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Experimental studies on the B_7 phase of a banana-shaped achiral mesogen

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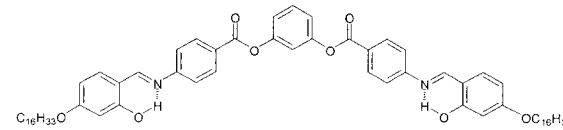
We report optical, X-ray, polarization and response time measurements on a new 'banana-shaped' mesogen. The material has a salicylaldimine segment in the linear part of the core, but is otherwise structurally similar to the mesogen first reported to show a banana mesophase. Textural and X-ray studies show that this mesophase has all the characteristics of the recently discovered B_7 phase. It is observed that the voltage required to obtain electrical switching is quite low compared with values for the few other materials exhibiting the B_7 phase.

1. Introduction

Till recently, the domain of ferroelectric liquid crystals [1] was limited to systems containing chiral molecules and having a tilted smectic phase. Subsequent findings of ferrielectricity and antiferroelectricity [2] supported this rule. Exceptions started to appear about a decade ago, the most interesting being that of bent-core 'banana-shaped' molecules [3]. When packed in smectic layers, the bent-core molecules result in layers with a polar character. Further, if the molecules become tilted, it will lead to chiral layer symmetry, although the molecules themselves are not chiral. Despite being a recent finding, results from a large number of investigations [4–6] have been reported on the mesophases formed by such banana-shaped molecules. As the molecular structural arrangement is yet to be fully established, the seven distinct phases of this type, observed to date, have been assigned temporarily the labels B_1 to B_7 [4, 5, 6]. Of these, the B_7 phase has attracted attention as it exhibits a spiral domain texture with single, double and triple coiled patterns [7]. In fact, the observation of such a pattern is direct evidence of the chiral nature of the phase. Till now this phase has been observed in only a few compounds [7–10]. In this paper we report X-ray, textural, spontaneous polarization $\mathbf{P}_s$ and switching time studies on a compound which exhibits the B_7 phase over a 70°C temperature range.

2. Results and discussion

The molecular structure of the compound used for this study is shown below. It is similar to that for the compound first reported [3] to show a B mesophase (the prefix B indicates that it is of the type exhibited by banana-shaped molecules), except for the fact that in the linear part of the core the Schiff's base segment is replaced by a salicylaldimine segment.



$$\mathrm{Cr} \xrightarrow{112.7^{\circ}\mathrm{C}\ [73.9\ \mathrm{J\,g^{-1}}]} \mathrm{B_7} \xrightarrow{172.7^{\circ}\mathrm{C}\ [23.8\ \mathrm{J\,g^{-1}}]} \mathrm{I}$$

The DSC thermogram obtained using heating and cooling modes (5°C $\mathrm{min^{-1}}$) is shown in figure 1. Only one mesophase, which as we shall see later has all the

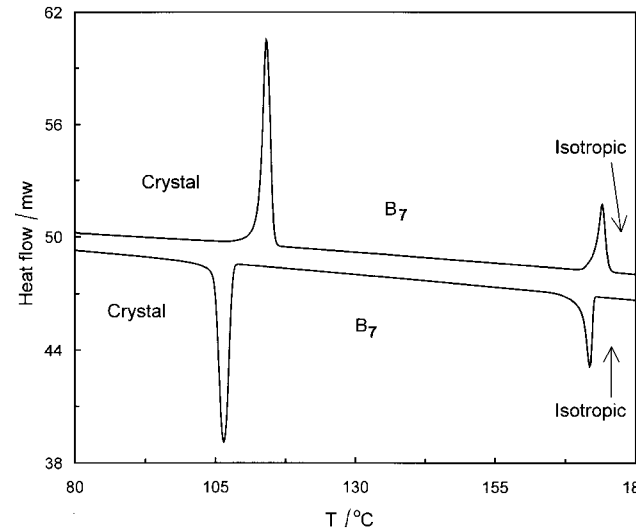


Figure 1. DSC traces showing the crystal to mesophase and the mesophase to isotropic transition. Heating/cooling rate is 5°C $\mathrm{min^{-1}}$.

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characteristics of the B_7 phase, is observed in both cycles. The enthalpy change associated with the melting transition seems to be larger than that for the B_7-isotropic transition. A similar observation was made for the B_7 phase of a fluoro substituted compound reported by Heppke *et al.* [10]. It must be remarked, however, that this feature is at variance with the behaviour observed for the homologous series first reported [7] to show the same phase sequence, viz., Cr–B_7–I.

On cooling the sample from the isotropic phase, the most commonly observed texture was the twisted filamentary texture (see figure 2). In fact, this texture indicates the presence of a helical structure although the system contains only achiral molecules. The pitch of the helix was 11 μm, and was roughly the same for several filaments. In contrast, a range of values varying from 2.5 to 9.8 μm was obtained for the diameter of the filaments. Such a variation in the diameter was also observed by Jakli *et al.* [11]. Figure 3 shows the time-dependent length and growth velocity for one of the filaments when the sample is cooled to 1°C below the isotropization temperature. The trends observed are typical of growth morphologies driven by diffusion transport [12]. The temporal variation of the length and the velocity can be well described by a power-law expression with the exponents 0.22 and -0.78, respectively. In the same sample preparation, we observed at least two other types of texture, viz. a focal-conic texture having a low birefringence and a myelinic texture. On cooling the sample further, the different textures coalesced into a non-specific pattern.

X-ray diffraction experiments were carried out on a non-oriented sample, using an image plate set-up (Mac Science, Japan). The pattern obtained at 165°C, along with the extracted intensity vs. 2θ profile, is shown in figure 4. The diffuse character of the wide angle ($\sim 20°$)

Figure 2. Microscopic texture of the B_7 phase exhibiting the spiral domains at 171.5°C. Notice a small region (right of centre) where a myelinic texture is also seen. Magnification × 320.

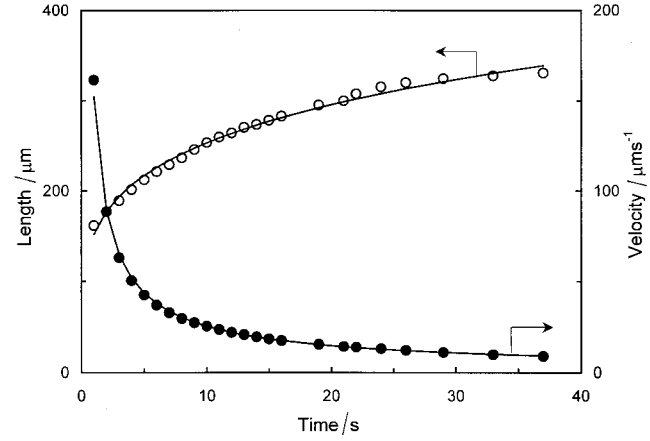
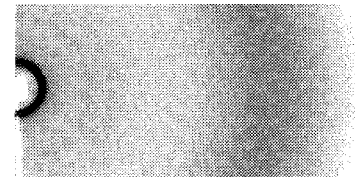


Figure 3. Time dependence of length (open circle) and growth velocity (filled circle) of a filament when the sample is cooled to 1°C below the isotropic $-B_7$ transition temperature. The solid lines represent a power-law behaviour.



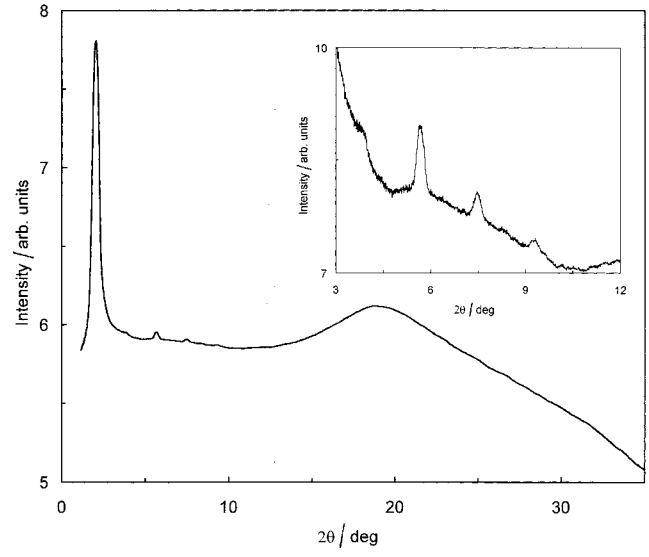
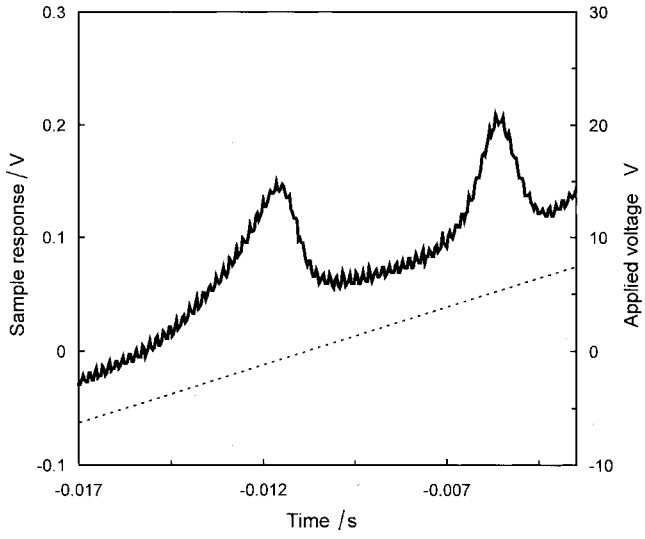


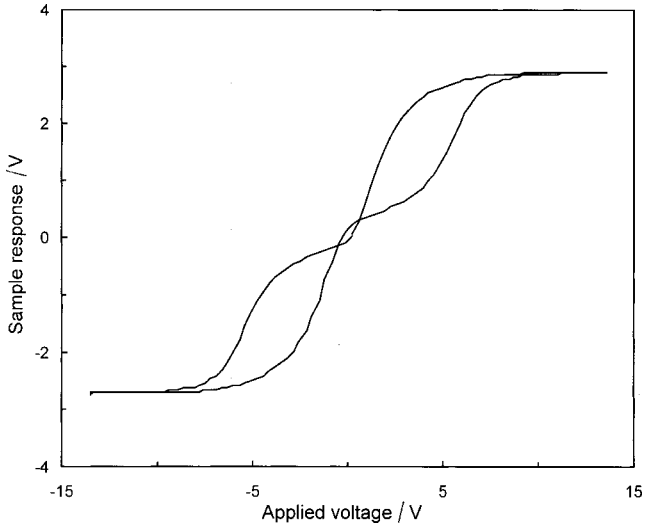
Figure 4. X-ray diffraction pattern (top) and the intensity versus 2θ profile (bottom) of the sample at 165°C. The profile shows a diffuse peak at wide angle indicating a liquid-like order and four sharp peaks at low angles corresponding to a two-dimensional structure.

peak indicates a liquid-like order within the smectic layer. In the small angle region, four sharp reflections were seen. As we were unable to obtain a monodomain sample, we have not indexed these reflections. However, their presence rules out a simple layered phase and points towards a two-dimensional structure. Most of the above mentioned features have been reported [7] for the B_7 phase and we therefore believe that the mesophase observed in the present case is indeed the B_7 mesophase. One must point out that the X-ray characterization of the B_7 phase is not yet uniquely established. For example, the B_7 phase reported by Pelzl *et al.* [7], showed a two dimensional modulation within the layer. In contrast, the mesophase studied by Heppke *et al.* [8], although showing a spiral domain texture, exhibits a simple layer structure.

The electrical switching properties were investigated by the current response method. Measurements were done by sandwiching the sample between ITO-coated glass plates giving a thickness of about 10 μm. The sample was cooled slowly from the isotropic phase before commencement of the measurements. On application of a triangular wave electric field, the non-specific texture cleared to show the fan-shaped focal-conic texture, which contained a mixture of 'bright' and 'dark' regions. On reversing the sign of the applied field, these domains showed a clear switching with the bright regions becoming dark and vice versa. The monitored current response, figure 5 (*a*), showed that even at a very low field strength (~ 1 V μm^{-1}), the switching was antiferroelectric having two peaks per half cycle of the applied field. The 'double hysteresis loop' obtained by applying a sine wave field, figure 5 (*b*), confirms this feature. As the field strength was increased, the time separation between the two peaks decreased, as shown in figure 6. The combined area under the peaks is a measure of the $\mathbf{P}_s$, for which the value is plotted as a function of the applied field in figure 7. The magnitude of $\mathbf{P}_s$ increases with increasing applied field and saturates for values higher than 3 V μm^{-1}. The saturated value of $\mathbf{P}_s$ is comparable to that for the



(*a*)



(*b*)

Figure 5. (*a*) The current response peaks of the sample at 165°C on applying a relatively low triangular wave field of 1.2 V μm^{-1}, 20 Hz (solid line: sample response, dotted line: applied voltage). (*b*) The double hysteresis loop obtained at the same temperature on applying a sine wave field of 1.2 V μm^{-1}, 40 Hz using the Diamant Bridge method.

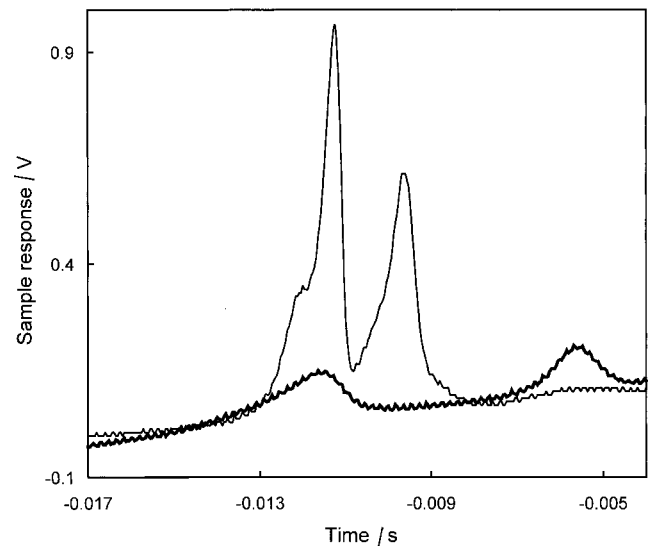


Figure 6. The current response curves obtained for two different values of the triangular wave field (thick line: 1.2 V μm^{-1}, thin line: 3.6 V μm^{-1}, 20 Hz). Notice that the time separation between the two peaks has decreased when the field is high.

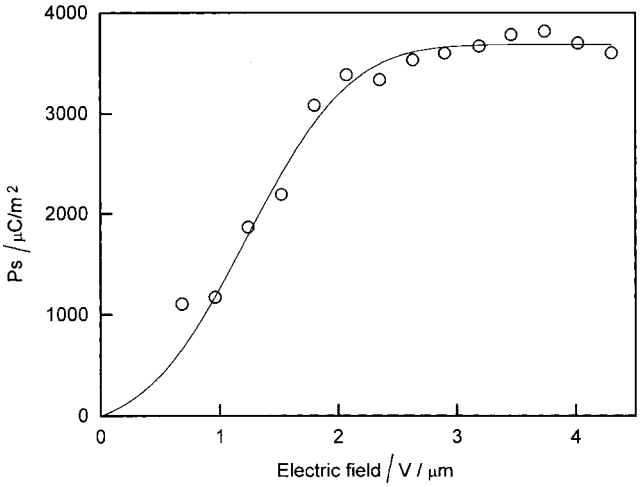


Figure 7. The field dependence of the spontaneous polarization $\mathbf{P}_s$ at $T = 165°C$, measured using the current response peaks when a triangular wave field of 20 Hz was applied to the sample. The solid line is a guide to the eye.

B_7 phase reported earlier [9, 10] and also for the commonly observed B_2 banana phase [4, 5]. The $\mathbf{P}_s$ values measured for increasing and decreasing field modes showed a very small hysteresis. The temperature dependence of $\mathbf{P}_s$ obtained with a 4 V μm^{-1} field is shown in figure 8. Conforming to the first order character of the I-B_7 transition, the $\mathbf{P}_s$ shows an abrupt and large increase immediately below the transition and has a very weak temperature dependence at lower temperatures.

The dynamics of the polarization switching were studied by monitoring the current response of the sample to an applied square wave field. A typical time dependence of the sample output is shown in figure 9. Using such traces, the response time τ was estimated from the time elapsed between the appearance of the maximum of the current signal and the field reversal. The temperature dependence of τ (figure 10), shows an abrupt increase

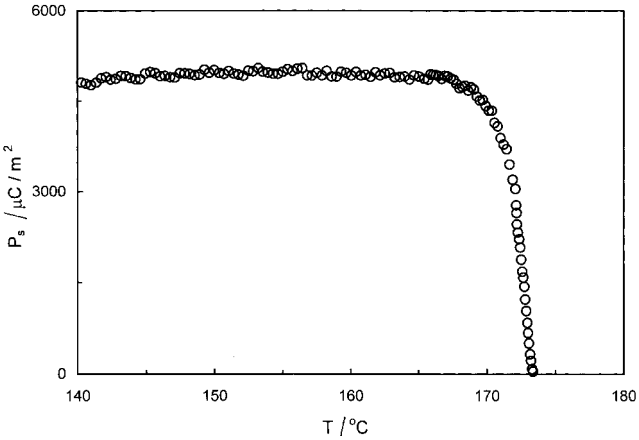


Figure 8. Temperature variation of $\mathbf{P}_s$ for a fixed triangular wave field of 3.8 V μm^{-1}, 20 Hz.

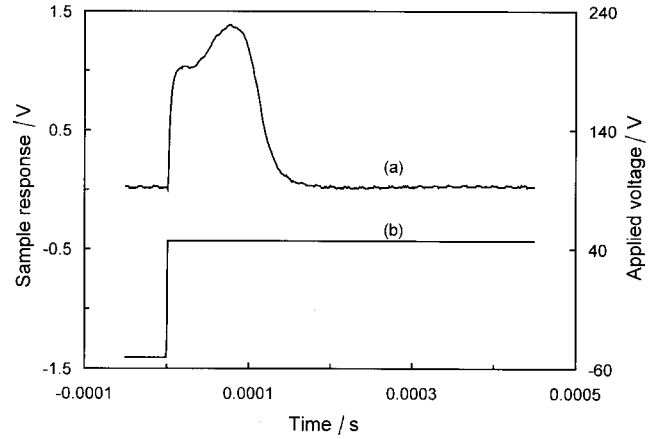


Figure 9. Current response curve of the sample (curve a) on application of a square wave field of 4.2 V μm^{-1}, 20 Hz (curve b). The switching time τ was estimated from the time elapsed between the appearance of the maximum of the current signal and the field reversal.

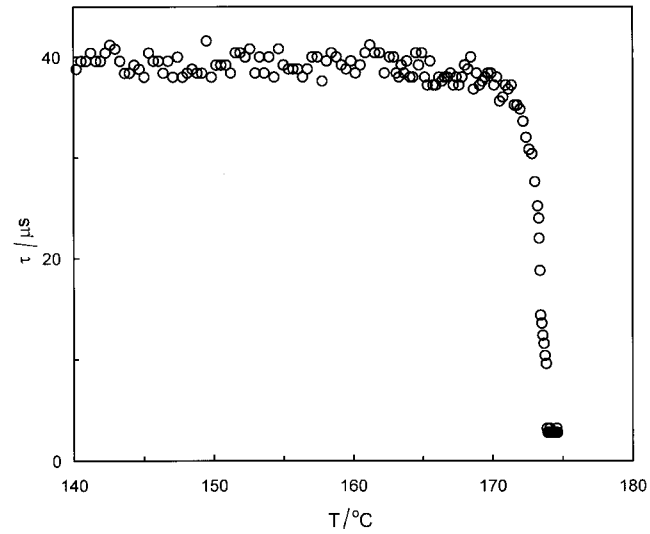


Figure 10. Thermal variation of the switching time τ under a square wave field of 4.2 V μm^{-1}, 20 Hz.

near the transition, but has an Arrhenius type behaviour away from it. The magnitude of the activation energy that was calculated from the region with the Arrhenius behaviour is 3.3 ± 0.4 kJ mol^{-1}, a value lower than that for the B_2 phase [13].

Details of the synthetic procedure for the compound studied will be published elsewhere, but we mention briefly the following points. 1,3-Dihydroxybenzene was treated with 4-nitrobenzoyl chloride to give 3-(4-nitrobenzoyloxy)phenyl 4-nitrobenzoate. This dinitro compound was then catalytically hydrogenated to 3-(4-aminobenzoyloxy)phenyl 4-aminobenzoate, which upon condensing with 2-hydroxy-4-hexadecyloxybenzaldehyde furnished the final product.

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