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Vitrification and water induced crystallization of zinc(II) dodecylbenzene sulphonate

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Crystallization of zinc(II) dodecyl benzene sulphonate has been suppressed by either the removal of water of hydration or the rapid cooling of the compound from the liquid crystalline state. The anisotropic structure is preserved in the solid state when the hydrated compound in the LC phase is rapidly quenched, while removal of the water of hydration at temperatures in or above the LC phase and the subsequent slow cooling produces a stable isotropic structure.

1. Introduction

Liquid crystals have established themselves as technologically important materials in several now mature fields such as LC displays where they function in the fluid phase which renders their molecular orientation susceptible to external fields. There are also potentially important and emerging technologies, such as optical information storage [1] and control of the polarization of light [2], where it is desirable to have a high degree of anisotropy frozen in a solid matrix, such as vitrified films. Vitrified glasses have been known in polymeric materials, and in recent years [3], due to the ease of processing offered by low molar mass liquid crystals, vitrification in these systems has gained interest as evident from recent publications [4, 5]. For example, several studies [6, 7] have attempted to correlate vitrification processes with structure and mesogenity of low molar mass compounds.

In the majority of these compounds, crystallization is suppressed through an appropriate choice of cooling rate, from the LC to below the glass transition temperature. Recrystallization ensues when these compounds are heated, followed by the usual crystal–LC and LC–isotropic transitions. In this paper, we report on the phase transitions and the retention of anisotropy of zinc dodecylbenzene sulphonate [$Zn(DBS)_2$], in the quenched, the dried and the hydrated cases.

The mesomorphic behaviour of metal dodecylbenzene sulphonates including $Zn(DBS)_2$ has been observed previously [8, 9]. Lyotropic liquid crystals possessing lamellar structures were reported from the reaction product of dodecylbenzene sulphonic acid (DBSA) and metal nitrates. Interplanar spacings for solid $Zn(DBS)_2$ samples crystallized from supernatant solutions were found to be 30·9 Å. Its complexes with poly(vinylpyridine) [10] and polyamide-6 [11] have also been found to possess mesomorphic characteristics.

This communication reports on the finding that crystallization of $Zn(DBS)_2$, both in its dried and hydrated states, can be suppressed. Upon absorption of a small amounts of water, the dehydrated isotropic $Zn(DBS)_2$ crystallizes. This behaviour is quite unique and to our knowledge has not been reported previously.

Zinc(II) dodecylbenzene sulphonate [$Zn(DBS)_2$] was prepared according to the reaction

$$2\ \mathrm{DBSA} + \mathrm{ZnO} \rightarrow \mathrm{Zn(DBS)_2} + \mathrm{H_2O}.$$

DBSA was dissolved in anhydrous ethanol and added to a suspension of ZnO in ethanol. The stoichiometry was exactly 2 moles DBSA to one mole ZnO. The mixture was sonicated at room temperature for several hours at the end of which all the ZnO had disappeared and a completely clear solution obtained. The solution was filtered, the ethanol evaporated and the resulting material was dried under vacuum at 80°C for two weeks. The structure was confirmed to be $Zn(DBS)_2$ by proton solution NMR in deuteriated methanol and FTIR.

For the purpose of this communication, dry denotes materials placed in vacuum oven at 120°C for several days while hydrated is $Zn(DBS)_2$ that has been exposed to air for several days. The cross-polarized optical microscopy was performed with samples sandwiched between glass slides. X-ray diffraction was performed in a high powered rotating anode generator. Powder samples were mounted on a four-circle goniometer in 1 mm glass

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capillaries. The X-ray out-of-plane resolution in this case was ~0·14. For the dry experiment, $Zn(DBS)_2$ powder was initially dried in a vacuum oven at 80°C for two weeks, inserted into the capillary, further dried in a vacuum oven at 120°C for one day. The capillary was then cooled slowly to room temperature under vacuum and sealed. For the hydrated $Zn(DBS)_2$ sample, the powder was allowed to absorb moisture from the air for several days prior to loading into the capillary. The capillary was kept in air and unsealed prior to and during the experiment. For quenched samples the open capillary was quenched very quickly from 90°C (LC state) to subambient temperatures with liquid nitrogen and tested at 30°C.

The transitions for the hydrated $Zn(DBS)_2$ were observed in the differential scanning calorimeter to be crystalline solid to LC at 82°C and LC to isotropic at 134°C. Figure 1 shows a cross-polarized optical micrograph of the hydrated $Zn(DBS)_2$. The sample was sheared between glass plates in the liquid crystalline (LC) phase and annealed at 105°C for 48 h. The texture exhibits a few focal conics and a high density of striated bands known as oily streaks. Both types of defects are characteristic of the smectic A mesophase. In contrast the dried sample, under the same conditions, was observed to be completely dark between the cross-polarizers, indicative of an isotropic state. When the dried sample was exposed to air, textures similar to figure 1 developed in a matter of minutes.

Figure 2 shows X-ray diffraction data for $Zn(DBS)_2$ in the dry as well as the crystallized and the quenched hydrated samples. The equilibrium water uptake of the hydrated sample was thermogravimetrically measured to be ~13 wt%. The hydrated crystallized $Zn(DBS)_2$ exhibits multiple diffraction peaks. The first peak represents a long period $d=30{\cdot}7$ Å, almost identical to the value reported by Tezak *et al.* [8]. Several well-defined orders of reflections can be seen for the hydrated $Zn(DBS)_2$. There are also numerous other peaks, some of which have been observed previously [10].

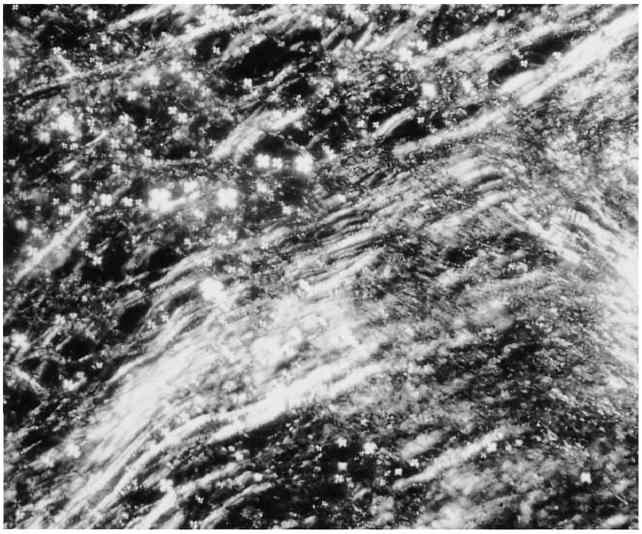

Figure 1. Cross-polarized optical micrograph of the hydrated zinc(II) dodecyl benzene sulphonate sheared between glass slides, annealed at 105°C.

In contrast, the dry $Zn(DBS)_2$ showed a single peak at $d=26{\cdot}5$ Å with its corresponding harmonic appearing as a shoulder at 13·3 Å followed by the typical broad liquid peak centered around 4·6 Å. A single peak also appears in diffraction experiments performed in the isotropic phase at 170°C and is most probably due to periodicity between the zinc centres which remain in the isotropic liquid state. Also the difference of approximately 4·2 Å in the long period between the dry and the hydrated cases is expected in view of the extra space occupied by the water of hydration.

It is not the object of the present study to investigate the possible structures arising from diffraction peaks in figure 2. The data are shown merely to demonstrate the difference between the dry, the hydrated and the quenched $Zn(DBS)_2$. However we remark that the drying process was carried out at temperatures where the material was in the LC state and it is rather surprising that the isothermal removal of water in the LC phase caused a LC–isotropic phase transformation. This transformation was reversed upon absorption of moisture by $Zn(DBS)_2$ from the atmosphere at room temperature. The hypothesis for such a reversible transformation is that hydration of the molecules releases the configurational restrictions, placed upon the molecular packing during the drying process, leading to the unexpected crystallization of the surfactant molecules. This hypothesis can be justified since the interactions between the $zinc^{2+}$ and the $sulphonate^{1-}$ ions are quite different in the dry and the hydrated cases. In the former the ionic interactions occur directly between the species, and are thus quite strong. In the latter, it occurs through the sphere of hydration formed around the $zinc^{2+}$ cation by six water molecules, creating a less rigidly bound structure and allowing the molecules to rearrange to a more thermodynamically stable state. Both the isotropic and the crystalline states of the surfactant were however stable and it was possible to switch from one to the other by the simple drying or hydration processes. This reversibility was confirmed by alternative X-ray diffraction experiments not included here and performed in the reflection mode at different temperatures. The structure for hydrated $Zn(DBS)_2$ was observed to be lamellar at 90°C with $d=23{\cdot}9$ Å. Repetitive heating and slow cooling of the sample between 30 and 90°C would transform the structure between the LC and the crystalline phases. At 170°C a single peak at $d=22{\cdot}6$ Å remained

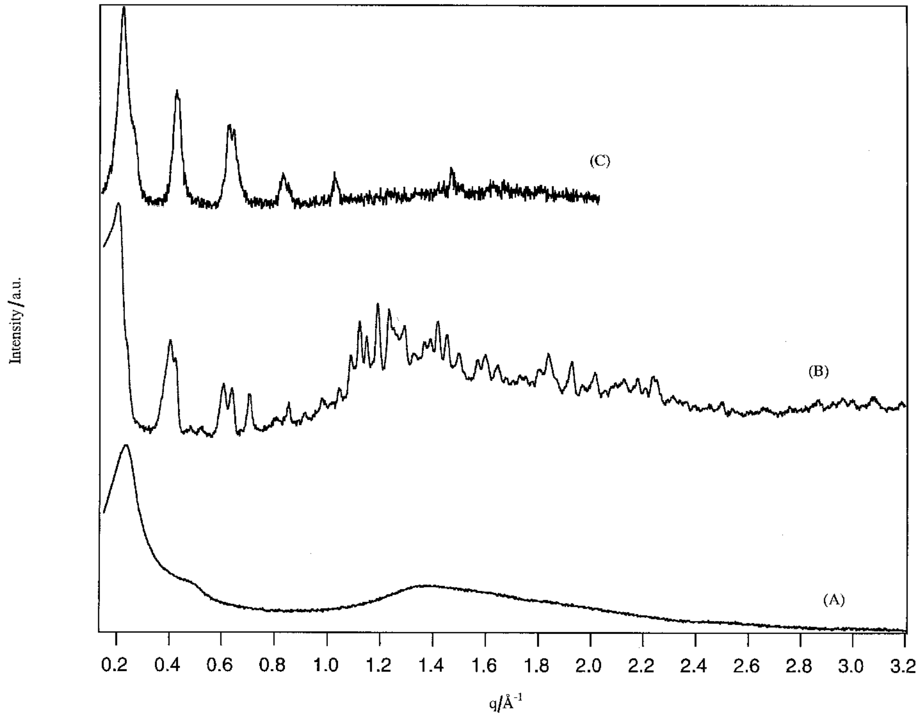

Figure 2. X-ray diffraction patterns for Zn(DBS)$_2$ taken at 30°C, (*A*) dry, (*B*) hydrated in air at room temperature, (*C*) rapidly quenched from LC phase at 90°C.

corresponding to the distance between zinc centres in the liquid state.

Pattern (*C*) in figure 2 shows X-ray diffraction data taken from the sample that was very rapidly quenched from 90°C to subambient temperatures, held there for a period and tested at 30°C. Retention of the mesomorphic structure is evident from the unique presence of the diffraction peak at $d=27{\cdot}8$ Å and up to the seventh harmonic peak associated with the lamellar structure. However, the layer spacing was increased in the solid anisotropic sample (by 3·9 Å) compared with that in the LC state. When this sample was placed in air for extended period of time, the diffraction pattern returned to that associated with the crystalline state. A possible explanation is that crystallization was suppressed during the cooling process, however, the T_g of the vitrified compound is probably below room temperature. Thus keeping the sample above its T_g had allowed significant molecular mobility for crystallization to occur. As yet, it has not been possible to prove vitrification by differential scanning calorimetry, due to instrument cooling rate limitations. However the X-ray data suggests that crystallization has been suppressed during the cooling process and that the mesomorphic structure was retained in the solid state. Further investigation of the effects of water on the structural transition of Zn(DBS)$_2$ are being performed.

References

[1] Eichler, H. J., Heppke, G., MacDonald, R., and Schmid, H., 1992, *Mol. Cryst. Liq. Cryst.*, **223**, 159.

[2] Schadt, M., 1993, *Ber. Bunsen. phys. Chem.*, **97**, 1213.

[3] Attard, G. S., 1991, *High Value Polymers*, edited by A. H. Fawcett (London: Royal Society of Chemistry).

[4] Bruce, D. W., Donnio, B., Guillon, D., Heinrich, B., and Ibn-Elhaj, M., 1995, *Liq. Cryst.*, **19**, 537.

[5] Attard, G. S., Imrie, C. T., and Karasz, F. E., 1992, *Chem. mater.*, **4**, 1246.

[6] Chen, S. W., Mastrangelo, J. C., Blanton, T. N., Bashir-Hashemi, A., and Marshall, K. L., 1996, *Liq. Cryst.*, **21**, 683.

[7] Wedler, W., Demus, D., Zaschke, H., Mohr, K., Schafer, W., and Weissflog, W., 1991, *J. Mater. Chem.*, **1**, 347.

[8] Tezak, D., Strajnar, F., Milat, O., and Stubicar, M., 1984, *Prog. Coll. Polym. Sci.*, **69**, 100.

[9] Tezak, D., Popovic, S., Heimer, S., and Strajnar, F., 1989, *Prog. Coll. Polym. Sci.*, **79**, 293.

[10] Ruokolainen, J., Tanner, J., Brinke, G., Ikkala, O., Torkkeli, M., and Serimaa, R., 1995, *Macromolecules*, **28**, 7779.

[11] Motamedi, F., and Smith, P., (in preparation).