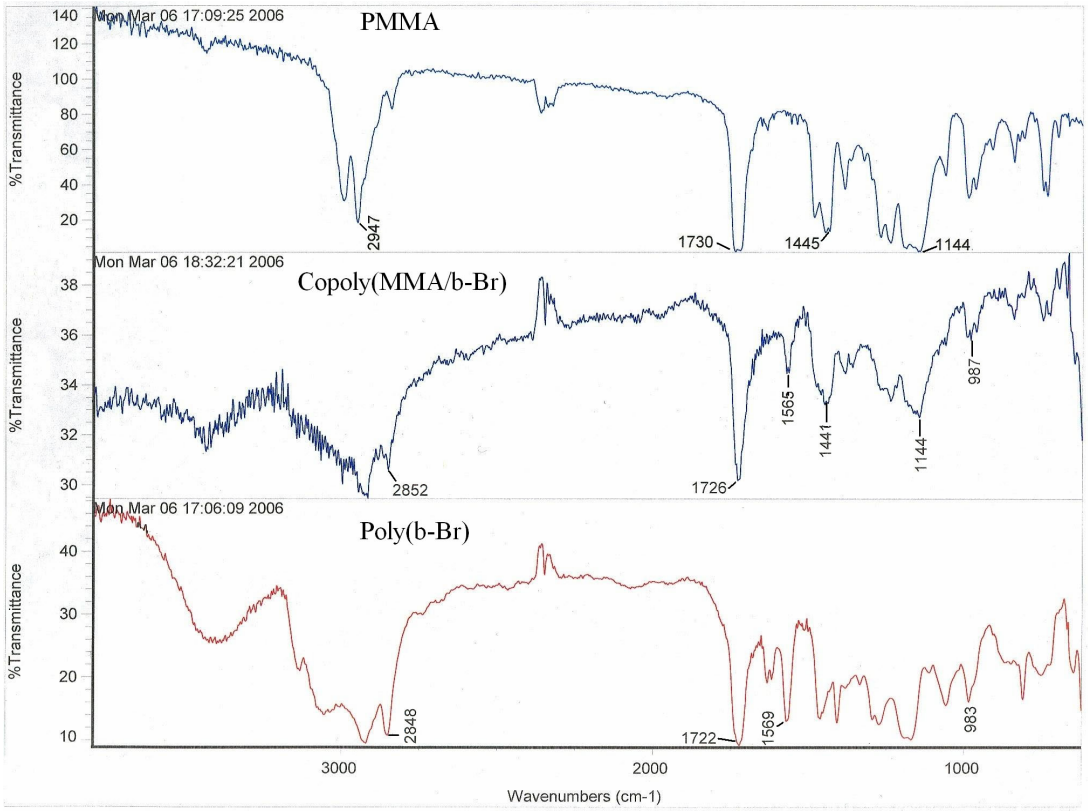


Figure S3 FT-IR spectra of PMMA (top), Copoly(MMA/**b-Br**) nanoparticles (middle) and poly(**b-Br**) (bottom).