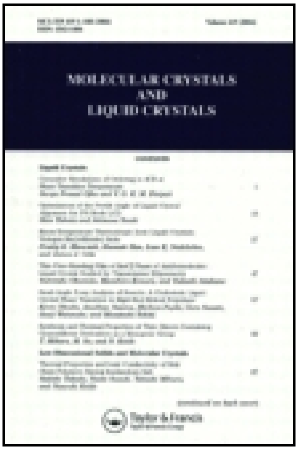

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Effect of the Surface Anchoring on the Electro-Optic Response of Bi-Mesogen Organosiloxane Liquid-Crystal Materials

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Effect of the Surface Anchoring on the Electro-Optic Response of Bi-Mesogen Organosiloxane Liquid-Crystal Materials

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The electro-optic response of a bi-mesogen organosiloxane liquid crystal material confined in a cell with strong surface anchoring is investigated. The specimen displays an increase in the apparent tilt of the optic axis as the temperature is increased and a mono-stable electro-optic response with different response times for switching on and switching off. The cell takes 5 ms to be switched on and 200 µs to be switched off. A stripe-switching regime is observed at high field, with the rate of propagation of the stripes decreasing as the field is increased. A tentative interpretation of this unexpected behaviour is proposed.

Keywords: bi-mesogen; ferroelectric cell; stripe-switching

1. INTRODUCTION

In low molar mass organosiloxane liquid-crystal materials the molecules consist of mesogenic moieties attached via alkyl chains to a short siloxane chain. The siloxane chain has usually less than five repeat units, typically between two and five. Mono-mesogens and bi-mesogen where the molecule has respectively one and two mesogenic moieties [1–3] as well as cyclic tetramers [4] have been reported in the

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literature. In the mesophases the siloxane moieties tend to micro-separate from the mesogenic moieties favouring a layered structure with alternating mesogen-rich and siloxane-rich layers. 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].

When an electric field is applied to the material the molecule may either respond as one entity as in conventional low molar mass materials or only the mesogenic moieties respond to the field as in side-chain polymeric materials. In the latter case the switching, which is the change in the orientation of the average optic axis of the specimen, is achieved through a change of conformation of the molecules. An intermediate situation where the siloxane and the mesogenic moieties have independent and possibly conflicting response to the electric field cannot be excluded a priory.

The optical and electro-optic properties of a specimen cell of low molar mass organosiloxane liquid crystal material depend therefore on the conformation of the molecules in the cell. The conformation may be controlled either by the alignment layer in the cell or by doping the material [6]. The present paper is a preliminary investigation of the unusual electro-optic response of some of the bi-mesogen materials synthesised by Kaeding and Zugenmaier [1]. The observed behaviour is tentatively interpreted as the result of a very strong surface anchoring.

2. BI-MESOGEN ORGANOSILOXANE MATERIALS

The bi-mesogen low molar mass organosiloxane molecules consist of two identical mesogenic moieties attached symmetrically via an alkyl chain to the siloxane group as illustrated schematically in Figure 1. The mesogenic moieties are represented symbolically by an ellipsoid and the siloxane group by a rounded corners rectangle.

In a smectic phase the molecules adopt the conformation of lowest energy that is compatible with the preferred packing of the mesogens [6]. Possible conformations compatible with a smectic phase are shown in Figure 2. In the hairpin and in the linear conformation the two mesogenic moieties of the molecule have their long axis parallel to

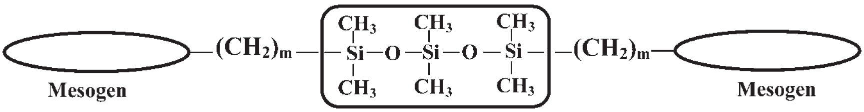

FIGURE 1 The schematic representation of a bi-mesogen molecule.

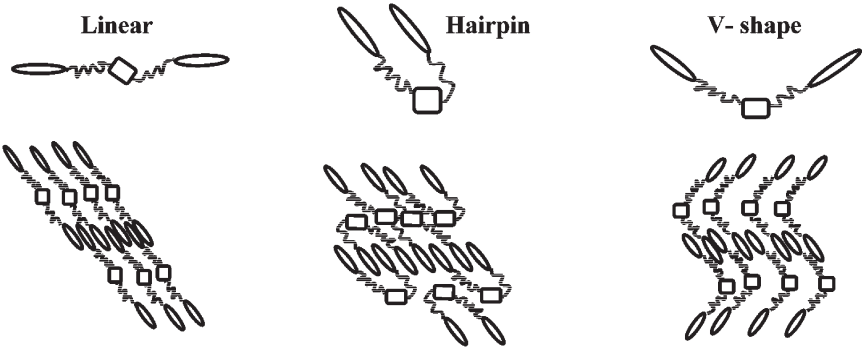

FIGURE 2 Conformations of the bi-mesogen molecule compatible with the smectic phase. The mesogens are symbolised by ellipsoids and the siloxane chain by rounded rectangles.

each other. The optic axis of the material coincides with the average long axis of the mesogens. With these two conformations in smectic phases there is a synclinic arrangement of the mesogenic moieties. If the mesogenic moieties are chiral, a ferroelectric order can be observed in tilted phases.

In the V-shaped conformation the long axis of the mesogenic moieties are not parallel to each other. This conformation in a smectic phase leads to an anticlinic arrangement of the mesogenic moieties. The average axis of the molecule does not coincide with the axis of the mesogenic moieties. If the plane of the molecule is normal to the layers then the symmetry of the phase is that of a S_A phase. However, if the mesogenic moieties are chiral, the anticlinic arrangement of the mesogenic moieties imposed by the conformation leads to an antiferroelectric ordering of the local dipole moments of the mesogenic moieties. Each smectic layer can be regarded as consisting of three sub-layers, two mesogen-rich layers on each side of the siloxane rich layer. The two mesogen rich layers have equal but in opposite direction electric dipoles.

With the V-shaped and the hairpin conformations there is the possibility of order of the plane of the molecule and of a tilt of this molecular plane with respect to the layer normal. In this case the direction of tilt of the mesogenic moiety and that of the molecule as a whole are no necessarily the same. The relevant spontaneous polarisation to be considered for the electro-optic response depends on whether the mesogenic moieties alone or the molecule as a whole respond to the applied field.

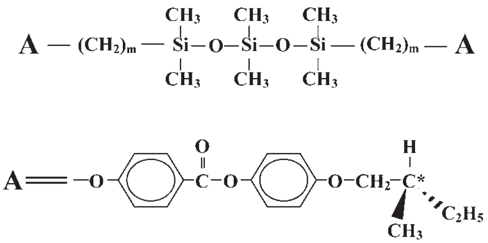

FIGURE 3 Schematic diagram of the molecules in the materials investigated. For 11 Dim, m = 11 and for 10 Dim, m = 10.

3. THE MATERIAL INVESTIGATED

The materials investigated here are 10 Dim and 11 Dim from the series synthesised by Kaeding and Zugenmaier [1]. The diagram of the molecules is given in Figure 3.

The siloxane moiety contains three silicon atoms. As it is usually the case [2,4] with low molar mass organosiloxanes, on cooling the materials display a transition from the isotropic phase directly into a smectic C phase.

4. OBSERVATIONS

The observations were carried out using a polarised-light microscope in conjunction with a heating stage and temperature controller (Linkam TMS 94) with a temperature resolution of 0.1°C. The specimens were contained in 5 μm thick cells treated for planar alignment. The electric field could be applied to the specimen via ITO electrodes. The observed transition temperatures given in Table 1 are in agreement with the values quoted by Kaeding and Zugenmaier [1].

No electro-optic response was observed in the material 11 Dim at any temperature in the mesomorphic range. Low fields and high fields up to 35 V/μm were applied to the specimen but there was no

TABLE 1 The Phase Sequence of the Materials. The Last Two Columns Give the Calculated Molecular Length and the Measured Layer Spacing (Kaeding and Zugenmaier [1])

	Phase sequence	L(Å)	d(Å)
10 Dim	$K \xleftrightarrow{-7.6^\circ C} S_X \xleftrightarrow{11.3^\circ C} S_C \xleftrightarrow{71.3^\circ C} I$	62.0	30.85
11 Dim	$K \xleftrightarrow{-0.3^\circ C} S_X \xleftrightarrow{21.6^\circ C} S_C \xleftrightarrow{76.7^\circ C} I$	64.6	32.77

observable response. Further work to establish the lack of response in this material is in progress and will be reported elsewhere.

The material 10 Dim responds to an electric field. A reasonably good alignment was achieved by cooling slowly the specimen from the isotropic phase with an applied triangular AC field.

The response of 10 Dim is that of a ferroelectric material. A weak single polarisation reversal current peak is observed when a triangular wave is applied to the specimen. There are two possible interpretations for this observation. The packing of the mesogens could be synclinic and the conformation is therefore either linear or hairpin or, the conformation is either V-shaped or hairpin, there is a tilt of the plane of the molecule and the molecule responds a one whole entity to the field. In the series of materials described by Robinson *et al*. [2] the three-silicon atoms siloxane moiety always favours the V-shaped conformation. However, the x-ray data and the molecular lengths obtained by Kaeding and Zugenmaier [1] and given in Table 1 suggested that the conformation is hairpin with a tilt angle of about 12 degrees. This is would be in agreement with the measurements presented in this work. The exact determination of the conformation is still under investigation and will not be discussed any further in this paper.

4.1 Measurement of the Tilt Angle

The tilt angle was determined as half the angle between the two positions of optical extinction when the sample is switched between crossed polarizers. A low frequency (50–100 mHz) bipolar square wave was applied to the specimen to switch the material between the two positions. This method gives the tilt of the average optic axis of the specimen. Usually the average optic axis coincides with the long axis of the mesogens however, this is not necessarily the case with bi-mesogens. Moreover, with this method one cannot directly ascertain that the angle measured is the tilt θ or the complementary (45-θ) with respect to the layer normal.

Usually the temperature dependence of the measured angle enables one to determine which angle is being measured. The tilt is expected to decreases and vanish at the smectic C to smectic A transition. In the present material there is no smectic A phase and the X-ray measurements [1] show that the layer spacing is constant in the smectic C temperature range suggesting that the tilt angle is also temperature independent.

The observed temperature dependence of the tilt of the average optic axis is given in Figure 4. At low temperatures the tilt is about 7 degrees and increases steadily with temperature; above 65°C the tilt

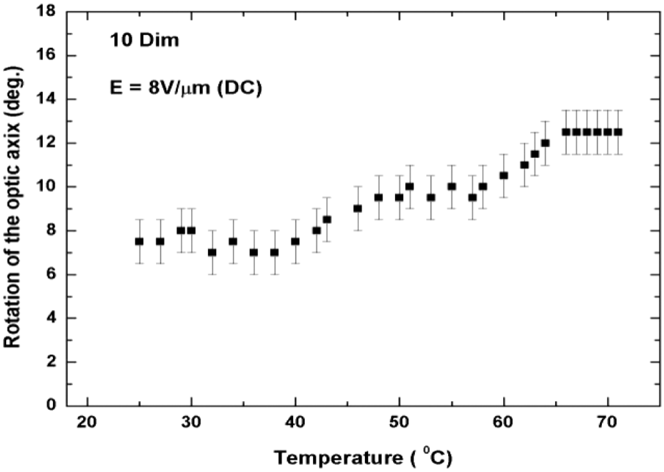

FIGURE 4 The variation of the tilt angel in 10 Dim as a function of temperature.

is almost temperature independent and close to 12 degrees. This unexpected behaviour can be explained if there is a very strong anchoring at the surface (Fig. 8). To verify this assumption the tilt angle was measured in a cell with no alignment layer. A temperature independent angle close to 12 degrees was obtained in the untreated cell. A strong surface anchoring also explains the asymmetric response time presented in the next section.

4.2. The Response Time

The optical response time was measured by observing the changes in the intensity of the transmitted light when the specimen is switched between crossed polarisers. The response of the specimen to a bipolar square-wave field is not symmetrical. The two positions at the intersection between the tilt cone and the plane of the cell are not equivalent. Figure 5 shows the intensity of the transmitted light when the square wave is applied. The specimen is oriented between the crossed polarisers in the position where extinction is observed in zero field. The positive field switches *on* the material in a time of the order of 5 ms. The material returns to the zero-field state in a time of the order of 200 μs when the field is reversed.

When switching the material *on*, we have observed two different switching regimes as a function of the amplitude of the applied field. At low fields the material switches uniformly. At fields larger than

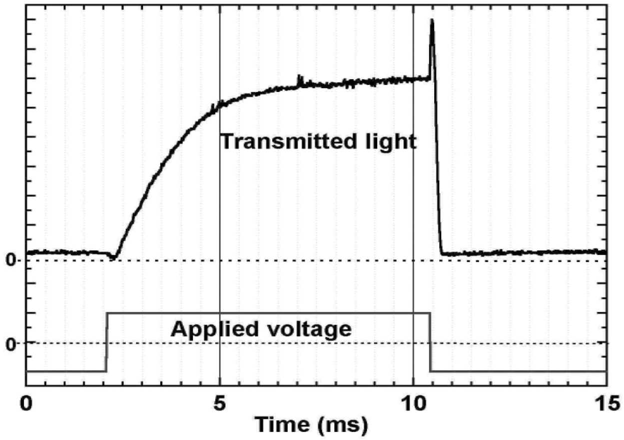

FIGURE 5 The asymmetric electro-optic response of 10 Dim to a square-wave field.

about 10 V/μm the material switches in stripes. The photograph shown in Figure 6 was taken a few milliseconds after a 32 V/μm positive field was applied to the specimen. The position of the specimen between the crossed polarisers is such that the extinction position corresponds to the *on* state; the progressing stripes therefore appear dark.

The stripes nucleate at various places in the specimen and grow parallel to each other in the plane of the layers until the entire

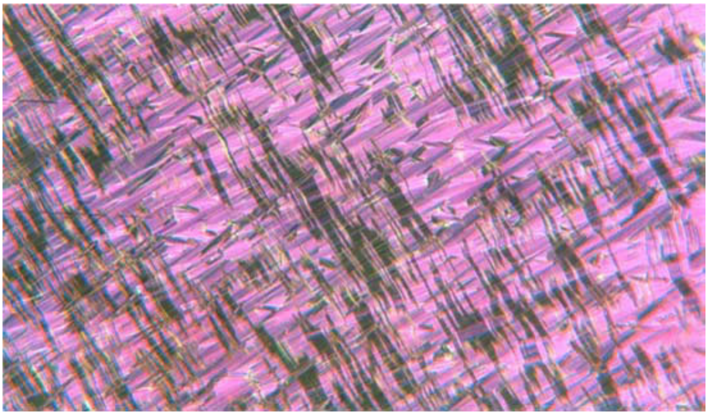

FIGURE 6 The stripes observed during the switching process at high fields. The position of the specimen between the crossed polarisers is such that the extinction position corresponds to the *on* state.

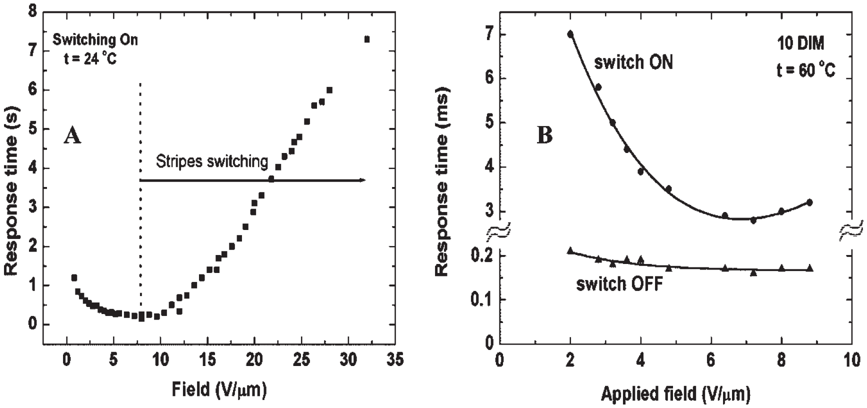

FIGURE 7 The behaviour of the response times as function of the amplitude of the applied square wave field. A: two regimes are observed in the switching *on* process. B: switching-*on* and switching-*off* times are compared to each other. Note the change of scale.

specimen is switched. The rate of progression of the stripes decreases as the field is increased. Therefore the response time for switching *on* in this regime increases as the field is increased.

The behaviour of the switching-*on* response time at 24°C as a function of the applied field is shown in Figure 7A. The response times quoted are the optical response times. In the low field regime the response time decreases as expected with increasing field. In the high field regime the response time increases with the field and reaches seven seconds at the 32 V/μm, the highest field available.

The switching-*off* response time decreases monotonically as the field is increased. The behaviour of the switching-*off* response time

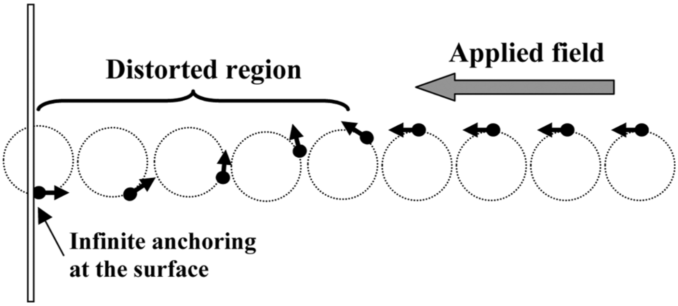

FIGURE 8 Proposed arrangement of the mesogens near the surface in the presence of an electric field.

is compared to that of the switching-on time in Figure 7B. The switching-*off* response time is not affected by the regime in which the specimen has been switched on.

5. TENTATIVE INTERPRETATION

Most of the unusual observations reported could be explained by assuming a strong surface anchoring of either the siloxane or the mesogenic moiety.

In a surface stabilised ferroelectric cell, the spontaneous polarisation will be anchored perpendicular to the surface. When an electric field is applied in the direction opposite to the spontaneous polarisation on expects that like in the Friedricks transition above a threshold the specimen will be distorted so that the direction of the polarisation in the middle of the cell becomes parallel to the field. Because of the distorted regions, the average optic axis of the specimen will appear rotated by an angle less than the cone angle. One can reasonably expect that the distorted region in the cell will decrease as the temperature is increased. This will lead to and *increase* in the angle by which the average optic axis is rotated, in agreement with our observations.

The strong anchoring also explains the asymmetric response to the field and the mono-stable response. To switch the specimen on, one needs to distort the specimen whereas when the field is reversed the elastic force and electrostatic forces combine to switch the specimen off. However, the observed response at high field cannot not explained by this simple model. The stripe-switching regime could be explained by assuming that at high fields the electrostatic forces locally overcome the anchoring and molecule flips to the other side of the cone. This flipping would cause the neighbouring molecules to flip causing the propagating stripes. However this interpretation is not consistent with the facts that we observed that the stable orientation is not altered after the stripe-switching and that the rate of propagation of the stripes decreases as the field is increased. A possible interpretation consistent with these observations would be that at high field the molecule switches to different conformation that is elastically more favourable in the distorted specimen but with a higher electrostatic energy. More work is in progress to confirm or discard this proposed interpretation.

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