Surfactant ionic liquid-based microemulsions for polymerization†

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Surfactants based on imidazolium ionic liquids (ILs), including polymerizable surfactant ILs, have been synthesized and used to stabilize polymerizable microemulsions useful for producing polymer nanoparticles, gels, and open-cell porous materials.

Ionic liquids (ILs) are organic salts with melting points at or near-room temperature.[1] They are attracting much interest in many fields of chemistry and industry because of their chemical stability, thermal stability, nonvolatility and high ionic conductivity.[2] These properties of ILs qualify them as alternatives to traditional organic solvents, and ILs have already found use in organic/inorganic synthesis,[3] catalysis,[4] electrosynthesis,[5] and polymer synthesis.[6] ILs can provide highly polar environments for materials synthesis. The synthesis of novel nanostructures in ILs has recently been gradually realized.[7]

To explore applications of ILs, the incorporation of surfactants with/within ILs has been investigated by several groups in micellar solution and emulsion compositions.[8,9] Some nonionic surfactants, such as polyethylene glycol dodecyl ether (Brij-35), polyethylene glycol sorbitan monolaurate (Tween-20) and 4-(1,1,3,3-tetramethylbutyl)phenyl polyethylene glycol (Triton X-100) are able to form amphiphilic aggregates in a "conventional" IL, 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide solution.[8] It has also been demonstrated that ILs formulated from imidazole cations with appended perfluoro tails could act as surfactants in conventional imidazolium-based ILs, facilitating the emulsification of fluoroalkanes within IL continuous phases.[9] Microemulsions composed of bmim-BF_4, cyclohexane and surfactant Triton X-100 have been recently prepared and characterized by Han and coworkers,[10] Eastoe *et al.*[11] and Chakrabarty *et al.*[12] A recent work presented by Gao *et al.* demonstrated that the bmim-PF_6/water/Triton X-100 system can also form microemulsions under suitable conditions.[13]

Here, we report the synthesis of surfactant ILs, that consist of an imidazolium cation polar group and a hydrophobic tail (Fig. 1). We use these surfactant ILs to stabilize microemulsions. To our knowledge, this is the first report of microemulsions stabilized by IL-based surfactants that also are ILs near room temperature.

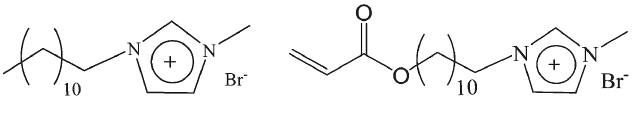

Fig. 1 Structures of ionic liquid surfactants investigated in this work. (left) **a-Br**, mp: 39.7 °C; (right) **b-Br**, mp: 37.2 °C.

The IL surfactants were synthesized and characterized as described in the ESI.† 1-Dodecyl-3-methylimidazolium bromide (**a-Br**) was synthesized by the reaction of 1-bromododecane with 1-methylimidazole. To synthesize 1-(2-acryloyloxyundecyl)-3-methylimidazolium bromide (**b-Br**), acryloyl chloride and equimolar 11-bromo-1-undecanol were firstly reacted in tetrahydrofuran in the presence of triethylamine to prepare the bromoalkane acrylate. The reaction of bromoalkane acrylate with 1-methylimidazole produced polymerizable **b-Br**. Both compounds are ILs near room temperature.

The critical micelle concentration (c.m.c.) of **a-Br** in water determined by surface tension (pendant drop) measurements is 10.31 mM at 24 °C. The partial phase diagrams of the **a-Br**/H_2O/methyl methacrylate (MMA) ternary system at 24 and 60 °C are illustrated in Fig. 2. Samples within the one-phase microemulsion region (to the left of the indicated boundaries) were transparent. Bulk microemulsion polymerization in the **a-Br**/MMA/H_2O (0.04/0.04/0.92) system was initiated by 2,2-azobisisobutyronitrile (AIBN) at 60 °C. However, turbidity from particle aggregation could be observed during the polymerization. The polymerization produces monodisperse polymer latexes with diameters of $\sim$50 nm (Fig. 3).

The c.m.c. of **b-Br** was found to be 15.35 mM at 24 °C. Similarly to the nonpolymerizable surfactant IL **a-Br**, **b-Br** can be used to stabilize H_2O/MMA systems, and form transparent and stable microemulsions (Fig. 2) to the left of the illustrated boundaries. It has been observed that polymerizable surfactants have advantages over nonpolymerizable surfactants in capturing nanoscopic length scales and structures in microemulsions during polymerization.[14] Bulk polymerization of the **b-Br**/MMA/H_2O (0.07/0.07/0.86) microemulsion system resulted in polymer latexes without any apparent aggregation. Copolymerization between MMA and **b-Br** in microemulsions was confirmed by FTIR spectra (see ESI†). Fig. 4(A) shows a transmission electron microscopy (TEM) image of the produced polymer latexes. The average diameter of these nanoparticles is $\sim$30 nm. Since **b-Br** is more polar than MMA, it likely forms a polymerized polar shell around the resulting particles, which increases particle stability and allows the particles to be easily redispersed in water and in NaBr solution without any evident aggregation, indicating that the latex surface is hydrophilic. These latexes start to aggregate in $NaBF_4$ solution, and dramatically aggregate in KPF_6 solution (Fig. 4(B), (c) and (d)). This aggregation is due to the surface being transformed from hydrophilic to hydrophobic, by the anion exchange of the Br^- to BF_4^- to PF_6^-.[15]

Transparent gels can be produced by polymerization when surfactant and MMA concentrations are higher (**b-Br**/MMA/H_2O

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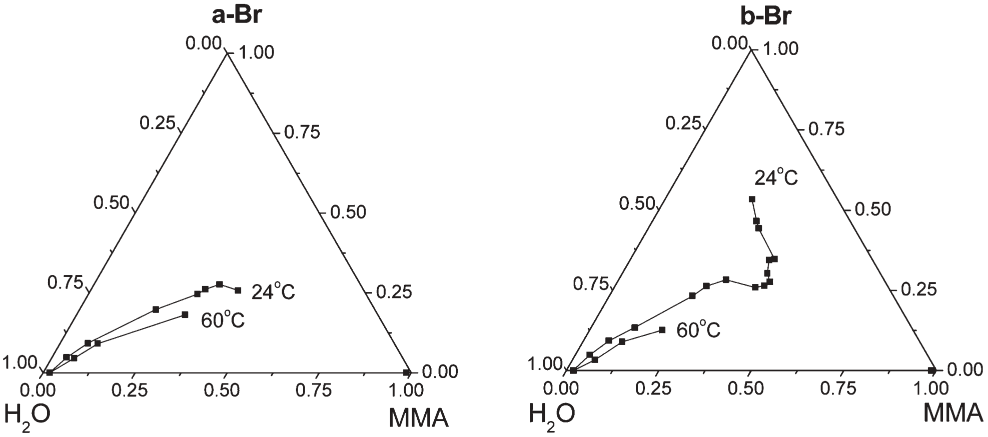

Fig. 2 Partial phase diagrams (weight fraction) of **a-Br** and **b-Br**/water/MMA systems. The single-phase microemulsion domains were determined visually on the basis of transparency and absence of phase separation (in PTFE-lined, screw-capped culture tubes). The partial phase diagrams at 60 °C were 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.

(0.15/0.10/0.75)). Such a transparent polymer gel shrinks and becomes opaque after being immersed in aqueous KPF_6 (Fig. 5(A), (B)). This opaque material can be converted back to a semi-transparent gel by further treatment with aqueous NaBr (Fig. 5(C)). Scanning electron microscopy (SEM) images of the transparent gel (Fig. 6(A)) show some weak stripes due to the shrinkage of the gel surface under the vacuum in the SEM. However, pores with diameters of ~3–8 μm can be observed in the opaque gel (Fig. 6(B)). Most of these pores connect to others through small circular "windows", with diameters of ~1–3 μm. These pores can be partially closed (self-healed) by further immersion in NaBr solution. The formation of the pores seen in the opaque gel is due to the shrinkage of the copolymer at the interfaces between aqueous and polymer domains. The polymerizable surfactant **b-Br** molecules are situated along these interfaces

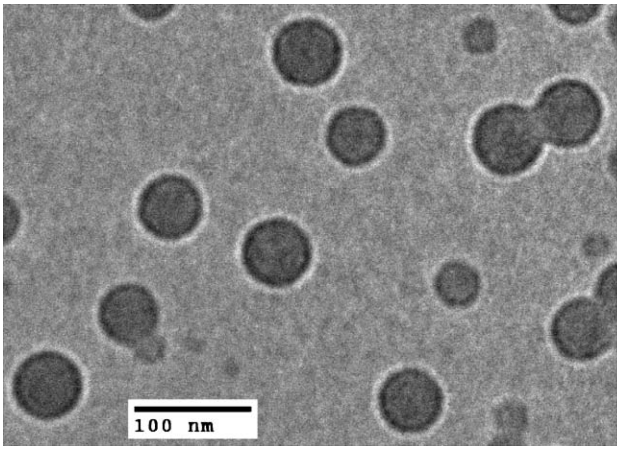

Fig. 3 TEM image of polymer latexes produced from microemulsion polymerization of **a-Br**/MMA/H_2O (0.4/0.4/0.92), initiated by AIBN at 60 °C.

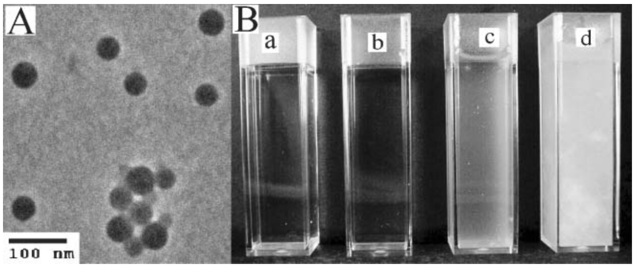

Fig. 4 (A) TEM image of polymer latexes produced from microemulsion stabilized by **b-Br**, (B) polymer latexes dispersed in (a) water, (b) 0.1 M NaBr solution, (c) 0.1 M $NaBF_4$ solution and (d) 0.1 M KPF_6 solution.

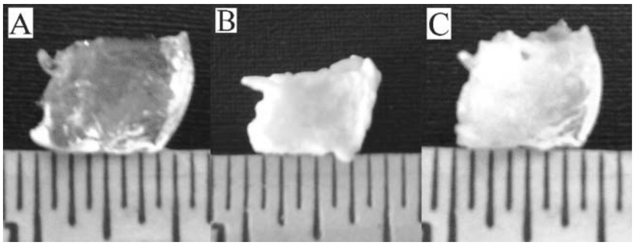

Fig. 5 Photographs of polymer gels: (A) after microemulsion polymerization; (B) gel in (A) treated with 0.1 M KPF_6 solution; (C) gel in (B) treated with 0.1 M NaBr solution.

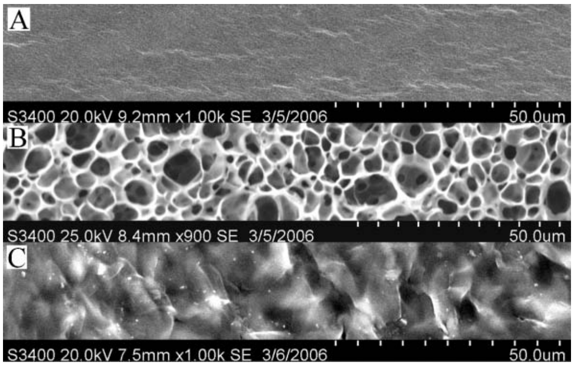

Fig. 6 SEM images of polymer gels (A) after microemulsion polymerization; (B) gel in (A) treated with aqueous 0.1 M KPF_6; (C) gel in (B) treated with aqueous 0.1 M NaBr solution.

between aqueous and MMA domains prior to polymerization. Once the vinyl groups of **b-Br** and MMA are copolymerized, the hydrophilic portions of **b-Br** protrude into the aqueous domains or channels in the gel. The anion exchange from Br^- to PF_6^- changes the copolymer from being hydrophilic to being hydrophobic at these interfaces between aqueous and polymer domains, and thus causes shrinkage at the interface to make pores. This shrinkage results from condensation of surfactant IL chains on themselves and on the polymeric backbone as the polar imidazolium headgroups are transformed from being hydrophilic to being hydrophobic. The shrunken polymer domains at the interface can be converted back to hydrophilic and expanded in water again after anion exchange from PF_6^- to Br^-, and thus swell by imbibing water and partially healing or closing the pores.

In conclusion, we have demonstrated the preparation of microemulsions stabilized by surfactant ILs, including polymerizable or reactive surfactant ILs. Polymerization in these microemulsions can produce polymer particles, gels and open-cell microporous materials. The surface properties of the resulting copolymers can be modified *via* anion exchange. These new applications of ILs expand the potential of ILs and microemulsions, and demonstrate a single-pot avenue to open-cell microporous copolymers *via* bulk polymerization.

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