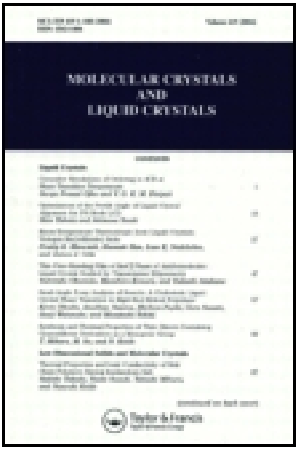

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C. Carboni [a] [b] & H. J. Coles [a]

[a] Department of Physics and Astronomy, Southampton Liquid Crystal Institute, The University of Southampton, Southampton, SO17 1BJ, UK

[b] Department of Physics, Sultan Qaboos University, P.O. Box 36, Al-Kohd, 123, Muscat, Sultanate of Oman

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Antiferroelectric Low Molar Mass Organosiloxane Liquid Crystals: a Phenomenological Model

C. CARBONI* and H.J. COLES†

Department of Physics and Astronomy, Southampton Liquid Crystal Institute, The University of Southampton, Southampton, SO17 1BJ, UK.

We have established that the antiferroelectric order observed in low molar mass organosiloxane liquid crystal materials with chiral bi-mesogen molecules is due to the bent conformation of the molecules rather than to co-operative antiferroelectric interactions. The switching between antiferroelectric and ferroelectric order involves a change of conformation of the molecules. We show that in mixtures of antiferroelectric and ferroelectric molecules this concept can be used to vary continuously the threshold field for antiferroelectric switching. We propose a simple model to describe the behaviour of the materials and to predict the threshold field.

Keywords: Antiferroelectric; organosiloxane; thresholdless switching

INTRODUCTION

The antiferroelectric order observed in materials with bi-mesogen organosiloxane molecules is not due to an antiferroelectric coupling between molecules in adjacent layers but to the V-shaped conformation of the molecules. The V-shaped conformation forces the electric dipole moments of the two chiral mesogenic moieties to be antiparallel to each other as illustrated in figure 1A. The packing of such molecules in a smectic phase results in an anticlinic arrangement of the long axis of the mesogenic moieties and therefore in a long-range antiferroelectric-like order of the dipole moments[1-3].

It is a peculiarity of the low molar mass organosiloxane liquid-crystal materials that their characteristics are, to a large extent, determined by the conformation

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* Present address: Department of Physics, Sultan Qaboos University, P.O.Box 36, Al-Kohd 123, Muscat, Sultanate of Oman.

† Author for correspondence

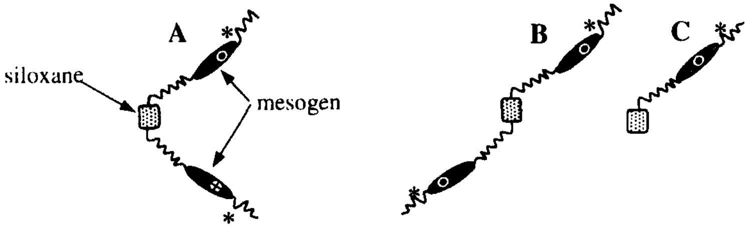

Figure 1. The bi-mesogen molecules **A**: V-shaped (antiferroelectric), **B**: linear (ferroelectric) and the mono-mesogen molecule **C**.

of the siloxane moiety[2,4]. The conformation adopted by the siloxane moiety is the one with the lowest energy that is compatible with the packing requirements of the mesogens. That conformation depends on the number of silicon atoms [2,3]. Because of the relatively low conformational energy barriers in siloxane chains the conformation of the siloxane moiety and therefore the characteristics of the material can be readily modified by controlled external influences such as the application of an electric field or mixing with molecules with a different conformation. In the present paper we show how this concept can be used to induce the antiferroelectric order in a material that would otherwise be ferroelectric. We propose a model to describe the behaviour of mixtures and to predict the threshold field for the antiferroelectric switching.

THE MATERIALS

The model presented here is illustrated using the new series of materials described in references [1-3] that are based on biphenyl benzoate mesogenic moieties. However, the chemical details of the mesogenic moiety are not relevant for the model; the only requirements on the mesogenic moiety is that it should be chiral, that it possess a transverse electric dipole moment and that it favours a SmC* phase. We also assume that in the smectic phase there are no significant antiferroelectric interactions between adjacent layers. With these conditions the materials with mono-mesogens (figure 1C) and linear bi-mesogens (figure 1B) are ferroelectric whereas the materials with V-shaped bi-mesogens (figure 1A) are antiferroelectric. In the present materials the only V-shaped bi-mesogen molecules are those containing three or five silicon atoms.

We shall consider mixtures of the V-shaped bi-mesogen molecules with mono-mesogen and with linear bi-mesogen molecules. In both cases the *anticlinic* alignment of the mesogens in the V-shaped molecule is incompatible with the *synclinic* arrangement of the molecules in the host. There are two possible ways by which this incompatibility can be resolved. Either the V-shaped molecules are switched to a linear conformation in which case the material remains ferroelectric or the V-shaped molecules impose the anticlinic arrangement to all the other molecules and the material becomes antiferroelectric.

THE MODEL

Following Robinson et al[1] we label respectively, the mono-mesogen and the bi-mesogen molecules X-n and X-n-X; n indicates the number of silicon atoms in the siloxane group, and X refers to the mesogen.

The template parameter

In the bi-mesogen molecules we call the link between the two mesogens *the template*[2,3]. This is the three-block chain consisting of the siloxane moiety and the two alkyl-chain links. We label the templates Si_n where n is the number of silicon atoms in the siloxane moiety. We define the template parameter W_n as the energy required to switch the template Si_n from a V-shaped conformation to a linear conformation. With this definition W_n is positive if the bent conformation has the lowest energy and negative if the straight conformation has the lowest energy. We do not want to consider, at this stage, what are the contributions to W_n, it may be that the mesogen contributes to W_n, this will be considered in a separate publication. Note that an isolated template has several template parameters because there are several V-shaped and several linear conformations. However, when the template is linked to the mesogens in a smectic phase one needs to consider only the one V-shaped and the one linear conformations with the lowest energy compatible with the packing of the mesogen; W_n is thus uniquely defined in a given organosiloxane material.

In mono-mesogen molecules we call the template the two-block chain consisting of the siloxane moiety and the alkyl chain. We shall assume that there is no change of conformation when switching a mono-mesogen and set W_n equal to zero for all mono-mesogen molecules[5].

We also define a mesogen parameter U_X which is the energy required to force the molecules in a unit volume of the mesogen X from their preferred synclinic (ferroelectric) arrangement into the anticlinic (antiferroelectric) arrangement. We do not consider here what are the contributions to U_X; a price has to be paid to force the anticlinic arrangement and that price is U_X.

The free energy of a mixture

Consider a material which is a mixture of several types of organosiloxane molecules, let Si_n be the templates of the different types of molecules. We write the energy density of such a mixture

$$f=\sum_{n}(\sigma_n-\varepsilon)\alpha_n W_n+\varepsilon U_X \qquad [1]$$

α_n is the concentration of the Si_n template, $(\sum\alpha_n=1)$.

$\sigma_n = 1$ if $W_n > 0$ and $\sigma_n = 0$ if $W_n < 0$; $\varepsilon = 1$ if the molecules are in an anticlinic arrangement and $\varepsilon = 0$ if the molecules are in a synclinic arrangement. The summation is carried out over all the types of templates present in the mixture. All the terms not relevant to the antiferroelectric / ferroelectric behaviour have been omitted. The coefficient $(\sigma_n - \varepsilon)$ is introduced to ensure that only those templates that have been switched to a conformation of higher energy contribute to the free energy.

We can write the energy of the mixture in the synclinic arrangement ($\varepsilon = 0$)

$$f_S = \sum_n \sigma_n \alpha_n W_n \qquad [2]$$

and the energy of the mixture in the anticlinic arrangement ($\varepsilon = 1$)

$$f_A = \sum_n (\sigma_n - 1)\alpha_n W_n + U_X \qquad [3]$$

The quantity of interest is

$$\Delta f = f_S - f_A \qquad [4]$$

If Δf is positive then the anticlinic molecular arrangement is preferred and the material is *antiferroelectric*. The material remains ferroelectric when Δf is negative. The sign of Δf can be changed by varying the concentration of the appropriate template. One can readily verify that, at any concentration, Δf is negative for mixtures of mono-mesogens ($W_n = 0$ for all n), for mixtures of linear bi-mesogens ($W_n < 0$ for all n) and for mixtures between linear bi-mesogens and mono-mesogens. The mixtures in which a change of sign of Δf can be observed are those containing V-shaped molecules ($W_n > 0$).

If the antiferroelectric material is subjected to an electric field **E** then equation 4 becomes

$$\Delta f = f_S - \left(f_A + \tfrac{1}{2}\Sigma \alpha_n (\mathbf{p}_n \cdot \mathbf{E})\right) \qquad [5]$$

where $\mathbf{p}_n$ is the effective electric dipole moment of the mesogen attached to the template Si_n. There is a threshold field

$$E_{th} = \frac{2\Delta f}{\Sigma \alpha_n p_n} = \frac{2\Delta f}{P} \qquad [6]$$

at which Δf changes sign and the material switches from antiferroelectric to ferroelectric. At the critical concentration y_c, which makes f_S equal to f_A the threshold field vanishes, the material becomes thresholdless antiferroelectric[6].

EXAMPLES

As a first example, let us consider a binary mixture between two bi-mesogen materials, one consisting of V-shaped molecules with template Si_n ($W_n > 0$ and $\sigma_n = 1$) and the other of linear molecules with template Si_m ($W_m < 0$ and $\sigma_n = 0$). Let y be the concentration of Si_n and (1- y) that of Si_m. In this particular case equations 1-4 become

$$f = (1 - \varepsilon)y W_n + (-\varepsilon)(1 - y) W_m + \varepsilon U_X \qquad [7]$$

$$f_S = yW_n \quad \text{and} \quad f_A = (1 - y)(-W_m) + U_X \qquad [8]$$

$$\Delta f = f_S - f_A = (W_m - U_X) + (W_n - W_m)y \qquad [9]$$

The change of sign of Δf , that is the crossover between ferroelectric and antiferroelectric order occurs at the critical concentration

$$y_c = \frac{W_m - U_X}{W_m - W_n} \qquad [10]$$

The cross over is illustrated in figure 2 where we have plotted on the same graph f_S and f_A as function of the concentration y. The material always adopts the arrangement of lowest energy.

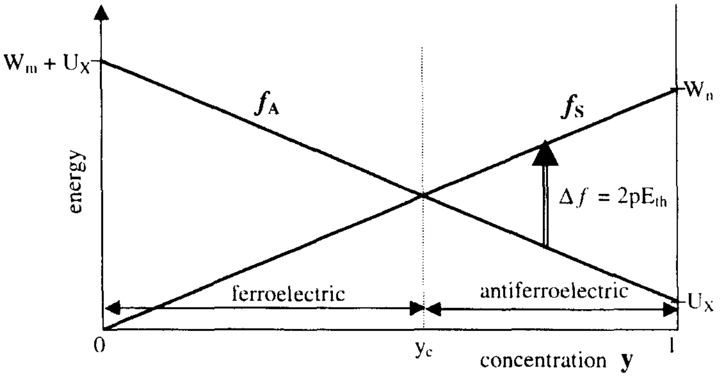

Figure 2. The energy of a binary mixture of V-shaped and linear bi-mesogen molecules. The material always adopts the arrangement of lowest energy. There is a phase transition at the critical concentration y_c.

In the range of concentrations where the material is antiferroelectric, the threshold field for switching to the ferroelectric state is

$$E_{th} = \frac{1}{2P}\left((W_m - U_X) + (W_n - W_m)y\right) \qquad [11]$$

E_{th} varies linearly with the concentration y and vanishes and at y_c. One can see that if $|W_m|$ is of the same order than $|W_n|$ and both are much larger than U_X then the crossover between ferro and antiferroelectric order occurs for $y = ½$.

As a second example, consider now a binary mixture where one of the constituents has V-shaped molecules with template Si_n ($W_n > 0$ and $\sigma_n = 1$) and the other mono-mesogen molecules with template Si_m ($W_m = 0$). Let y be the concentration of Si_n and (1- y) that of Si_m. The energies given by equation 1-3 are, in this case,

$$f = (1 - \varepsilon)y\,W_n + \varepsilon U_X \qquad [12]$$

$$f_S = yW_n \qquad \text{and} \qquad f_A = U_X \qquad [13]$$

The change of sign of Δf occurs at the concentration $y_c = \frac{U_X}{W_n}$

The threshold field for switching $E_{th} = \frac{1}{2p}\left(W_n\,y - U_X\right)$ varies linearly with the concentration y and vanishes at y_c. If W_n is much larger than U_X then the crossover occurs at very low concentrations.

EXPERIMENT

We have investigated two series of mixtures using materials described in references [1-3]. We have mixed the V-shaped bi-mesogen Cl11-Si3-11Cl with the mono-mesogen Cl11-Si3 and with the linear bi-mesogen Cl11-Si4-11Cl.

All the mixtures with the mono-mesogen are antiferroelectric. In the mixtures of bi-mesogens a transition between ferroelectric and antiferroelectric order is observed at a concentration of about 45% of Si_3 templates. In both cases the threshold field as a function of concentration (figure 3) decreases linearly with

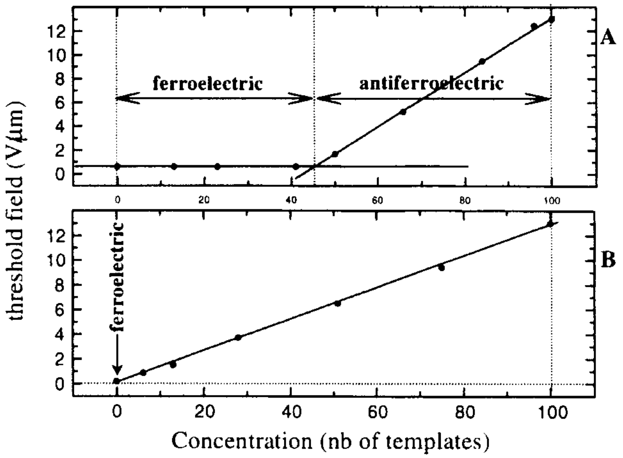

Figure 3. The behaviour of the threshold field as a function of the concentration of V-shaped molecules in mixtures with linear bi-mesogen molecules (**A**) and with mono-mesogen molecules (**B**)

decreasing concentrations. These observations are in agreement with the model presented and confirm the assumptions made in reference [3] that U_X is much smaller than W_3 and W_4 and that W_4 is smaller but of the same order than W_3.

ACKNOWLEDGEMENTS

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