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Liquid Crystals

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Online publication date: 11 November 2010

To cite this Article Ema, K. , Yao, H. , Takanishi, Y. , Takezoe, H. , Kusumoto, T. , Hiyama, T. and Yoshizawa, A.(2002) 'Anomalous behaviours of the heat capacity in a liquid crystal showing a re-entrant isotropic phase', *Liquid Crystals*, 29: 2, 221 – 225

To link to this Article: DOI: 10.1080/02678290110099448

URL: <http://dx.doi.org/10.1080/02678290110099448>

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Anomalous behaviours of the heat capacity in a liquid crystal showing a re-entrant isotropic phase

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(Received 30 May 2001; accepted 2 August 2001)

High resolution a.c. calorimetric measurements have been carried out on a liquid crystal 2-{4-[(R)-2-fluorohexyloxy]phenyl}-5-{4-[(S)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine (RSFPPY), determined the present measurement revealed precise temperature dependence of the heat capacity over a wide temperature range including the phase transition temperatures. The isotropic–chiral smectic C transition was anomalous in that it showed quite different behaviours depending on whether the measurement was made on heating or cooling that is attributed to the relaxational character of the transition. A new non-transitional feature in the isotropic phase was found, corresponding to a very broad heat capacity peak over a 30 K temperature range. This indicates an existence of a new phase, possibly some kind of blue phase, at the lower temperature side of the isotropic phase.

1. Introduction

Re-entrant optically isotropic phases have been observed in several liquid crystal systems, including some discotic crystals [1], a double swallow-tailed compound [2], etc. It has been recently found that the dichiral ferroelectric liquid crystal 2-{4-[(R)-2-fluorohexyloxy]phenyl}-5-{4-[(S)-2-fluoro-2-methyldecanoyloxy]phenyl}pyrimidine (RSFPPY) is another example

which exhibits a transition from an anisotropic smectic phase to a re-entrant optically isotropic phase [3]. The molecular structure and phase sequence of RSFPPY are shown in figure 1 [3]. Here Iso is the isotropic phase, IsoX is the re-entrant optically isotropic phase, SmX* and SmC* phases are smectic phases different from each other, and Cr is a crystal phase. We note that the phase sequence shown here were based on measurement by differential scanning calorimetry (DSC) with rapid temperature scanning [3], so that the transition temperatures do not always agree well with the present results,

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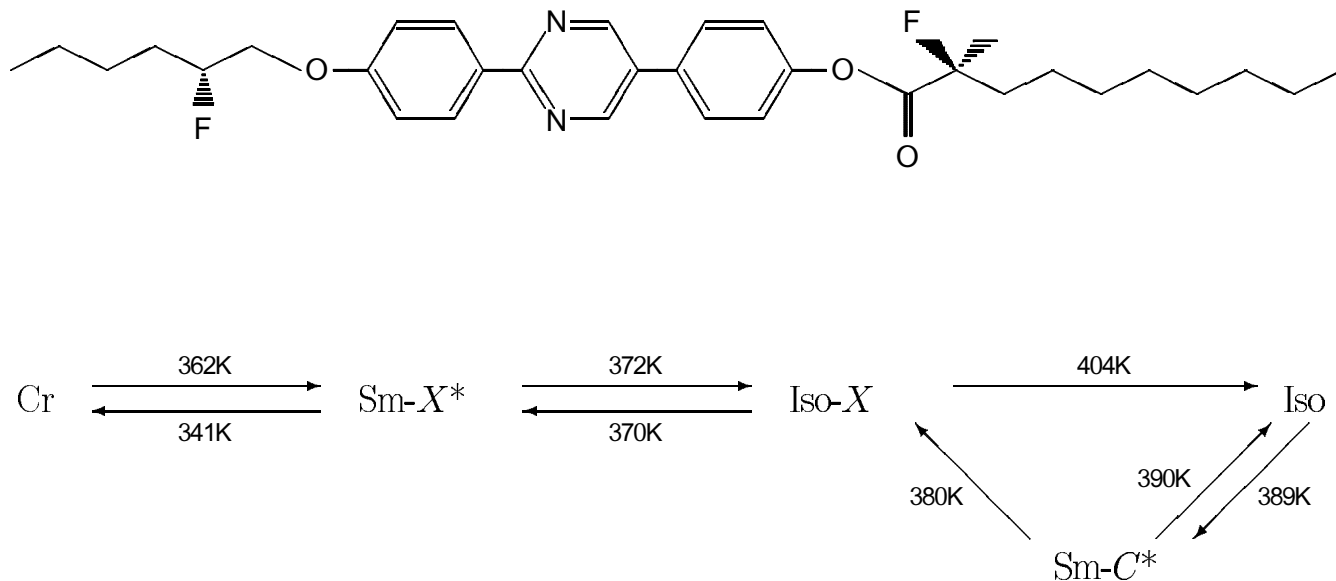


Figure 1. Molecular structure and phase sequence of RSFPY. The transition temperatures are based on the measurements in [3].

obtained with much slower scan rates. A significant result in the early DSC measurement was that an endothermic transition was observed on cooling from the SmC* phase to the IsoX phase. This quite unusual behaviour indicates the existence of marked supercooling in the appearance of the IsoX phase. Two possibilities were proposed in [3]: (1) the formation of the IsoX phase is very slow, (2) the formation and growth of the IsoX phase does not occur in the Iso phase. Scenario (2) has since been discarded since direct transition from the Iso to IsoX was observed in some cases. A preliminary X-ray diffraction (XRD) measurement did not identify the structure of the IsoX phase [3]. Very recently, Takanishi *et al.* [4, 5] carried out XRD measurements which revealed that the IsoX phase is cubic. The detailed character of the IsoX phase is, however, still not understood well.

So far, thermal measurements have been carried out only by DSC. Because very rapid temperature scan rates (0.1 K min^{-1} or higher) were used, the detailed temperature dependence of the heat capacity was not determined accurately. In this paper we report the results of high resolution a.c. calorimetric measurements on RSFPY. The present measurements have revealed precise temperature dependences of the heat capacity including anomalies accompanying the phase transitions. The results also show that the SmC* and SmX* phases may both be metastable and may only occur under special circumstances. In addition, a new non-transition al feature has been found in the Iso phase, corresponding

to a very broad heat capacity peak over 30 K. This may possibly be related to a supercritical evolution of some kind of blue phase structure, at the lower temperature side of the Iso phase.

2. Experimental

The heat capacity was measured using an a.c. calorimeter described elsewhere [6]. The liquid crystal samples were hermetically sealed into gold cells; three sample cells, containing 22.2, 16.0, and 5.9 mg of sample were studied. These will be referred to as the sample cells 1, 2, and 3. The results obtained for these cells were essentially identical except for some detailed behaviour in the immediate vicinity of the transition; the results for the cell 1 will therefore be given unless otherwise stated. The temperature was scanned very slowly during the measurement. The scan rate was about 2.5 mK min^{-1} in the transition region, which is slower than usual DSC scans by more than one order of magnitude. In a.c. calorimetry, the sample temperature is made to oscillate by an a.c. heat input, and the heat capacity is determined from the amplitude of the oscillation, T_{ac} . In the present measurements T_{ac} was several mK, which allows a very high temperature resolution in determining the temperature dependence of the heat capacity. The C_p values were determined as $C_p = (C_p^{obs} - C_p^{empty})/m$, where C_p^{obs} and C_p^{empty} are the heat capacities of the filled and empty cells, respectively, and m is the mass of the liquid crystal sample in grams.

3. Results and discussions

3.1. IsoX–SmX*–Cr transitions

The C_p data at relatively low temperatures are shown in figure 2. The anomaly due to the SmX*–IsoX transition is seen around 369 K on heating, and around 368 K on cooling, thus showing a thermal hysteresis of about 1 K. The Cr–SmX* phase transition occurs around 356 K on cooling, where a step-like anomaly in C_p is seen. On heating, the anomaly due to the Cr–SmX* phase transition is not seen clearly. Further, there is no temperature range where C_p data on heating match those assigned to the SmX* phase on cooling. Therefore it is probable that a direct transition from the Cr phase to the IsoX phase occurs on heating. This shows that the SmX* phase may be metastable and may only occur in special circumstances.

It is seen that the C_p shows no anomalous behaviour and remains at relatively low values in the IsoX phase. This suggests that the structure does not change significantly in the IsoX phase. On the other hand, particularly on cooling, the C_p anomaly due to the IsoX–SmX* transition can be seen as a lambda-shaped Landau-type anomaly. This implies that some kind of order is present in the SmX* phase, increasing with decreasing temperature.

3.2. Iso–SmC*–IsoX transitions

Anomalies due to the Iso–SmC*–IsoX phase transitions are observed around 387 K on cooling as seen in figure 2. The C_p data in this temperature region are shown with enlarged scales in figure 3. In this figure, closed circles represent typical behaviour observed on cooling, while open circles show typical behaviour on

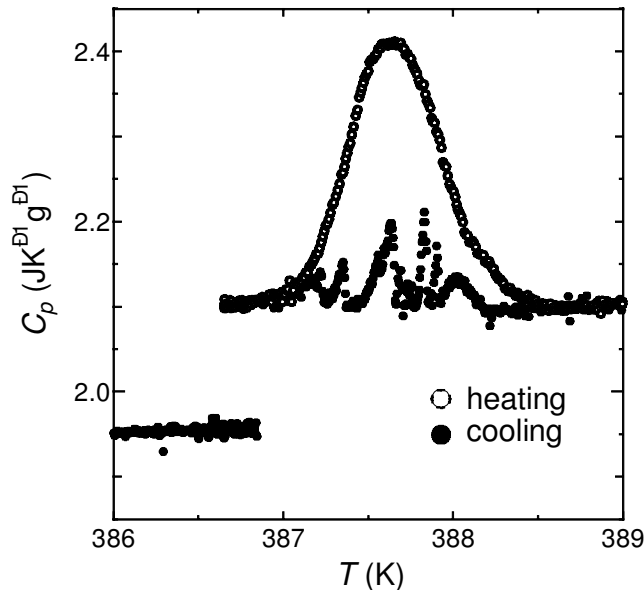


Figure 3. Temperature dependence of the heat capacity C_p near the Iso–SmC*–IsoX phase transitions. Closed circles represent data observed on cooling; open circles show heating data obtained by turning to heating from a cooling run within the SmC* phase.

heating, as seen on turning to heating from a cooling run within the SmC* phase. The heat anomaly accompanying the Iso–SmC* transition on cooling has a complicated structure with several peaks distributed over the range 387–388 K. On heating, C_p shows a single broad peak which is much larger in comparison with that seen on cooling. The detailed behaviour of the heat anomaly at the Iso–SmC* transition was not reproducible and differed for each run and each cell. However, the following general trends were found: (1) for each cell, the heating data always show larger anomalies than the cooling data; (2) one single peak is always observed on heating; (3) the shape of the anomaly on cooling becomes more complicated in the cell order 3, 2, and 1, i.e. in the order of increasing amount of liquid crystal contained; (4) the overall magnitude of the anomaly, on both heating and cooling, becomes smaller in the same order, i.e. the cells with smaller sample give larger anomalies.

A rough estimation of the apparent transition enthalpy obtained by the integration of the observed heat anomaly, assuming a somewhat arbitrary base line, yielded 0.2–0.3 J g⁻¹ on heating and 0.04–0.08 J g⁻¹ on cooling for cell 1, and 0.5–0.6 J g⁻¹ on heating and 0.2–0.3 J g⁻¹ on cooling for cell 3. All these values are much smaller than the former reported value 2.3 kJ mol⁻¹ = 4.3 J g⁻¹ based on a DSC measurement [3].

These results can be understood by assuming that the Iso–SmC* transition is first-order, and the observed anomaly corresponds to two-phase coexistence. In the

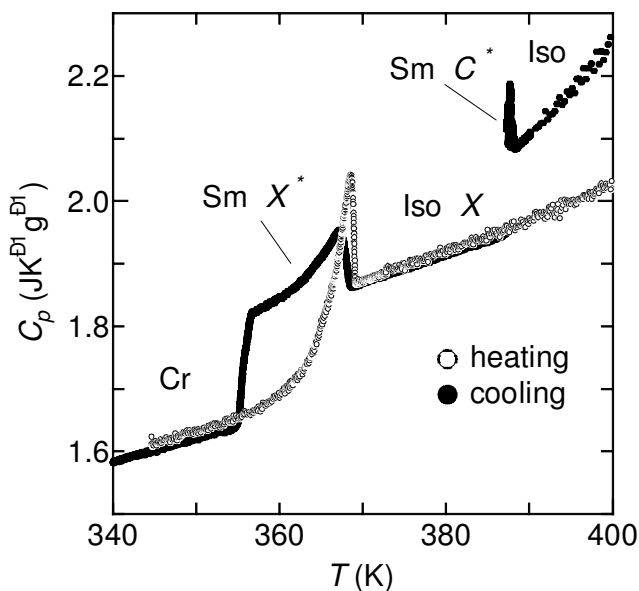


Figure 2. Temperature dependence of the heat capacity C_p of RSFPY in the low temperature region.

two-phase coexistence region, the temperature response of the sample includes a component from the normal heat capacity and one from the heat transfer due to the phase conversion which accompanies transfer of the latent heat. When the rate of the phase conversion is much slower than the heating period of the a.c. calorimetry, the contribution from the latent heat becomes negligible and the response of the sample is simply determined by the normal heat capacity. On the other hand, if the phase conversion rate is rapid enough, the integrated anomaly will coincide with the latent heat [7]. The present result indicates that the conversion rate, or the speed of phase boundary movement, is slower in comparison with the measuring frequency. The discrepancy of the observed data for heating and cooling implies that the conversion rate is slower in the cooling process than in the heating process. Qualitatively similar phenomena were also found, for instance, at the main transition of phosphatidylcholines [7, 8]. The explanation given above is also supported by the fact that the observed heat anomaly became larger, by about 20%, when the measurement frequency was lowered to $f_0/2$, where $f_0 = 0.03125$ Hz is the normal measurement frequency. As another indication of two-phase coexistence, it has also been found that the phase lag of sample temperature oscillation with respect to the a.c. heating shows an anomalous behaviour [9] over the same temperature range as that of the C_p anomaly.

In most cases reported so far for liquid crystal transitions, the width of the two-phase coexistence region is not so wide, being of the order of 100 mK. Therefore the present coexistence region in the Iso–SmC* transition of RSFPY, about 1 K, is rather wide. Because some other transitions in the present sample, such as the SmC*–IsoX, are rather sharp, it is unlikely that the broadness of the coexistence region of the Iso–SmC* transition is due to sample imperfection or inhomogeneity.

The SmC*–IsoX phase transition occurred at 386.9 K in the cooling run shown in figure 3, where an abrupt decrease in the C_p value is seen. It was found that the temperature of transition from the SmC* to the IsoX phase was not reproducible but depended on the thermal treatment history. When the sample had been kept in the SmC* phase or the Iso phase, especially at higher temperatures, it transformed into the IsoX phase more easily, showing a higher SmC*–IsoX phase transition temperature. In some cases, a direct transition from the Iso to the IsoX phase was observed on cooling. Such a tendency is in agreement with the fact that the SmC* phase is metastable and eventually transforms to the more stable IsoX phase. It was noted that the temperature range of the SmC* phase is much narrower than the DSC result [3, 10]. This discrepancy can be ascribed to the different temperature scan rates used in the

measurements. In the present measurement, the temperature scan rate was about 2.5 mK min^{-1} in this region, while the DSC data were taken with scan-rates not slower than 100 mK min^{-1} . We also note that the width of the SmC* phase observed in dielectric measurements diminishes as the cell thickness increases [5].

3.3 Anomalous behaviour in the Iso phase

Figure 4 shows the C_p data at higher temperatures obtained for cell 2. On heating, the IsoX–Iso phase transition is located at about 401 K, where a step-like anomaly is seen. In this case, the SmC* phase did not appear on cooling, and a direct transition from Iso to IsoX phase was observed around 389 K. It is noticed that C_p shows a very broad peak around 410 K over a temperature range of more than 30 K.

A qualitatively similar peak has been found in the isotropic phase of some chiral liquid crystals, and is supposed to correspond to a continuous (or supercritical) evolution from the blue-III phase (or ‘fog phase’) to the isotropic phase [11–14]. Recent observation by Takanishi *et al.* [4, 5] of a blue-coloured texture in the polarized microscope for RSFPY also gives evidence for a similarity between such systems. These facts establish that the broad C_p peak observed here for RSFPY corresponds to a non-transitional feature, possibly related to a supercritical evolution of some kind of blue ‘fog’ structure. A quantitative comparison of these systems deserves attention. A rough estimation of the integrated enthalpy associated with this broad peak has been made, assuming the normal part as shown by the dashed line

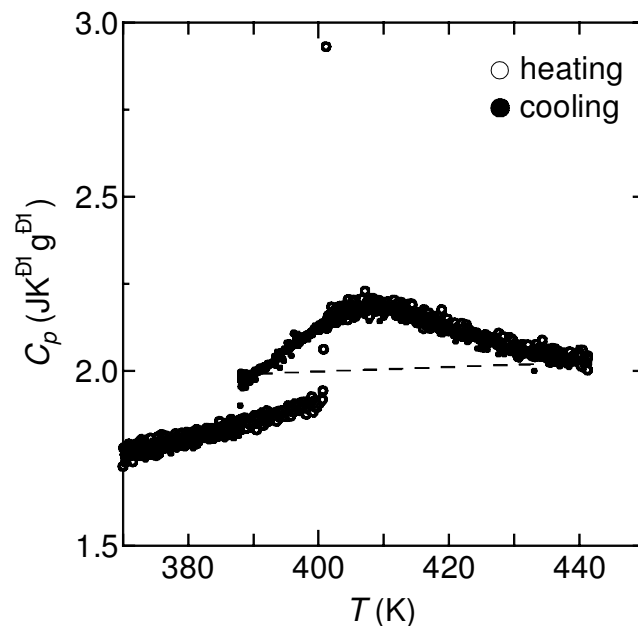


Figure 4. Temperature dependence of the heat capacity C_p of RSFPY in the high temperature region.

in figure 4, which gives 2.8 kJ mol^{-1} . This value is comparable with $0.344 \text{ kJ mol}^{-1}$ for S,S-MBBPC [12, 13], and $7.09\text{--}7.52 \text{ kJ mol}^{-1}$ for the trimesogen (R)-Cycle11(HF) [14].

On the other hand, the 30 K width of the peak observed in RSFPY is much wider than in other systems; 3–4 K or less in every case. At present we have no clear idea why the anomaly is so broad in RSFPY. It is to be noted, however, that the blue-coloured phase in RSFPY is definitely different from the ‘cholesteric’ blue phase in the sense that a layer structure is clearly observed for RSFPY by XRD [5]. It was also found that the correlation length in this temperature region is longer than for the normal blue and TGB phases. Further, a large CD signal was observed, indicating the existence of a macroscopic helical structure. From these considerations, it is probable that RSFPY exhibits a new kind of blue phase-like ordering.

This work was partly supported by Grant-in-Aid for Scientific Research from the Ministry of Education and Science, Japan, No. 12129204.

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