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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Young, M. , Pitsi, G. , Li, M. -H. , Nguyen, H. -T. , Jamee, P. , Sigaud, G. and Thoen, J.(1998) 'An adiabatic scanning calorimetry study of a chiral liquid crystal tolane with blue phases and twist grain boundary phases', *Liquid Crystals*, 25: 3, 387 – 391

To link to this Article: DOI: 10.1080/026782998206191

URL: <http://dx.doi.org/10.1080/026782998206191>

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An adiabatic scanning calorimetry study of a chiral liquid crystal tolane with blue phases and twist grain boundary phases

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(Received 26 February 1998; accepted 14 April 1998)

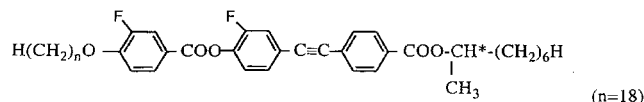
High resolution adiabatic scanning calorimetry (ASC) was employed to study the phase behaviour exhibited by the chiral liquid crystal material (*R*)-1-methylheptyl 3'-fluoro-4'-(3-fluoro-4-octadecyloxybenzoyloxy)tolane-4-carboxylate (FH/FH/HH-18BTMHC). We report on the heat capacity of the different phases and phase transitions as well as the enthalpy changes of the material showing a phase sequence Cr–SmC*–TGBC–TGBA–BPI–BPII–BPIII–I. While the presence of the BPI phase was observed in previous DSC studies only on cooling the sample, our ASC measurements detected this phase also in the heating runs at sufficiently slow scanning rates. Indications of smectic order still present in the blue phases, as recently reported from X-ray scattering experiments, are also observed.

1. Introduction

Chiral liquid crystals are an important class of materials, not only because of their complex polymorphism, but also because they exhibit an elaborate array of phenomena which have very fundamental connections to other problems encountered in condensed matter physics research. It is a well known fact that the transition from the nematic phase to the smectic A phase is analogous to the transition from a normal metal to a superconducting metal. Analogies such as this one are an interesting feature of liquid crystal systems and have led to the prediction of some new phases found to occur only in chiral liquid crystal systems. Among these phases are the so-called defect phases, or blue phases (BPs), typically occurring between the chiral nematic (N*) and the isotropic phase, and the twist grain-boundary phases (TGBs) [1].

Recently, the Bordeaux group [2] reported the observation of a completely new phase sequence I–BPs–TGBA–TGBC–SmC* in a fluoro substituted chiral tolane derivative where the blue phases are observed for the first time between the isotropic phase and the TGBA phase in the absence of a cholesteric phase. The chiral compound is (*R*)- or (*S*)-1-methylheptyl 3'-fluoro-4'-(3-fluoro-octadecyloxybenzoyloxy)tolane-4-carboxylate (simply named FH/FH/HH-18BTMHC). The core is benzoyloxytolane (BT) and the chiral centre

is linked to the core via an ester group in the 1-methylheptyl carboxylate moiety (MHC), while FH/FH/HH describes the fluorine substitution in the three aromatic rings and 18 refers to the number of carbons in the aliphatic chain. The chemical structure of the compound is as follows:



Apart from the fluorine substitution, this molecule has basically the same chemical structure as those compounds previously investigated by Nguyen *et al.* [3] which exhibit the TGBA phase.

The mesomorphic properties investigated by polarizing optical microscopy, differential scanning calorimetry (DSC) and X-ray structural analyses, as well as helical pitch measurements of a number of members of the FH/FH/HH-*n*BTMHC series have been described very recently by Li *et al.* [4]. In this paper we report on the results obtained by high resolution adiabatic scanning calorimetry (ASC) employed to study the phase behaviour exhibited in the chiral liquid crystal material FH/FH/HH-18BTMHC. From the optical microscopy and DSC study by Li *et al.* [2, 4] we know that this material exhibits a novel phase sequence Cr–SmC*–TGBC–TGBA–BPII–BPIII–I on heating and Cr–SmC*–TGBC–TGBA–BPI–BPII–BPIII–I on cooling. It should be noted that the DSC technique is inadequate

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for determining whether these phase transitions are continuous (i.e. second order) or weakly first order (discontinuous). Moreover, the enthalpy changes associated with the different phase transitions, and/or the effect of fluctuations on the behaviour of C_p in pre-transitional temperature regimes, as well as the details of the C_p anomalies can only be determined with the use of high resolution calorimetry (ASC or AC) [5, 6]. The ASC method that is used here has already proven its merits in our earlier calorimetric investigations on liquid crystals [7–10] and on the fullerite C_{60} [11].

2. Theoretical background

Chirality in liquid crystals produces a fascinating array of equilibrium phases with orientational structures at length scales much larger than typical molecular dimensions. While the N* and SmC* phases are very well known liquid crystal phases, the BP (BPI, BPII and BPIII) and TGB phases (TGBA, TGBC and TGBC*) are less known due to the fact that the evidence for their existence is of recent date.

The structure of the blue phases can be described as a cubic, columnar arrangement of molecules, and within these columns local nematic order is retained. The BPI structure is body-centred cubic (bcc) while BPII is face-centred cubic (fcc). The microscopic structure of BPIII has yet to be elucidated by structural studies.

The twist grain boundary phases (TGB) are other kinds of frustrated phase exhibited by chiral molecules. The TGBA phase was predicted on the basis of de Gennes's paper [12] from an analogy between the cholesteric to smectic transition and the normal to superconductor transition in metals under an external magnetic field. The theoretical structure of this new phase was predicted by Renn and Lubensky [1(e)] and first demonstrated in 1989 by Goodby *et al.* [13]. The TGBA phase consists of slabs of smectic A material regularly stacked in a helical fashion along the axis parallel to the smectic layers. Adjacent slabs are continuously connected via a grain boundary which consists of a grid of parallel equispaced screw dislocation lines to allow for the helical twist.

Renn and Lubensky also proposed the existence of the TGBC and TGBC* phases [14] in which the smectic slabs are respectively, SmC and SmC*. Our sample possesses both TGBA and TGBC structures. The analogies, as described by Renn and Lubensky [15], between TGB phases and superconducting materials naturally provide motivation for these calorimetric studies on this liquid crystal compound.

3. Experimental

The measurements have been carried out with the same adiabatic scanning calorimeter as that used pre-

viously for measurements near the NAC-multicritical point in mixtures of 8O5 and 8O6 [16(a)] and later on for studies of chiral–racemic mixtures of the cholesteryl ester CE6 [16(b)]. Full details of such a calorimeter and its possible modes of operation can be found elsewhere (Thoen *et al.* [5]). In our principal modes of operation of the scanning calorimeter, we apply (or extract) a constant heating (cooling) power P to (from) the measuring cell. The temperature versus time curve $T(t)$ is the principal experimental result. The $T(t)$ experimental curve directly results in the enthalpy of the sample [8]:

$$H(T) = H(T_s) + P(t - t_s) \quad (1)$$

where the index s refers to the starting conditions of the heating (cooling) run. The specific heat capacity $C_p(T)$ can also be derived from the direct $T(t)$ data by means of the relation

$$C_p = P/T. \quad (2)$$

The rate \dot{T} is obtained via numerical differentiation of $T(t)$. With this method, it is thus possible to obtain information on the temperature dependence of the enthalpy and the specific heat capacity and it also allows us to measure the latent heats if a first order phase transition is involved. This is one of the main advantages compared either with the AC-calorimetric method, where no latent heats can be measured, or to DSC, where true latent heats can hardly be distinguished from pre-transitional increases of the enthalpy related to specific heat capacity anomalies.

During a temperature scan, the temperature of the shield (surrounding the cell which is suspended by thin threads inside this evacuated shield) is controlled to follow the sample temperature. This is achieved to within 0.2 mK by a computer controlled feedback system. Heating as well as cooling runs have been carried out at very slow scanning rates, typically of the order of 1 mK min⁻¹. The measuring cell has a maximum sample volume of about 0.5 cm³ and contained a sample mass of 399.2 mg. The FH/FH/HH-18BTMHC sample studied was obtained from the 'Centre de Recherche Paul Pascal'†.

4. Results

We have conducted ASC measurements for the chiral material (*R*)-FH/FH/HH-18BTMHC over the temperature range 60 to 80°C. Typical ASC scans showing the specific heat capacity anomalies [as defined in equation (2)] are shown in figures 1 and 2, recorded at 2 and 3.8 mK min⁻¹ (mean scanning rates), respectively.

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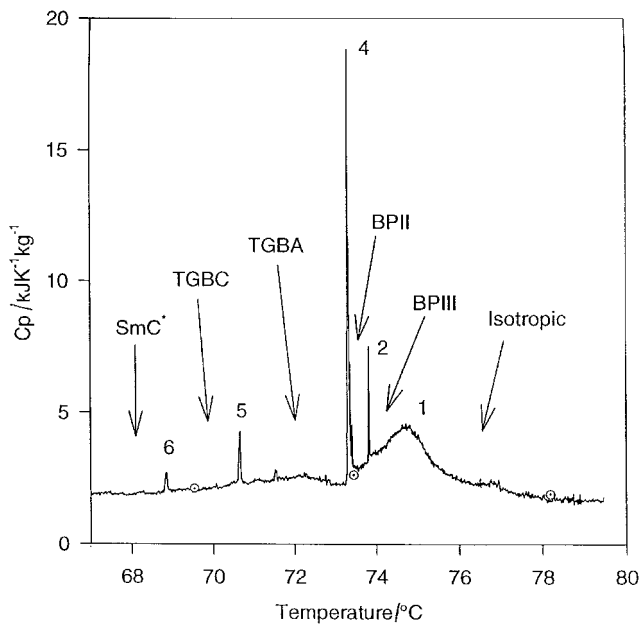


Figure 1. General overview for the specific heat capacity for the entire temperature range investigated and covering all phase transitions involving TGB phases and blue phases in FH/FH/HH-18BTMHC. Note that the narrow BPI phase and the BPI–BPII transition occurring between peaks (2) and (4) are shown in the detailed plot of figure 3. The data are obtained for a heating run (mean scanning rate 2.0 mK min^{-1}). The circles with dots represent data points obtained by the classical pulse method on the same sample confined to the same sample holder.

The heating scan of figure 1 shows the specific heat capacity anomalies associated with the phase transitions SmC^* –TGBC, TGBC–TGBA, TGBA–BPI, BPI–BPII and BPII–BPIII. The corresponding peaks are labelled 6, 5, 4, 3 and 2, respectively. The broad peak 1 is associated with the supercritical behaviour in the vicinity of the BPIII–Isotropic critical point and is not a phase transition as also observed in other compounds [17]. Our data confirm that no latent heat could be associated with this transition while also the data describing this peak 1 could not be fitted at all with a power law expression.

It is clear from figure 2 that the BPI–BPII phase transition (peak 3) is enhanced on cooling, while its presence in a warming scan can hardly be distinguished from peak 4 if plotted on the same temperature scale. Careful investigation only reveals the existence of a rather small peak (see figure 3), most likely corresponding to the BPI–BPII transition. This suggests that a stable BPI phase can exist between TGBA and BPII on heating. This was not observed in the DSC measurements of Li *et al.* [2] where a 200 mK min^{-1} heating rate was used (i.e. 100 times faster than the mean scanning rate in our ASC measurements). Supercooling of the TGBC phase

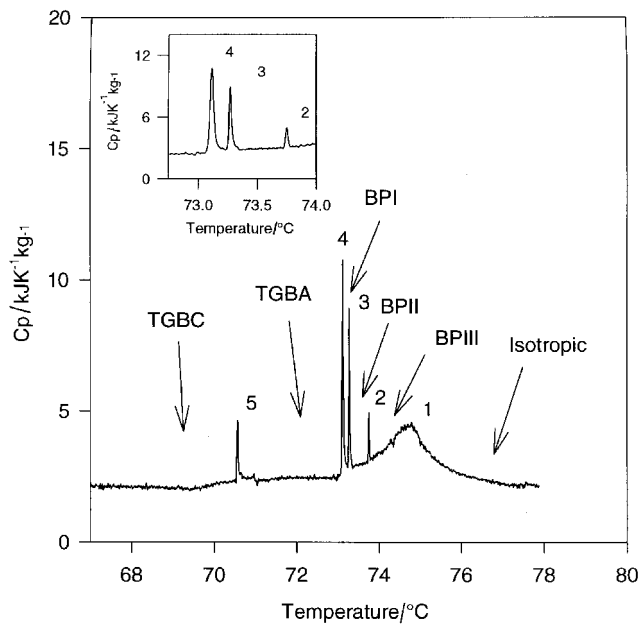


Figure 2. General overview for the specific heat capacity for the entire temperature range investigated as obtained from a cooling run (mean scanning rate 3.8 mK min^{-1}). The inset represents a detailed view of the BPI–BPII transition (peak 3) (with respect to peak 4) not so clearly present in the heating run.

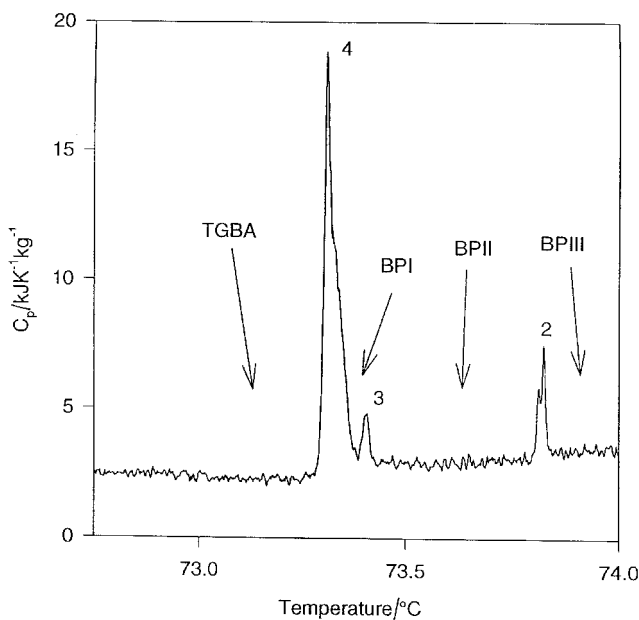


Figure 3. Detailed plot of the temperature dependence of the specific heat capacity of FH/FH/HH-18BTMHC near the TGBA–BPI and BPI–BPII transitions as obtained from a heating run.

extending down to crystallization explains why the TGBC– SmC^* transition is not displayed in the cooling run (figure 2).

Furthermore, a magnification of the TGBA–BPI transition peak (peak 4 in figure 1) clearly shows a shoulder on the right side (see figure 4) which might be attributed to some sort of smectic order still present in the blue phase, as recently found by Pansu *et al.* [18] in the same chiral compound. In their X-ray experiments it was found that smectic ordering still persists in blue phases with correlation lengths lower than the pitch. Kamien [19] proposed a general defect structure that can produce a smectic double twist that can be responsible for short range smectic order in blue phases.

In some low rate heating scans we found that the BPII–BPIII transition peak 2 showed some structure, as also shown in figure 3. Whether this is also due to some smectic order still present in the BP phase or has some other cause, e.g. some kind of surface melting effect, is not clear.

All our data indicate separate discontinuous phase transitions occurring for SmC*–TGBC, TGBC–TGBA, TGBA–BPI, BPI–BPII and BPII–BPIII. Indeed one of the strengths of the ASC technique is the direct determination of the enthalpies (and thus of the latent heat ΔH_L). A composite plot showing the enthalpy changes associated with peaks 2, 3, 4, 5 and 6 on heating is presented in figure 5. In this graph the relative enthalpy change for each transition i is plotted versus a shifted temperature scale $(\Delta T)_i = (T - T_0)_i$ with T_0 chosen in such a way that the height and the temperature dependence of the different transition energies can be compared with one another. It can be clearly seen that all

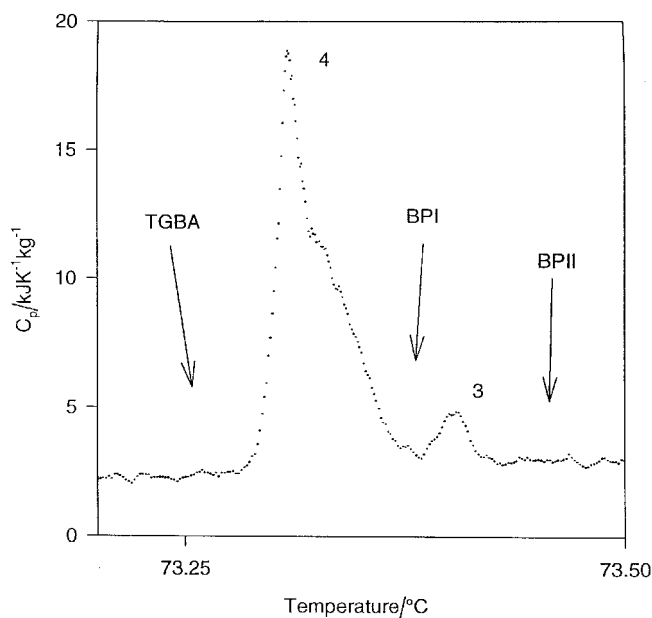


Figure 4. Blow up of the TGBA/BPI transition peak as obtained from a heating run and clearly showing a shoulder on the right side.

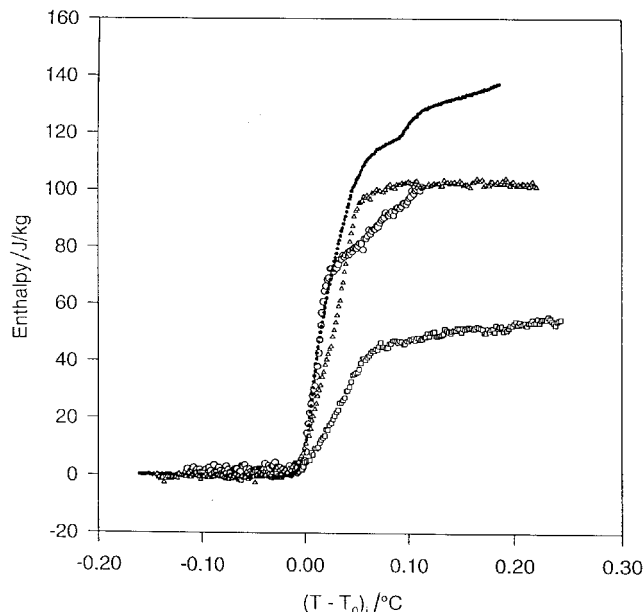


Figure 5. Enthalpy changes in the vicinity of the BPII–BPIII transition (open circles), the TGBA–BPI and BPI–BPII transitions (closed circles), the TGBC–TGBA transition (triangles), the SmC*–TGBC transition (squares). The enthalpy values for the TGBA–BPI and BPI–BPII transitions have been rescaled by a factor 0.2 for display purposes. The enthalpy changes for each transition i are plotted versus a shifted temperature scale for relative comparison.

transitions are first order. In the table, a summary is given of the values of the latent heats of the various transitions and the corresponding transition temperatures (corresponding to the C_p maxima), as well as the thermal hysteresis.

Theoretical calculations show that the TGBC–TGBA transition can be Ising-like [14] (as in the case of a liquid–gas critical point) in some chiral liquid crystal systems. This is not the case in our system. Our results for the enthalpy change show that this transition is definitely first order in this system. Our ASC results completely confirm the existence of a phase sequence I–BPs–TGBA–TGBC (in the absence of a cholesteric phase) in a relatively small temperature interval of about 10 K as recently observed by X-ray structural analysis and optical studies [4].

In on-going work, we are interested in determining the phase transition behaviour in binary mixtures of the right- and left-handed components of FH/FH/HH-18BTMHC. Such a mixture will naturally have a lower chirality than the pure, single-handed material, corresponding to a larger pitch for the twist phases. In this situation, one might expect to observe quite different behaviour at several of these phase transitions. Moreover, it should be possible to observe cross over

Table

Phase transition	T_{tr} heating ^a /°C	T_{tr} cooling ^b /°C	Thermal hysteresis/°C	Latent heat ΔH_L /J kg ⁻¹
1. BPIII–I	74.75	74.75	—	—
2. BPII–BPIII	73.823	73.750	0.073	60 ± 8
3. BPI–BPII	73.404	73.271	0.133	27 ± 8
4. TGBA–BPI	73.311	73.114	0.197	430 ± 45
5. TGBC–TGBA	70.659	70.564	0.095	86 ± 5
6. SmC*–TGBC	68.843	—	—	38 ± 4

^a Mean heating rate is 2 mK min⁻¹.

^b Mean cooling rate is 3.8 mK min⁻¹.

behaviour as a function of chirality, particularly in the vicinity of the BPIII–I transition. Recently, DSC measurements for a range of mixtures have determined the approximate concentration at which the BPIII–I critical end point occurs. Thus, we are currently extending our studies to such mixtures to determine precisely the heat capacity and enthalpy change in the vicinity of this critical point, as well as the behaviour at intermediate concentrations. Also the chirality effect on all the other transitions is under investigation.

This work was supported by the Fund for Scientific Research Flanders (Belgium) (FWO) (project no G.0264.97). The collaboration between the two laboratories was also supported through an exchange program between the Flemish Community and CNRS (France) (project no C97.003). M. Young thanks the Belgian American Educational Foundations and the FWO for postdoctoral fellowships.

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