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The Electro-Optic Response in a Series of Chiral Bi-Mesogen Low Molar Mass Organosiloxane Liquid-Crystal Materials

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The electro-optic response of a series of low molar mass bi-mesogen organosiloxane materials is presented. The materials display an unusual response to the electric field. It is argued that the observed behaviour can be explained if the material has two regimes for switching depending on temperature and the amplitude of the applied field. In one regime the two mesogenic moieties of the molecules respond independently of each other like side pendant in polymeric materials and in the other regime the bi-mesogen molecule responds as a single unit like a bent-core molecule.

Keywords Bent core molecule; bi-mesogen; ferroelectric; field induced phase transition; organosiloxane; smectic

1. Introduction

In low molar mass organosiloxane liquid-crystal materials the molecule consists of one or two mesogenic moieties attached via alkyl chains to a short siloxane chain. The siloxane chain has usually less than five repeat units, typically two or three. In the mesophase the siloxane moieties tend to micro-separate from the mesogenic moieties favouring a layered structure with alternating mesogen-rich and siloxane-rich layers [1–4]. It has been argued that the siloxane-rich layer can be regarded as an effective two-dimensional polymer backbone and the mesogen as side-chain pendants [2]. The low molar mass organosiloxane liquid-crystal materials are therefore somewhere in-between the conventional low molar mass and the polymeric materials. In that respect the bi-mesogens are particularly interesting because the same material can behave either as a low molar mass material or as a polymeric material.

In the smectic phase the molecules adopt the conformation of lowest energy compatible with the packing of the molecules in layers, with the boundary

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constraints and, if any, the applied electric field. Possible conformations compatible with a smectic phase and the micro-separation of the siloxane moiety are shown in Figure 1.

The mesogens are symbolised by ellipsoids and the siloxane group by rounded rectangles. In the V-shaped conformation the long axis of the two mesogenic moieties are not parallel to each other. This conformation in a smectic phase always leads to an anticlinic arrangement of the mesogenic moieties whereas with the linear and the hairpin conformation both the anticlinic and the synclinic arrangements of the mesogenic moieties are possible. In the V-shaped conformation the average axis of the molecule does not coincide with the long axis of the mesogenic moieties; the molecular axis may be normal to the layers whereas the axis of the mesogens are tilted. If the mesogenic moieties are chiral there is a local polarisation in each mesogen sub-layer; the direction of the polarisation is in opposite direction in alternate sub-layers. If the mesogenic moieties behave as independent entities as in the case of polymeric materials, the application of an electric field can change the conformation of the bi-mesogen molecule from V-shaped to linear [2,4]; the response is that of an antiferroelectric material. Because of this peculiarity J. Lagerwall has called these molecules '*chameleon molecules*' [5]. However, with short spacers between the mesogen and the siloxane moiety the molecule may respond as a whole single bi-mesogen entity like a conventional low molar mass material. In this case the molecule is a bent-core molecule. The total dipole moment of the molecule rather than the local moment on the mesogenic moiety couples to the field and banana types of behaviours are expected. The materials presented in this paper appear to

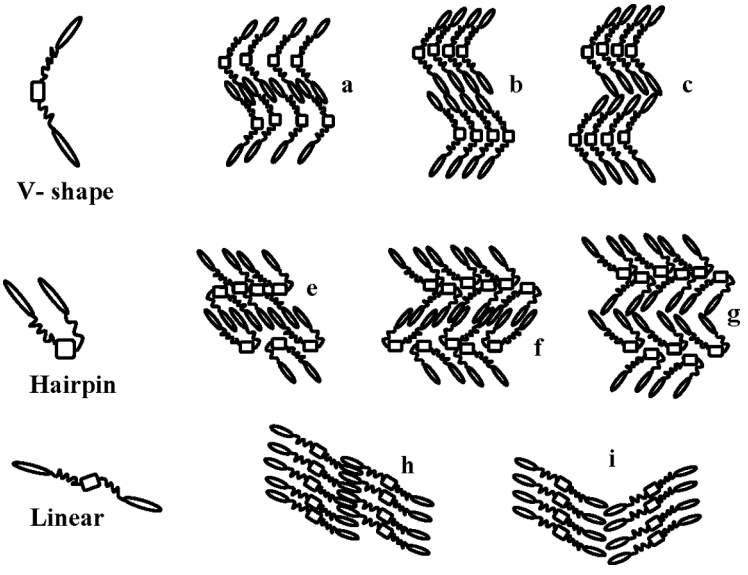

Figure 1. Conformations of the bi-mesogen molecule compatible with the micro-phase separation in the smectic phase. The mesogens are symbolised by ellipsoids and the siloxane chains by rounded rectangles. In the V-shaped conformation, if the mesogens are independent of each other, each mesogen layer has a polarisation perpendicular to the plane of the page; if the bi-mesogen molecule is rigid the polarisation of the smectic layer (= 3-sublayers) is in the plane of the page.

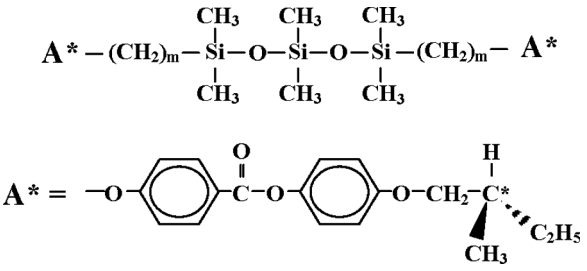

Figure 2. The schematic molecular structure of the molecule in the series of materials.

display both types of behaviours depending on temperature and the amplitude of the applied field.

2. The Materials

The materials investigated in this paper are from the series of bi-mesogens synthesised by Kaeding and Zugenmaier [1] details of the synthesis are given in references [1,6]. A schematic diagram of the molecular structure is given in Figure 2.

In all the materials the siloxane moiety has three silicon atoms. The mesogenic moiety is the same for all the compounds. The rigid core of the mesogen has two rings and the stereogenic centre is situated at the end of the short terminal chain. The parameter that is varied through the series is the length of the link between the mesogenic and the siloxane moieties. In the materials presented the link has 6, 10 and 11 carbon atoms.

3. Observations

The observations were carried out using a polarised light microscope in conjunction with a heating/cooling stage and temperature controller. The specimens were contained in cells of 5 μm cell-gap treated for planar alignment. The electric field was applied to the specimen via indium tin oxide (ITO) transparent electrodes. The orientation of the layers was identified by observing the layers undulation at the position of extinction. The tilt angle was measured by switching the material between the two positions of extinction using a low frequency (10 mHz) square wave. The observed transition temperatures given in Table 1 are in good agreement with the values quoted by Kaeding and Zugenmaier [1] however, the electro-optic measurements suggest some minor changes to the phase sequence inferred in reference [1].

The material 6Dim displays the most unusual behaviour. A smectic C* (SmC*) phase is observed at room temperature. Between −6°C and 34.6°C the material displays a ferroelectric response with a 35 degrees tilt of the optic axis; the tilt is almost independent of the temperature and also independent of the amplitude of the applied field. At a 34°C there is a *discontinuous* transition to a phase with the optic axis normal to the layers; this phase is most probably smectic A* however, since we were not able to ascertain that this phase is SmA* we have labelled it SmX*. Stripes of the SmX* phase appear at the transition. The stripes nucleate at the edge of the broken fans and grow in a direction parallel to the layers. The stripes increase in size and number and merge into each other until the entire specimen has changed

Table 1. The phase sequence of the materials. The phase S_X displayed by 6Dim is very likely a S_A^* phase. The low temperatures mesophase displayed by 10Dim and 11Dim could be according to Kaeding [1] a plastic crystal phase

Name	m	Phase sequence
6Dim	6	$Cr. \overset{-0.6^\circ C}{\longleftrightarrow} SmC^* \overset{34^\circ C}{\longleftrightarrow} SmX^* \overset{45^\circ C}{\longleftrightarrow} I$
10Dim	10	$Cr. \overset{-7.6^\circ C}{\longleftrightarrow} \widetilde{SmX}^* \overset{11.3^\circ C}{\longleftrightarrow} SmC^* \overset{71.3^\circ C}{\longleftrightarrow} I$
11dim	11	$Cr. \overset{-0.3^\circ C}{\longleftrightarrow} \widetilde{SmX}^* \overset{21.5^\circ C}{\longleftrightarrow} SmC^* \overset{76.7^\circ C}{\longleftrightarrow} I$

phase. The growing SmX* stripes are dull grey indicating a significantly different birefringence than in the deep purple coloured SmC* background. If a sufficiently large electric field is applied to the specimen in the SmX* phase the material switches to the SmC* phase. The threshold field for switching depends on the temperature.

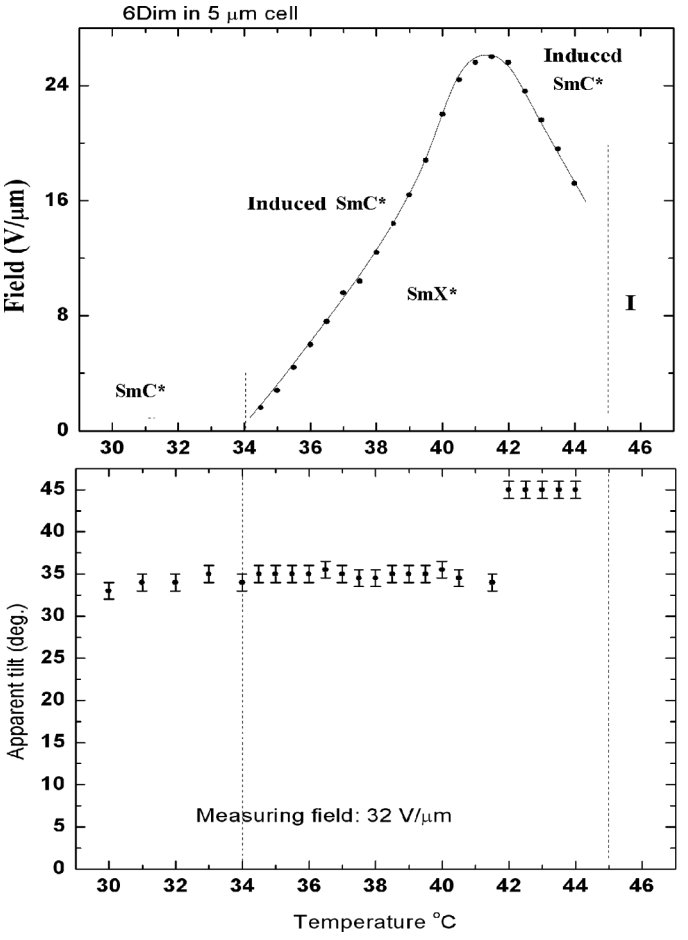

Figure 3. Top: the threshold field for switching 6Dim as a function of temperature. Bottom: the tilt of the optic axis as a function of temperature measured with a field above the threshold.

The variation of the threshold field and of the tilt angle as a function of temperature is shown in Figure 3. Between 34.6°C and 41.2°C the threshold field increases with temperature. The tilt of the optic axis in the switched state is 35 degrees. Above 41.2°C the value of the threshold decreases with temperature and the tilt of the optic axis in the switched phase is 45 degrees.

The material 10Dim responds to an electric field and displays ferroelectric switching in the SmC* phase; the tilt is almost independent of temperature and close to 36 degrees. We note in passing that the measurement of the tilt angle given here for 10Dim corrects the erroneous data given in reference [7]. As already reported in reference [7] at all temperatures in the SmC* range, the response time decreases with the amplitude of the applied field until about 6 V/μm. Above this value of the applied field the switching occurs in stripes similar to those observed at the transition in 6Dim and the response time increases dramatically with the amplitude of the applied field.

No electro-optic response was observed in the material 11Dim in fields up to 35 V/μm at any temperature in the mesomorphic range.

4. Discussion and Conclusion

The investigation of the series of materials presented in this paper is still in progress; the discussion in this section reflects our understanding at the time of the 23rd International Liquid Crystal Conference (ILCC) in Krakow. A definite interpretation of the observed unusual behaviour requires further work including X-ray studies of the specimen in the cell and in applied fields as well as dielectric studies and spontaneous polarisation measurements.

Before discussing our proposed interpretation for the behaviour of 6Dim we note that at the 23rd ILCC conference Kornek *et al.* [8] reported experimental observations of a field induced SmA to SmC transition with a threshold field in a non-chiral material. The theory based on a Landau–de Genes approach described by Eremin *et al.* [9] predicts that in non-chiral materials such a field induced transition with a threshold is possible. A similar argument cannot be invoked in the present case to explain the field induced transition in 6Dim because the materials is chiral and the term responsible for the threshold in the Landau expansion of Eremin *et al.* [9] is forbidden by symmetry in chiral materials.

Our proposed interpretation for the behaviour of 6Dim is as follows:

Below 34.6°C the conformation of the molecule is either linear (Fig. 2-h) or U-shaped (Fig. 2-e) with a synclinic arrangement of the mesogens tilted by 35 degrees. This is consistent with the observed ferroelectric response. At 34.6°C the conformation changes to V-shape (Fig. 2-a) with the average optic axis normal to the layers and the long axis of the mesogens remaining tilted by 35 degrees. The conformation change can nucleate on the defect at the edge of the broken fan and progresses in the plane of the smectic layer like falling dominoes hence the discontinuous transition and the progressing stripes. Above the transition the molecules are in the V-shaped conformation therefore the mesogenic moieties are in an anticlinic arrangement; the applied field which favours the synclinic arrangement switches the molecule into the linear conformation. The threshold field for switching depends on the energy barrier that must be overcome to cause the change of conformation of the molecule packed in the smectic phase. Since the V-shaped conformation is observed at high temperature it is expected to see the height of the barrier and therefore the threshold field for switching to increase with temperature.

At 41.2°C the energy barrier for the change of conformation is such that it becomes energetically more advantageous for the whole molecule to flip and bring the two dipoles associated with each mesogenic moiety perpendicular to the applied field. It is not clear yet why the optic axis after the flipping is at 45 degrees.

The lack of response observed in 11Dim could be simply explained if the molecules are in the V-shape conformation and the threshold for switching is larger than the maximum 34 V/μm available in our experiment.

At the time of writing only vague speculations can be made to explain the behaviour of the response time in 10Dim any meaningful interpretation must await further measurements. However; the switching in stripes at high fields and the increasing response time point to a change of conformation.

In conclusion this paper presents the electro-optic observations reported at the 23rd ILCC conference (Krakow). A sound interpretation of the observations requires further work already in progress and will be the object of a future publication.

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