

Lamellar Phases Formed in Brij97/Water/Ionic Liquids

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Abstract: Microstructure and dynamic rheological properties of lamellar liquid crystals formed in Brij97/water/bmim-BF₄ and Brij97/water/bmim-PF₆ systems were investigated by means of SAXS and small amplitude oscillatory shear measurements. It is shown that two systems exhibit gel-like and fluid-like rheograms respectively along with the different locations of bmim-PF₆ and bmim-BF₄ penetrating through the lamellar phase.

Key words: ionic liquid; Brij97; lamellar liquid crystals

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An important area of green chemistry is the replacement of hazardous solvents in chemical processes. Ionic liquids (ILs), as the primary candidates for such green replacement solvents, have been extensively investigated for many applications. However, the formation of supramolecular assemblies related to ILs remains to be explored and has been attracting increasingly interests in both the chemistry of ionic liquids and supramolecular assemblies of amphiphiles^[1]. In this work, lamellar liquid crystals formed in Brij 97/water/bmim-BF₄ and Brij97/water/bmim-PF₆ systems were investigated using small angle X-ray scattering (SAXS) and rheological methods to find any new properties between them.

1 Experiments

1.1 Materials

The nonionic surfactant Brij97 of purity > 99% was purchased from Sigma-Aldrich and used without further purification. Ionic liquids bmim-PF₆ and bmim-BF₄ were prepared using the procedures the same as our previous work^[2].

1.2 Experimental methods

The lamellar samples were prepared and stabilized according to literature^[3].

Small angle X-ray scattering (SAXS) were performed on a HMBG-SAX X-ray small angle system, and rheological measurements were carried with a HAAKE RS75 rheometer, as described previously^[3].

The lamellar structure dimensions were calculated using the equations reported^[3].

2 Results and discussion

According to the reported phase diagrams^[2], three lamellar liquid crystal samples L_{a1} (Brij97/water), L_{a2} (Brij97/bmim-BF₄/water) and L_{a3} (Brij97/bmim-PF₆/water) were prepared. The compositions of the samples are 80/20, 76/4/20 and 76/4/20 respectively. Dynamic rheology and SAXS investigations on the lamellar samples are made comparatively.

2.1 Microstructure

From SAXS data listed in Table 1, It is seen that at the same water content, the value of a_s is in order of L_{a3} > L_{a2} > L_{a1}; while the values of d_w follows L_{a2} >

Tab 1 Characteristic parameters for the lamellar phases

Lamellar Phase	d (Å)	d _w (Å)	d _{apolar} (Å)	a _s (Å ²)
L _{a1}	55.72	36.5	19.2	52.0
L _{a2}	56.52	37.9	18.6	53.7
L _{a3}	55.72	37.3	18.4	54.2

Note: a_s is the effective cross sectional area per surfactant at the interface; d_{apolar} is the thickness of the apolar domain and d_w the polar domain.

$I_{\alpha 3} > I_{\alpha 1}$. Since a_s usually changes very slightly with the surfactant concentration when the type of liquid crystal is unchanged^[4], these differences should be related to the ways of bmm-PF₆ or bmm-BF₄ penetrating through the lamellar phase.

It is clear that there is an increase both in a_s and d_w for $I_{\alpha 2}$ and $I_{\alpha 3}$ comparing to $I_{\alpha 1}$, reflecting that both bmm-BF₄ and bmm-PF₆ are solubilized in the hydrophilic domain of the lamellar phases. Also from the microstructure parameters, it is reasonable to conclude that bmm-BF₄ is mainly localized in the water layer of the lamellar phases and resulting in a larger value in d_w ($I_{\alpha 2} > I_{\alpha 3}$), whereas bmm-PF₆ is dominantly penetrated between the EO chains of Brij 97 molecules which causing a larger value in a_s ($I_{\alpha 3} > I_{\alpha 2}$).

2.2 Dynamic rheological behavior

More information on the network structure of the lamellar phases can be obtained from small amplitude oscillatory shear measurements. The frequency dependence of both storage modulus (G') and loss modulus (G'') for the lamellar liquid crystalline samples are demonstrated in Figure 1.

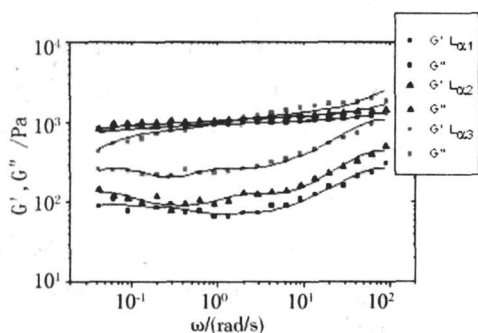


Fig 1 Dynamic rheograms for the lamellar samples at 25 °C

From Fig 1, two different mechanical spectrum are shown by the lamellar phases investigated. $I_{\alpha 1}$ and $I_{\alpha 2}$ are characterized by the same type of mechanical spectrum, typical gel-like rheogram. The rheogram of $I_{\alpha 3}$ is obviously different from that of $I_{\alpha 1}$ and $I_{\alpha 2}$. The slope of the frequency dependence of G' is far sharper, as a consequence it tends to "crossover" G'' at low frequency, and exhibits fluidlike viscoelastic property to some extent.

3 Conclusions

(1) SAXS data indicated that bmm-PF₆ is dominantly located between the oxyethylene part of surfactant and bmm-BF₄ is mostly solubilized in the water area.

(2) The frequency sweep spectrum of bmm-BF₄ containing lamellar phase is typical gel-like, whereas the bmm-PF₆ containing one shows viscoelasticity to some extent.

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Brij97/H₂O/离子液体体系层状液晶的研究

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摘要: 利用小角 X 射线散射和小幅振荡实验研究了 Brij97/H₂O/ bmm-BF₄ 和 Brij97/H₂O/ bmm-PF₆ 体系层状液晶的微观结构和动态流变性质。结果表明两层状液晶体系分别表现 gel-like 和 fluid-like 的动态流变行为, 而且 bmm-PF₆ 和 bmm-BF₄ 增溶在液晶结构的不同位置。

关键词: 离子液体; Brij97; 层状液晶

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