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Synchrotron X-ray investigation of the layer spacing in a series of low molar mass bi-mesogen organosiloxane smectic materials

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Abstract

The temperature dependence of the layer spacing of a series of chiral bi-mesogen organosiloxane liquid crystal materials is presented. The detailed measurements were taken at the Elettra Sincrotrone radiation source in Trieste on thin specimens contained between glass coverslips. In the materials with 10 and 11 spacers between the siloxane and the mesogenic moiety it is observed that the temperature dependence of the layer spacing is not monotonous. In the material with 6 spacers there is an abrupt change of 0.01 nm in the layer spacing between 35 and 36 ^{o}C. In this temperature range domains with both layer spacing coexist. This observation is in agreement with polarised light microscopy observations however, detailed DSC measurements show no heat associated with this transition.

Key words: Organosiloxane, Bimesogen, Synchrotron X-ray, Smectic liquid crystal

1. Introduction

Chiral bimesogen organosiloxane liquid crystal materials present the enigmatic characteristic of behaving either as a low molar mass material where the molecule responds as a whole unit to external stimuli or as a side-chain polymer where the two lateral mesogenic pendants respond independently of each other [1-3]. In the latter case a change in the conformation of the molecule is associated to the response. The work presented in this paper is an X-ray investigation of the temperature dependence of the layer spacing in three homologous bimesogen materials that display very different electro-optical responses.

2. The materials

The materials investigated are from the series of bi-mesogens synthesised by Kaeding and Zugenmaier [4, 5]. The schematic diagram of the molecule is shown in Fig. 1. The materials with n = 11, 10 and 6 carbon atoms in the alkyl chain (11Dim, 10Dim and 6Dim respectively) are investigated. The phase sequences and the transition temperatures are given in table 1 [4, 6].

Name	m	Phase sequence
6Dim	6	$K \xleftrightarrow{-0.6^oC} S_C{}^* \xleftrightarrow{35^oC} S_X{}^* \xleftrightarrow{45^oC} I$
10Dim	10	$K \xleftrightarrow{-7.6^oC} S_X{}^* \xleftrightarrow{11.3^oC} S_C{}^* \xleftrightarrow{71.3^oC} I$
11dim	11	$K \xleftrightarrow{-7.6^oC} S_X{}^* \xleftrightarrow{11.3^oC} S_C{}^* \xleftrightarrow{71.3^oC} I$

Table 1. The phase sequence and transition temperatures of 6Dim, 10Dim and 11Dim.

3. The electro-optic response

The unusual electro-optic response observed in these materials was presented in a previous paper [6]. The material 11Dim does no respond to fields up to 32 V/μm. In the $S_C{}^*$ phase the material 10Dim has an almost temperature independent tilt angle of 36 degrees. The material displays two regimes of response depending on the amplitude of the applied field. At low fields a uniform ferroelectric switching is observed whereas at high field the switching occurs as slowly progressing stripes. The material 6Dim displays a transition between two yet not unequivocally identified smectic phases. The transition occurs at 35 ^oC. A change of texture is observed at this temperature in polarized light microscopy. The change of texture occurs in the form of stripes of different birefringence nucleating and then progressing in a direction parallel to the smectic layers [6]. Ferroelectric switching with a polarisation reversal current peak is observed when the material is switched with a triangular wave in the low temperature smectic phase ($S_C{}^*$). As the temperature is increased the current peak broadens and its height decreases. The peak disappears at the transition. The tilt of the optic axis measured as half the angle between the two positions of extinction when the specimen is switched with a square wave is almost temperature independent and equal to about 31 degrees when switched with a field of 2 V/μm (larger than the field required to unwind completely the helix). There is a measurable electroclinic effect in this phase, the tilt increases gradually to 35 degrees as the field is increased to 32 V/μm. In the high temperature phase there is a threshold field for switching the material [6]. When a low frequency (10 mHz) square wave of amplitude above the threshold is applied the specimen displays first a transient texture with progressing stripes. This transient texture is observed for a few seconds (several alternances of the field) until the stripes have grown to occupy the whole specimen. The stripes are similar to those observed in zero-fields at the transition at 35 ^oC and also to those observed in the material 10Dim when switched with high fields.

The threshold for switching displays a non-monotonous dependence as a function of temperature. The threshold increases with temperature until about 43 ^oC. Between 35 ^oC and

43 ^{o}C the specimen, after the transient period, switches back to the texture observed at low temperatures. During the transient period the growing stripes are observed to switch whereas the background does not respond. Above 43 ^{o}C the threshold decreases with increasing temperature and there is a significantly different response to the electric field. After the transient period, a flash of light is observed each time the field is reversed but no polarisation reversal current peak is observed and no measurable change of the direction of the optic axis is observed. The interpretation of these observations is still an open ended question that requires time resolved X-ray measurements in applied fields in order to be clarified. In the present work all the measurements were done in zero fields.

4. Temperature dependence of the layer spacing

The measurements were performed at the Austrian Small Angle X-ray Scattering (SAXS) Beamline at ELETTRA. The unaligned specimens were contained between two glass cover slips; the gap between the cover slips was 5 – 10 μm. The temperature of the specimen was controlled using a Linkam heating stage modified as described in reference [7]. The beam size was 1.5 x 0.3 mm therefore a large number of domains of the unaligned specimen were illuminated. The detector was calibrated using a silver behenate (AgBeh) sample.

In the materials 10Dim and 11Dim it is observed that, as the temperature is increased from room temperature, there is first a small but significant decrease in the layers spacing until a temperature of about 15 ^{o}C below the transition to isotropic. Above this temperature, the layer spacing increases until the transition to the isotropic phase as shown in Fig. 2. This somewhat unusual decrease of layers spacing with increasing temperature has been observed in other smectic materials [8, 9] however, in the present materials there is no transition to a S_A phase at higher temperatures. The decrease in the layer spacing could be explained here by assuming that at low temperature the molecule is in the almost fully stretched linear conformation and, as the temperature increases, the conformation evolves towards the V-shape [1] therefore reducing the layer spacing. However, the change in layer spacing is only 0.02 nm and the proposed interpretation is only one plausible possibility to be confirmed.

Using the fully extended conformation molecular length calculated by Kaeding [5], the tilt of 36 degrees [6] and the measured layer spacing it is found that in 10Dim there is only a small amount of interdigitation of the order of 1 nm. This is in agreement with the X-ray measurements on the corresponding monomesogens in the S_A phase performed by Kaeding [5]. We note in passing that Robinson et al [1] proposed a complete interdigitation of the mesogenic moieties in their materials where the mesogenic moiety has a laterally attached halogen.

At 30 ^{o}C the difference between the layer spacing of 10Dim and 11Dim is 0.19 nm. The difference in molecular length in the fully extended conformations of the two molecules is 0.26 nm. Assuming the tilt angle is the same in both materials one would expect a difference in layer spacing of 0.21 nm. This significant difference is not yet fully understood but is very likely due to a different molecular conformation and related to the fact that 11Dim does not respond to the electric field.

The behaviour of the layer spacing in the material 6Dim is quite different from that observed in 10Dim and 11Dim. The temperature dependence of the layer spacing is shown in Fig. 3. The spacing increases with increasing temperature and there is an abrupt increase at the transition at 35 ^{o}C then the layer spacing continue to increase until the transition to isotropic.. Fig. 4 shows the intensity as a function of the magnitude of the scattering vector q at various temperatures between 35 and 36 ^{o}C; it can be seen that the two phases coexist during the transition with one phase growing at the expense of the other. This is consistent with the growing stripes observed by polarised light microscopy. However, there is no measurable heat associate with this transition. Fig 5 shows the DSC trace recorded on cooling the specimen from the isotropic phase; a detailed scan (not shown) between 34 and 37 ^{o}C shows no peak in this temperature range. This somewhat unexpected observation could be due either to the fact that the transition occurs over some time through the growing stripes and therefore the heat peak becomes too broad to be observed or to the fact that this transition is not a thermodynamic transition but a rearrangement of the molecular packing induced by the surface and therefore not observed in bulk measurements.

5. Conclusions

The X-ray measurements presented in this work emphasise the complexity in the behaviour of bimesogen organosiloxane liquid-crystal materials. In the present series it would appear that the molecular arrangement and therefore the electro-optic response is the result of delicately balanced conflicting constraints that can be altered by a small external action. In order to clarify the behaviour of 6Dim X-ray measurements in applied field are needed.

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Figure legends

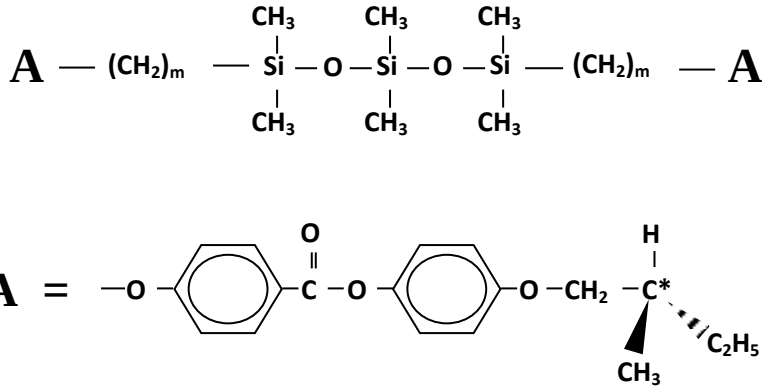
Figure 1: The schematic diagram of the molecule in the material.

Figure 2. The temperature dependence of the layer spacing in 10Dim and 11Dim.

Figure 3. The temperature dependence of the layer spacing in 6Dim

Figure 4: The scattered intensity as a function of q at the transition. Two types of domains with different layer spacing coexist in the specimen.

Figure 5: DSC trace observed on cooling 6Dim from the isotropic phase.



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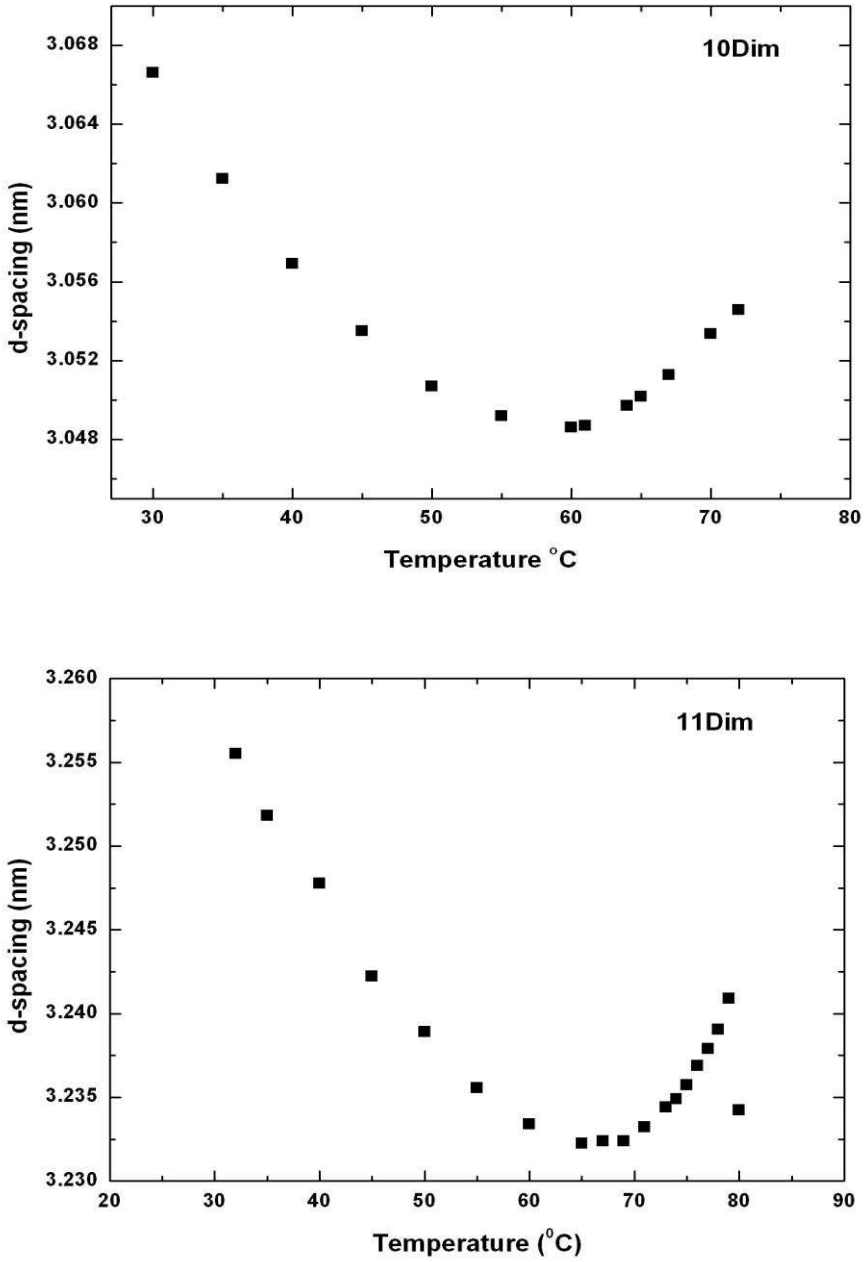

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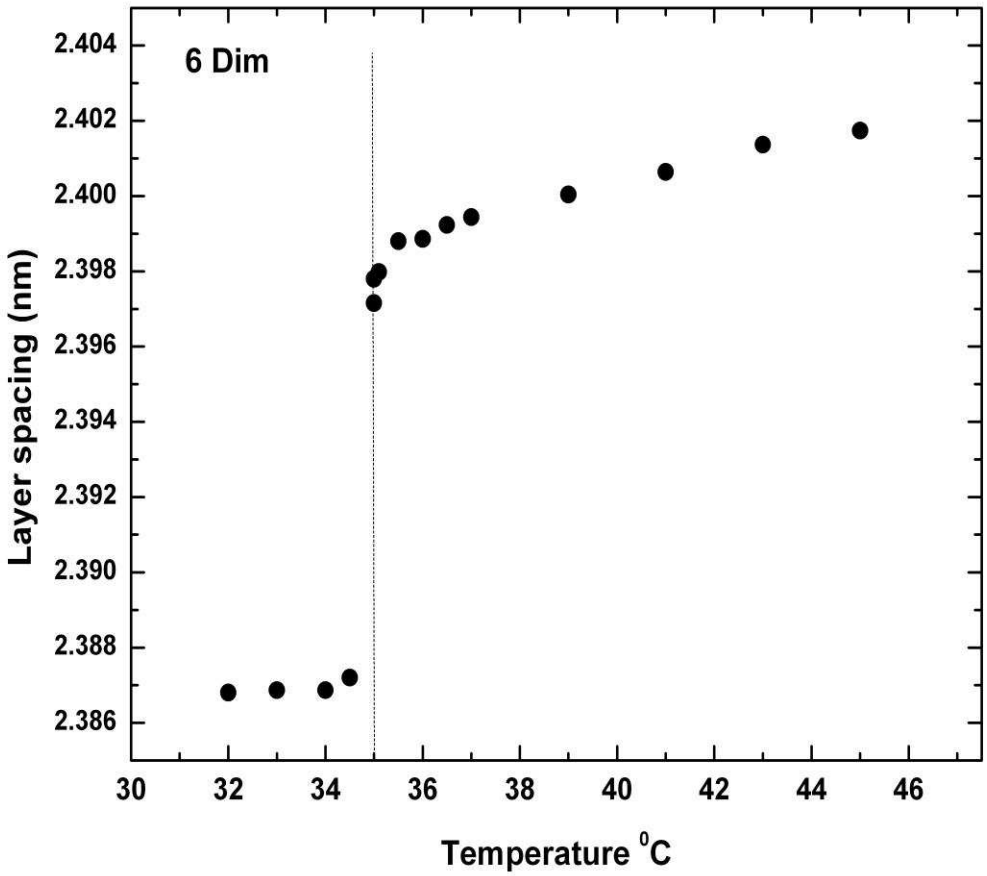

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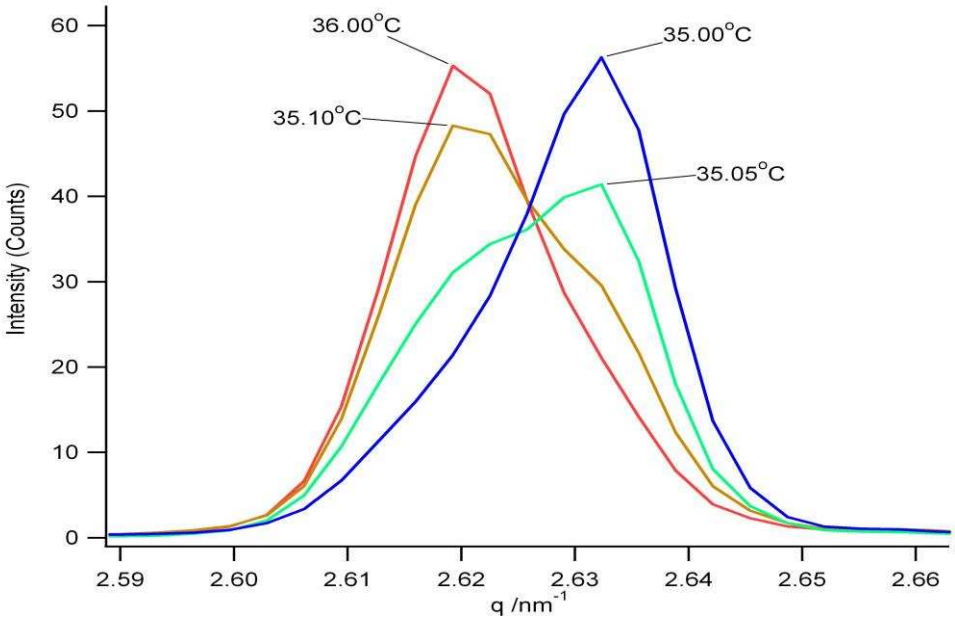

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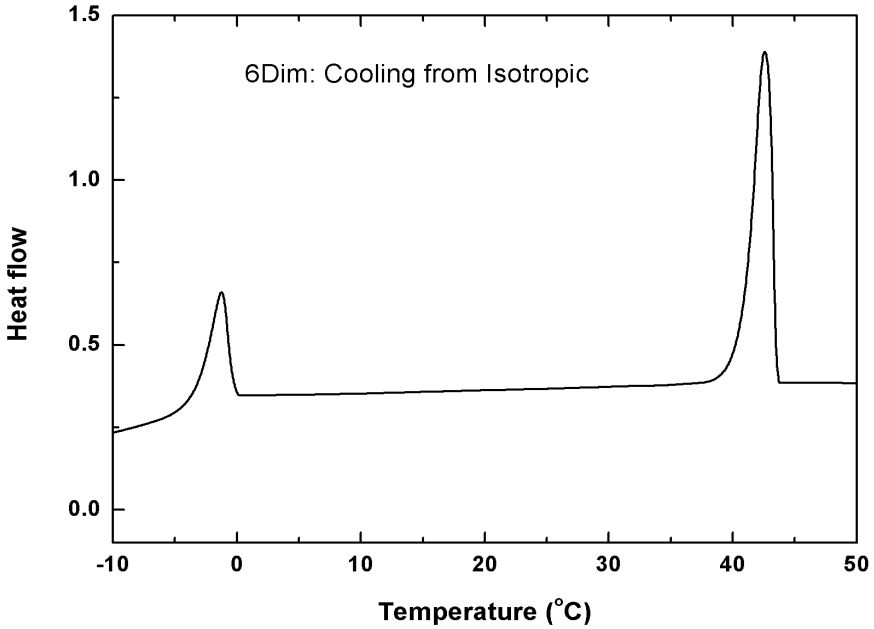

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