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Lyotropic liquid crystalline phases formed in an ionic liquid†

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Lyotropic liquid crystalline phases of an amphiphilic block copolymer are constructed and characterized in an ionic liquid with comparison of component and temperature effects.

Ionic liquids (ILs), a class of organic salts with unusually low melting temperatures, have attracted much attention. Due to their unique characteristics such as non-volatility, thermal stability, non-flammability, extremely high ionic conductivity, and catalytic properties, ILs can be used as environmentally-benign solvent media to replace conventional organic solvents in many industrially chemical process.[1,2] In addition, ionic liquid crystalline materials (*i.e.* ILs with some long-range molecular order, or systems with ionic liquid and functional mesogenic molecules) have been reported for their properties including macroscopic uniform orientation and ionic conductivity.[3,4] Studies on lyotropic mesophases obtained from ILs in aqueous solution have also been reported.[5] However, studies on supramolecular assemblies of traditional surfactants like micelles, vesicles, emulsions and liquid crystals, *etc.*, in ILs are rare.[6] Vesicle formation of dialkyldimethylammonium bromide is observed in ether-containing ILs.[6a] Fletcher and Pandey investigated the aggregation behavior of common anionic, cationic, and nonionic surfactants when solubilized within 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide.[6b] Micelle aggregates of different amphiphiles in two ILs were also reported by Anderson *et al.*[6c] A microemulsion of Triton X-100 mixed with ionic liquid and cyclohexane was produced and characterized by Gao *et al.*[6d] For liquid crystal, an important type of self-assembled supramolecular aggregate, although its formation in ILs has been achieved by Kato *et al.*[4] as mentioned above, they are mainly made of compounds containing functional mesogens, which are specially designed and synthesized for a specific purpose, or show anisotropic characteristics only at much higher temperature. Up to now, room temperature lyotropic liquid crystals (LLC), made of common surfactants in ILs, have not received much attention although the liquid crystal phase of distearoylphosphotidylcholine in *N*-ethylammonium nitrate was found twenty years ago.[7]

Here we report nonaqueous lyotropic liquid crystalline phases of an amphiphilic triblock copolymer formed in an ionic liquid, 1-n-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6).‡ Our aim is to find if common surfactants can also be self-assembled in ILs, and show new properties in such nonaqueous assemblies.

The copolymer we use is Pluronic P123($EO_{20}PO_{70}EO_{20}$), belonging to the PEO–PPO–PEO block copolymer series, which has been extensively used in pharmatics, foods, cosmetics, *etc.*[8] Its phase behavior in water has been investigated by Alexandridis *et al.*,[8] with PPO block aggregates as the hydrophobic domain and hydrophilic PEO blocks spreading in water. The liquid crystal properties in IL are studied through polarized optical microscope (POM) and small angle X-ray scattering (SAXS) techniques and compared with those in aqueous systems.

From POM and SAXS measurements, two birefringent regions appear clearly respectively at 38–52% and 65–87% (weight percentage) P123 in [Bmim]PF_6. Fig. 1 shows textures of samples with different P123 concentrations in ionic liquid (b, d) and in water (a, c). We can observe obvious differences between the nonaqueous and aqueous systems. When water is replaced by IL, the textures change greatly and rhombic bright domains appear for 45% P123 (Fig. 1b), though no such clear anisotropic textures (Fig. 1d) appear for the 75% P123 system.

Further structural information can be obtained by SAXS measurements (Fig. 2). Three SAXS peaks emerge in the anisotropic region at lower surfactant concentrations with relative positions of $1 : \sqrt{3} : 2$, which is characteristic of a hexagonal liquid crystal phase (H_1).[8] At higher P123 concentration, these SAXS peak positions accord with the ratio 1 : 2 : 3, indicating a lamellar phase (L_α).[8] The extracted structure parameters are listed in Table 1. It is clear that the lattice spacings (*d*, calculated from the first peak position) are all smaller than those of aqueous systems, which can be explained by the density difference between [Bmim]PF_6 and water. the greater density of [Bmim]PF_6 (1.37 g cm^{-3}) makes its volume in LLC smaller than that in water at the same weight percentage composition,[2] which may lead to shrinking of polar domains as well as the lattice spacings.

The effect of temperature on the phase behavior is also investigated. Fig. 3 shows SAXS curves of anisotropic phases

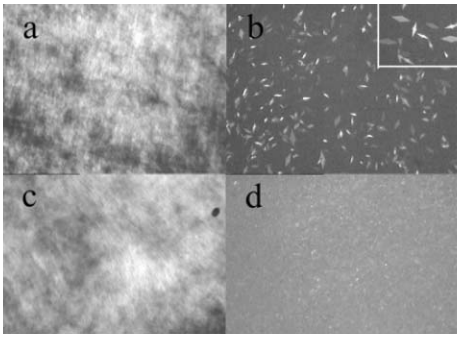

Fig. 1 Textures of anisotropic phases formed in water (a, c) and [Bmim]PF_6 (b, d) with 45% (a, b) and 75% (c, d) P123. Inset is an enlarged image of b.

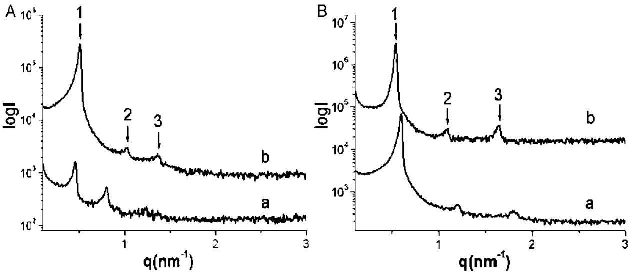

Fig. 2 SAXS diffraction patterns of anisotropic phases formed in water (a) and [Bmim]PF_6 (b) at 25 °C, with P123 concentrations of (A) 45% (hexagonal phase) and (B) 75% (lamellar phase). 1, 2 and 3 represent 1st, 2nd and 3rd peaks respectively.

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† Electronic supplementary information (ESI) available: lattice spacings, SAXS patterns, optical microscopy details. See http://www.rsc.org/suppdata/cc/b4/b411163j/

Table 1 Anisotropic phase types and lattice spacings (*d*) varing with concentration of P123 in water and [Bmim]PF_6 at 25 °C

	Phase		*d*/nm	
Concentration (%)	Water	[Bmim]PF_6	Water	[Bmim]PF_6
40	H_1	H_1	14.57	12.70
45	H_1	H_1	13.57	12.30
50	H_1	H_1	13.38	11.97
68	L_α	L_α	12.11	10.82
75	L_α	L_α	11.58	10.50
85	L_α	L_α	10.94	10.00

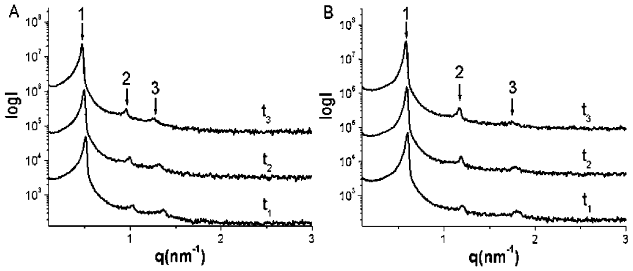

Fig. 3 SAXS diffraction patterns of anisotropic phases formed in [Bmim]PF_6 with P123 concentrations of (A) 45% and (B) 75%. t_1, t_2 and t_3 represent 25, 45 and 65 °C respectively.

measured at different temperatures. It is noted that higher temperature leads the first peak position to a smaller *q* value, corresponding to a larger lattice spacing (ESI 1†). This is easily understood by the volume swelling effect of IL when it is heated. Comparing 75% and 45% P123 systems, such an effect is more evident for the latter because it contains more IL. Fig. 3 also shows that LC phases in IL are stable to increasing temperature from 25 to 65 °C, while the corresponding aqueous samples are not. A phase transition (ESI 2†) will occur from hexagonal to lamellar in the 45% P123–water system at 65 °C.

What is the crucial role played in the formation of the LLC phase by the IL? One may be attributed to the strong solvatophobic interaction between IL and hydrophobic parts of surfactant, which has been reported.[6c] Despite the great difference in physicochemical properties between water and [Bmim]PF_6, and the low solubility of water in [Bmim]PF_6 or *vice versa*,[2,9] there are still some similarities between surfactant–water and surfactant–IL interactions. Such interactions, certainly, should vary with the type of surfactant and IL. We have noticed that, when SDS, CTAB and $C_{12}EO_4$ are used as substituent for P123 to mix with IL, the phases are not the same as those obtained above. SDS and CTAB are difficult to dissolve in [Bmim]PF_6 even at temperatures higher than 60 °C, while $C_{12}EO_4$–IL mixtures exhibit anisotropic properties just above a certain temperature (such as 70 °C, when containing 40% surfactant). In previous studies, Fletcher and Pandey found SDS is insoluble in [Emim]Tf_2N and no aggregation of CTAB is observed. Interestingly, possible aggregate formation is observed in this IL for nonionic surfactants with EO groups.

Now the answer becomes clear. From the above results, we conclude that the existence of the PEO group in the copolymer molecule may be the key point. In P123–[Bmim]PF_6, hydrogen bonds can occur between the end group of EO block and $[PF_6]^-$ anion. Interactions also occur between the cation moiety ($-N^+$) of IL and the lone pairs on oxygen atoms of EO groups.[6b,6c,10] Both effects may favor the appearance of long-range ordered structures when combining with the solvatophobic force. Therefore, the possible structural model of organized P123 assembly in [Bmim]PF_6 should be similar to that of aqueous systems: polar domains are formed with PEO blocks extending into the IL and PPO blocks form apolar or solvatophobic domains. In the hexagonal phase the amphiphiles form cylinders that pack in a hexagonal array, while in the lamellar phase the ordered structure exists in a bilayer fashion. The thermostability of a hexagonal phase containing IL can be explained first by its lower fluidity induced from the higher viscosity of the IL. On the other hand, the IL cation with a hydrophobic butyl group tends to act like a co-surfactant and cooperate with the block copolymer in forming interfaces,[8a] thus enhancing the structural order. In addition, as a melting salt, the IL may have a salting-out effect on the block copolymer system,[11] which is helpful for the formation of self-assembled structures. Based on equations and parameters obtained in reference 8, the thickness of the IL domain can be estimated as about 4.6 nm for the 45% P123 hexagonal system and 3.1 nm for the 75% P123 lamellar phase.

In summary, we report lyotropic liquid crystalline phases formed with a conventional nonionic surfactant in IL. Both PEO and IL play important roles in the formation and stabilization of the organized assembly. In particular the latter behaves not only as a specific solvent[12] but also as a co-surfactant and salt, promoting the formation of ordered mesophases, which are room-temperature formed, thermostable, ion-conveyable, nonaqueous, and long-range ordered. In addition, such an amphiphile is commercially available and easy to acquire. All these properties may provide novel functional materials and find various potential applications.

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‡ [Bmim]PF_6 was synthesized based on reference 13.

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