Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Zhou, B. , Iannacchione, G. S. and Garland, C. W.(1997) 'Calorimetric study of phase transitions for octylphenylthiolpentyloxybenzoate in silica aerogels', Liquid Crystals, 22: 3, 335 — 339
To link to this Article: DOI: 10.1080/026782997209405
URL: http://dx.doi.org/10.1080/026782997209405

LIQUID CRYSTALS, 1997, VOL. 22, NO. 3, 335–339

Calorimetric study of phase transitions for octylphenylthiolpentyloxybenzoate in silica aerogels

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(*Revised version received 14 October 1996; accepted 6 November 1996*)

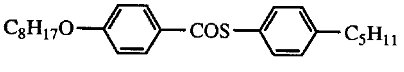
An a.c. calorimetric study has been carried out on octylphenylthiolpentyloxybenzoate (8S5) in three silica aerogels with mass densities $\rho = 0{\cdot}08$, $0{\cdot}17$ and $0{\cdot}36\,\mathrm{g\,cm^{-3}}$. Results for the least porous aerogel ($\rho = 0{\cdot}36$) are completely consistent with those reported previously for 8CB in the same aerogel. Freezing of 8S5 damaged the more porous $\rho = 0{\cdot}08$ and $0{\cdot}17$ aerogels by creating internal voids and cracks that are large compared with the intrinsic pore size. As a result, overlapping sharp bulk-like C_p features and rounded features due to 8S5 in residual aerogel pores were observed, and no quantitative separation of these features could be achieved.

1. Introduction

The behaviour of fluid systems confined in porous media is a topic of considerable current interest since it involves effects of quenched disorder as well as finite size. Numerous studies have been made using liquid crystalline materials [1]. In particular, the phase transitions of octylcyanobiphenyl (8CB) in silica aerogels have been investigated with light scattering [2–4], X-rays [5, 6], and a.c. calorimetry [2, 7]. The low density (high porosity) and fractal structure of silica aerogels makes them an attractive random porous medium.

Bulk 8CB exhibits nematic (N)–isotropic (I) and smectic A (S_A)–nematic transitions that have been well characterized [7]. The smectic phase is a partial bilayer (S_{A_d}), and the nematic range is moderately narrow (6·9 K). As a result of coupling between smectic and nematic order parameters, the second order N–S_A transition has an effective critical heat capacity exponent $\alpha_{\mathrm{bulk}} \simeq 0{\cdot}3$. In aerogels, both N–I and N–S_A heat capacity peaks are shifted to lower temperatures and are significantly rounded. This is especially true of the N–S_A C_p peak, which is strongly suppressed in magnitude, broadened, and severely rounded (see figure 7 in [7]). No N–S_A critical exponent analysis was possible for the 8CB/aerogel samples, and indeed, no true long range smectic order is achieved [6].

The present work involves a calorimetric study of the nonpolar liquid crystal 4-*n*-octylphenylthiol-4′-*n*-pentyloxybenzoate (8S5)



in three aerogels that are the same as those used in the earlier 8CB/aerogel study. Bulk 8S5 exhibits N–I, N–S_A, S_A–S_C and S_C–Cr transitions, where S_C is the tilted smectic C phase and Cr denotes a rigid crystalline phase [8]. Since the nematic range is fairly wide (~23 K), the N–S_A critical C_p exponent is consistent with the theoretical 3D-*XY* value $\alpha_{XY} = -0{\cdot}007$ [8, 9]. Furthermore, the integrated N–S_A enthalpy $\delta H_{NA}(\mathrm{bulk})$ is considerably larger than that for 8CB. The bulk S_A–S_C transition is well described by extended Landau theory [8, 10].

The goal of the present study was to characterize the effect of aerogels on the 8S5 liquid crystal phase transitions, with emphasis on S_A–S_C and N–S_A (where the bulk C_p exponent differs significantly from that of 8CB). This goal has been achieved for the lowest porosity aerogel (empty gel mass density $0{\cdot}36\,\mathrm{g\,cm^{-3}}$) but was frustrated by the severe effects of liquid crystal freezing on the two higher porosity aerogels (densities 0·08 and $0{\cdot}17\,\mathrm{g\,cm^{-3}}$). The freezing of 8S5 in these aerogels causes substantial damage to the gel, creating large internal cracks and voids that contain bulk-like pockets of liquid crystal. The latter seriously obscures the behaviour of 8S5 dispersed in the remaining porous network of the gel. No quantitative separation of C_p contributions from the large voids and the residual pores can be made. Furthermore, the nature of the pore structure remaining after freezing damage is not known.

2. Procedures

The aerogels used in the present study were from the same batches as those used for the calorimetric study of

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8CB/aerogels [7]. They were prepared by base-catalysed polymerization of tetramethylorthosilicate and have a fractal network structure in which the internetwork voids ('pores') have average pore chords L ranging from 700 ± 100 Å ($\rho=0{\cdot}08$) to 430 ± 65 Å ($\rho=0{\cdot}17$) to 180 ± 45 Å ($\rho=0{\cdot}36$), where ρ is the mass density of the empty aerogel in g cm^{-3} units. The volume fractions ϕ_P of pores in the gels are 0·945, 0·90 and 0·79, respectively. Further details are given in [7].

The filling procedure is of considerable importance. Aerogel samples were prepared in vacuum by heating 8S5 into the isotropic phase and allowing a thin slab of aerogel to fill slowly by capillary action. This gentle filling leaves the aerogel structure intact and does not create any empty regions [2,7]. Before sealing the filled aerogel into a silver cell, its surface was lightly dried with filter paper to remove superficial excess bulk liquid crystal. Sealing the cell and installing it in the calorimeter was carried out at room temperature. In the case of 8CB, the bulk material crystallizes at ~293 K but crystallization of 8CB in aerogels is suppressed to ~273 K [1]. Thus 8CB/aerogel samples do not freeze during the handling and mounting procedure. The melting point of bulk 8S5 is higher (~331 K), and our data for the $\rho=0{\cdot}08$ and $\rho=0{\cdot}17$ aerogel+8S5 samples indicate that freezing occurs at room temperature.

The a.c. calorimetry technique has been described elsewhere [11]. In essence, an a.c. power input causes an oscillatory temperature response $\Delta T_{\text{a.c.}}\, e^{i(\omega t+\phi)}$ for the sample, which is mounted in a sealed silver cell. The amplitude $\Delta T_{\text{a.c.}}$ determines C_P, and the phase shift ϕ provides a useful qualitative indication of two-phase coexistence if it occurs (at a first-order transition). The specific heat, C_P per gram of liquid crystal, is determined from equation (1):

$$C_P = \frac{C_P(\text{obs}) - C_P(\text{empty cell} + \text{empty gel})}{m} \qquad (1)$$

where m is the mass of liquid crystal (typically 30 mg) in the aerogel sample.

3. Results and discussion

Specific heat data for 8S5 in aerogels with densities $\rho=0{\cdot}08$, 0·17 and 0·36 g cm^{-3} are given over the range 320–365 K in figures 1–3. The inset in figure 1 shows bulk 8S5 C_P data from [8] over the range 321–350 K (data above 350 K are not available). The bulk 8S5 C_P data of Marinelli *et al.* [9] are high-resolution N–S$_A$ data over the narrow range 335·7–336·8 K which are described by the critical exponent $\alpha=-0{\cdot}022$. These data agree well over this limited range with the data from [8].

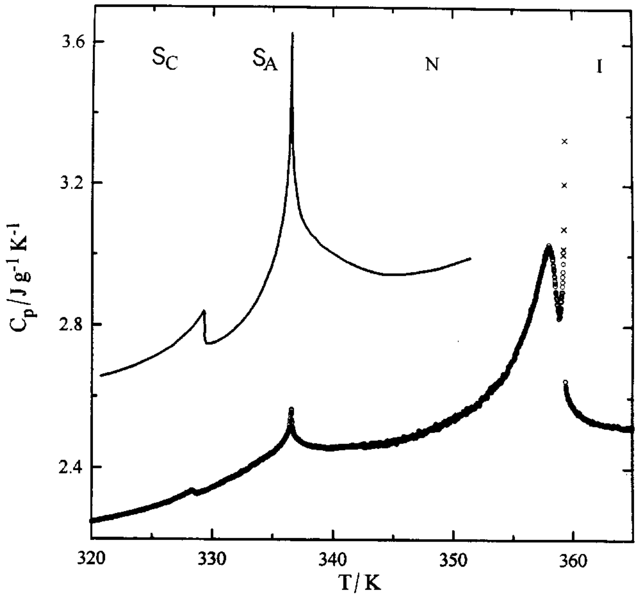

Figure 1. Temperature variation of specific heat C_P for 8S5 in an aerogel with density $\rho=0{\cdot}08$ g cm^{-3}. The solid curve shows C_P data for bulk 8S5 from [8]. The points denoted by × represent data obtained in a two-phase N + I coexistence region of bulk-like 8S5. See text for further details.

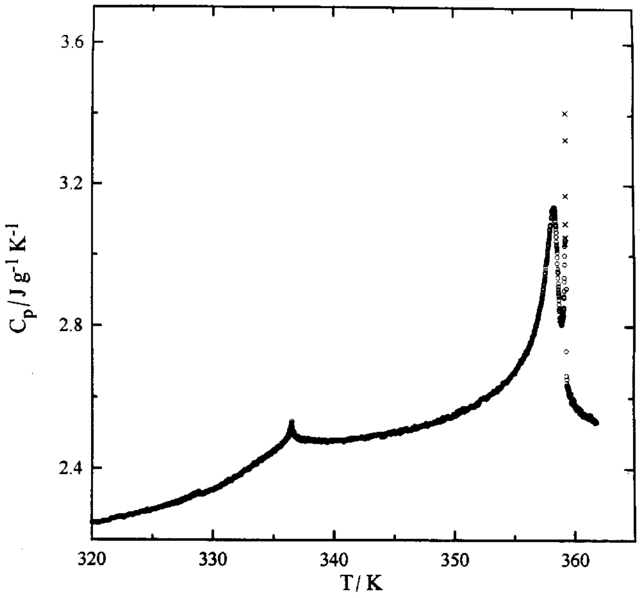

Figure 2. Temperature variation of C_P for 8S5 in an aerogel with density $\rho=0{\cdot}17$ g cm^{-3}. See figure 1 legend and text for further details.

3.1. *8S5 in $\rho=0{\cdot}36$ aerogel*

In figure 3 there is a very small sharp C_P spike at a temperature just above the large rounded N–I aerogel peak. The five points in this spike, denoted by ×, are due to a very small amount of excess bulk liquid crystal on the surface of the aerogel and represent artificial

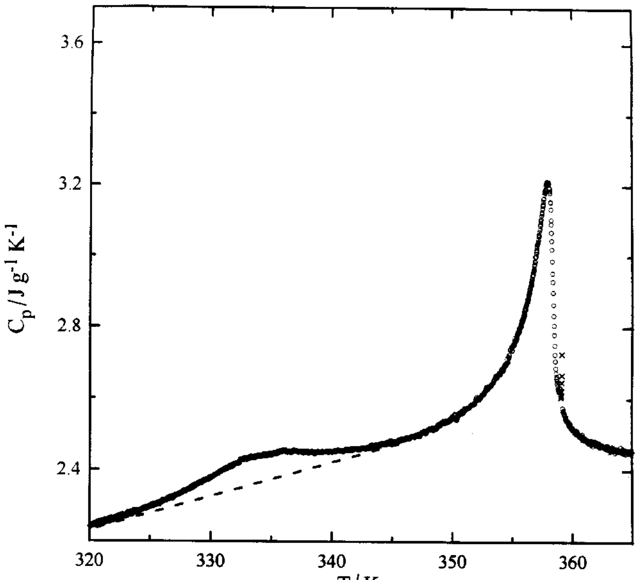

Figure 3. Temperature variation of C_p for 8S5 in an aerogel with density $\rho=0{\cdot}36\,\mathrm{g\,cm^{-3}}$. The five points at $\sim 359{\cdot}25$ K denoted by × are due to a very small excess of bulk liquid crystal on the surface of the aerogel. See text for further details.

C_p(coex) values in the bulk two-phase N–I coexistence region. This interpretation is confirmed by anomalous phase shift ϕ data, which are always seen when N and I phases coexist at the bulk first order N–I transition. Similar surface N–I C_p(coex) spikes were also observed for 8CB in aerogels [7]. The dashed curve drawn below the broad N–S$_A$ aerogel peak represent the tail of the N–I C_p curve and serves as the C_p(background) value that would be expected in the absence of a N–S$_A$ contribution.

The results presented for 8S5 in the $\rho=0{\cdot}36$ aerogel are completely consistent with 8CB data in this aerogel [7]. The size (integrated area) of the N–I peak associated with this transition for 8S5 in the pores of the gel ($4{\cdot}4\pm0{\cdot}1\,\mathrm{J\,g^{-1}}$) is comparable to that for 8CB ($5{\cdot}23\pm0{\cdot}05\,\mathrm{J\,g^{-1}}$). Also the shifts $\Delta T_{\mathrm{NI}}=T_{\mathrm{NI}}(\text{aerogel})-T_{\mathrm{NI}}(\text{bulk spike})$ are very similar: $-1{\cdot}23$ K for 8S5 and $-1{\cdot}31$ K for 8CB. The broad N–S$_A$ feature is larger in 8S5 as expected since $\delta H_{\mathrm{NS_A}}=\int\Delta C_p(\mathrm{N{-}S_A})\,\mathrm{d}T$ is larger for bulk 8S5 than for bulk 8CB. However, the ratio $\delta H_{\mathrm{NS_A}}(\text{gel})/\delta H_{\mathrm{NS_A}}(\text{bulk})$ is almost identical for these two materials: 0·285 for 8S5 and 0·298 for 8CB. Furthermore, the shift in the effective N–S$_A$ 'transition' temperature (centre of the broad N–S$_A$ peak) relative to the bulk critical temperature T_c is very similar: $T_{\mathrm{NS_A}}(\text{aerogel})-T_c(\text{bulk N–S}_A)=-2{\cdot}6$ K for 8S5 and $-2{\cdot}7$ K for 8CB [7]. No evidence was observed for a heat capacity feature associated with a S$_A$–S$_C$ transition for 8S5 in this aerogel.

There is no evidence of damage to this $\rho=0{\cdot}36$ aerogel due to 8S5 freezing. Either the crystallization temperature is sufficiently suppressed in this 180 Å pore size aerogel so that 8S5 does not freeze under our operating conditions, or this high density aerogel is mechanically strong enough to withstand 8S5 freezing without serious deformation.

3.2. $\bar{8}$S5 in $\rho=0{\cdot}08$ and $0{\cdot}17$ aerogels

Both figures 1 and 2 provide clear indications of the presence of substantial amounts of bulk-like 8S5 in the aerogel, as detailed below. The sharp high temperature N–I peak for these samples does not consist merely of a few N + I coexistence points with characteristic anomalies in the phase shift ϕ, as in figure 3 and in all the 8CB/aerogel samples reported in [7]. Here there are numerous points with C_p and ϕ behaviour corresponding to a bulk N–I pretransitional wing. Thus the N–I region is a composite of two comparable features—a bulk-like C_p(NI) and a temperature-shifted and rounded C_p(NI, aerogel) contribution. Even more dramatically, there is a bulk-like singular N–S$_A$ peak riding on top of a smeared and rounded aerogel N–S$_A$ feature. This double structure in the N–S$_A$ region is easiest to see in figure 2.

We feel confident that the bulk-like 8S5 resides in large (compared to the original pore size) cracks and voids internal to the aerogel and is not a surface excess. Several samples of 8S5 in the $\rho=0{\cdot}08$ aerogel were studied, and the sample shown in figure 1 was filled to only 70 per cent of its capacity and was carefully surface dried. After the experimental runs were complete, the sample was removed and microscopically examined. The surface was 'clean', showing no sign of a bulk liquid crystal coating, but the slab exhibited numerous visible cracks filled with solid 8S5. Furthermore, another $\rho=0{\cdot}08$ aerogel filled with 8S5 and surface dried exhibited a prominent melting transition at 331·07 K on heating. For that sample the N–S$_A$ specific heat peak was reproducible on heating and cooling runs and could be fitted with a power law expression involving either the 3D-XY critical exponent $\alpha=\alpha_{XY}=-0{\cdot}007$ or the effective bulk value $\alpha=-0{\cdot}022$ reported in [9]. However, this fit with a bulk critical exponent is suspect since (*a*) range shrinking is not too stable and the correction-to-scaling terms differ from bulk values and (*b*) the fit accounts for the entire N–S$_A$ excess heat capacity leaving no rounded aerogel-like contribution. This is unlikely in view of the rounded aerogel N–I peak for this gel and the qualitatively obvious presence of a rounded N–S$_A$ C_p peak lying under the sharp N–S$_A$ feature in the less porous $\rho=0{\cdot}17$ aerogel. Thus we believe that the N–S$_A$ transition for 8S5 in the large voids may not be completely the same as that for pure bulk 8S5, but a unique description of this feature cannot be achieved with the present data on damaged $\rho=0{\cdot}08$ and $\rho=0{\cdot}17$ aerogels.

Unfortunately, the sharp N–S_A peak and the underlying rounded aerogel N–S_A feature are impossible to separate into two well-defined contributions for the reasons described above. Furthermore, we do not know the relative masses of the two types of 8S5 (bulk-like liquid crystal in large cracks and voids created by the strain associated with 8S5 freezing and liquid crystal dispersed in the remaining narrow pores of the aerogel) and we have no information about the residual pore structure of a damaged aerogel. One indication that a significant fraction of 8S5 occupies the large voids and cracks in damaged $\rho=0{\cdot}08$ and $\rho=0{\cdot}17$ aerogels can be seen from the relative size of the temperature-shifted and rounded C_p(NI, aerogel) peaks in various aerogels. As shown in figures 1–3, the C_p(NI, aerogel) feature is *smaller* in the $\rho=0{\cdot}08$ and $\rho=0{\cdot}17$ gels than in the $\rho=0{\cdot}36$ gel. This trend is opposite to that observed for 8CB in these aerogels [7], which is consistent with the destruction of narrow pores and the creation of large voids due to 8S5 freezing. It should be pointed out that the bulk-like nematic range is the same in figures 1 and 2 (23·0 K), which agrees well with the bulk value (23·2 ± 0·2 K). Note also that there must be a substantial (but not quantitatively determinable) bulk-like N–I heat capacity tail in the N phase. This makes it impossible to extract well-defined ΔC_p(N–I) values for the aerogel contribution.

Figures 1 and 2 both exhibit a small mean-field S_A–S_C heat capacity feature at ~328 K. Since this feature is observed only when a singular N–S_A contribution appears, it is most likely that this S_A–S_C transition occurs only in the large bulk-like voids of damaged aerogels. This conclusion is supported by a recent study of heptyloxybenzylidene butylaniline (7O·4) in the same two aerogels where no freezing damage has occurred. No S_A–S_C heat capacity feature was observed in these aerogels when prepared so that no excess bulk 7O·4 remained on the surface [12]. Since $\Delta C_p(S_A$–$S_C)$ is a large peak in bulk 7O·4, this provides a sensitive test of the absence of this transition for liquid crystals in even the high porosity aerogels.

As a final test of the concept that freezing of a liquid crystal in a fragile (low density) aerogel can create large cracks and voids that give rise to bulk-like liquid crystal phase transition behaviour, we have carried out an experiment on 4O·8, butyloxybenzlidene octylaniline, in a $\rho=0{\cdot}08$ aerogel. Bulk 4O·8 exhibits the phase sequence CrK–plastic CrB–S_A–N–I, with the melting point for the rigid crystal K being 311·2 K [13]. Kutnjak and Garland [14] have carried out an extensive series of heat capacity measurements on such a 4O·8/aerogel sample covering the range from plastic crystal B to isotropic phases. These studies showed large aerogel features with very small and stable bulk spikes due to a very small surface excess of bulk 4O·8. The results were reproducible over a period of more than one month during which the temperature did not fall as low as 311 K (i.e., no crystal K freezing), although the system was cycled into and out of the plastic crystal B phase several times [14]. Indeed, the sample was originally prepared holding the temperature always above 311 K. After the experiments reported in [14] were completed, the sample was stored for more than two months at room temperature in a dessicator, during which time the 4O·8 froze into the crystal K phase. A new heat capacity run on this sample showed dramatic changes: all the liquid crystal/aerogel C_p features were markedly diminished in magnitude and bulk-like 4O·8 C_p features were now large and similar in character to those observed in pure bulk 4O·8 [13].

4. Conclusions

In conclusion, the N–I and N–S_A phase transition behaviours for 8S5 in the $\rho=0{\cdot}36$ aerogel are completely consistent with those reported for 8CB in the same aerogel [7]. This indicates that neither the nonpolar nature of 8S5 nor the 3D-XY character of the N–S_A heat capacity in bulk 8S5 play an important role in determining the N–I or N–S_A phase behaviour in this aerogel. However, higher porosity and more fragile aerogels ($\rho=0{\cdot}08$ and $\rho=0{\cdot}17$) were substantially damaged by the freezing of 8S5 into its rigid crystal phase. As a result, large voids and cracks were formed and the 8S5 in these regions exhibits phase transition behaviour qualitatively similar to that in bulk 8S5. The 8S5 remaining in the residual pore structure of these damaged high-porosity aerogels exhibited phase behaviour similar to that for 8CB in such aerogels, but detailed analysis is not possible due to the presence of the large bulk-like C_p features. The avoidance of freezing is, thus, a crucial condition for the study of liquid crystal phase behaviour in high-porosity aerogels.

Finally, the S_A–S_C transition seems to be completely suppressed by the random-field disorder induced by the aerogel network since no S_A–S_C transition was seen for 8S5 in the undamaged $\rho=0{\cdot}36$ aerogel and small S_A–S_C features in the damaged high porosity aerogels appears to arise from bulk-like material in the large-scale voids. This absence of S_A–S_C transitions for liquid crystals in undamaged aerogels is confirmed by recent studies of aerogel-confined 7O·4 [12].

The authors wish to thank N. A. Clark for stimulating discussions. This work was partially supported by the MRSEC program of the National Science Foundation under grant DMR-9400334 and partially under NSF grant DMR-9311853.

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