On the effects of doping calamitic and discotic nematics with materials of the opposite aspect ratio

T. J. Phillips[a]; V. Minter[a]; J. C. Jones[a]

[a] Defence Research Agency, Worcestershire, UK

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On the effects of doping calamitic and discotic nematics with materials of the opposite aspect ratio

by T. J. PHILLIPS*, V. MINTER and J. C. JONES

Defence Research Agency, St. Andrews Road, Malvern WR14 3PS, Worcestershire,
UK

In this paper the inter-mixing of calamitic and discotic materials is discussed. The systems are found to be immiscible near the middle of the phase diagram, as was predicted theoretically. However, a degree of miscibility is seen at each end of the phase diagram, allowing some interesting effects to be explored. A negative permittivity anisotropy is induced in a discotic material by dissolution of a polar calamitic dopant. The relaxation behaviour of the dopant in the material is studied and found to be similar to that in the pure calamitic, as far as can be determined in this experiment. The elastic constants of a calamitic mixture are enhanced by addition of a discotic dopant. This is believed to be due to the packing of the discotic molecules in such a way as to hinder director distortions, and may be useful for changing the values of calamitic elastic constants.

1. Introduction

Various workers have attempted to mix mesogens consisting of discotic (disc-shaped) and calamitic (rod-shaped) molecules, with limited success. In general, e.g. [1], they form a biphasic resultant, with small birefringent droplets of the minority material in the majority, looking rather like the droplets in polymer dispersed liquid crystals. The topic received theoretical interest for some time [2, 3], as it appeared that, were a 50/50 mixture to be achieved, it would be a biaxial nematic. Finally a theory that included immiscibility as a possibility [4, 5] concluded that this immiscible outcome was always of the lowest energy, and therefore that a 50/50 mixture was impossible—this certainly seems to have been borne out by experiment.

It is likely that the largest miscibility may be achieved with two species that are chemically similar. With this in mind, a mixture, **T2**, was formulated using DB126, a triphenylene benzoate ester [6, 7], and a Merck Ltd phenyl biphenyl carboxylate, MBOSF, [8], whose phase transitions are:

$$\text{Cr } 47 \text{ S}_C \text{ } 127 \text{ S}_A \text{ } 133\cdot5 \text{ N } 160 \text{ I } (^\circ\text{C})$$
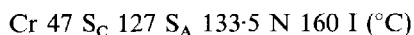
The relevant molecular structures are shown in figure 1. The phase diagram of **T2** is shown in figure 2, where the main points to note are the complex phase behaviour in the low wt % DB126 region, and the lack of any miscible mesophases near the centre of the diagram. However, there are two regions of interest.

One is where the discotic material appears to be miscible with the S_C phase at low concentrations ($<5\%$), discussed in the next section; the second is that, as shown on the right of figure 2, the calamitic material is soluble in the discotic material over a reasonable range (15–20%).

2. Control of discotic dielectric properties by doping with a calamitic

The second point above suggested that a calamitic dopant with a longitudinal dipole moment could be used to provide a perpendicular dipole moment in the discotic nematic phase, which is not easily achieved by other methods, as it requires asymmetric synthesis of a discotic, and would then provide material with a very low dipole relaxation frequency.† The calamitic molecules are expected to lie flat in the plane of the discs, because of the attractive interaction between benzene rings (figure 3), and therefore the longitudinal dipole moment of the calamitic contributes to the total dipole moment perpendicular to the director. This was attempted with **T5**, a mixture of a triphenylene nematic mixture **T1a** [9] and the material MH49 [10, 11], with structure shown in figure 1 and transition temperatures:

$$\text{Cr } 89 \text{ N } 121 \text{ I } (^\circ\text{C})$$
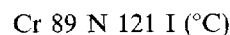
which has a large longitudinal dipole moment of $28\cdot7 \times 10^{-30} \text{ Cm}$ [12]. Mixture **T5c** had 8 wt % of

†Asymmetric synthesis is now being carried out by the Centre for Self-Organising Molecular Systems, University of Leeds.
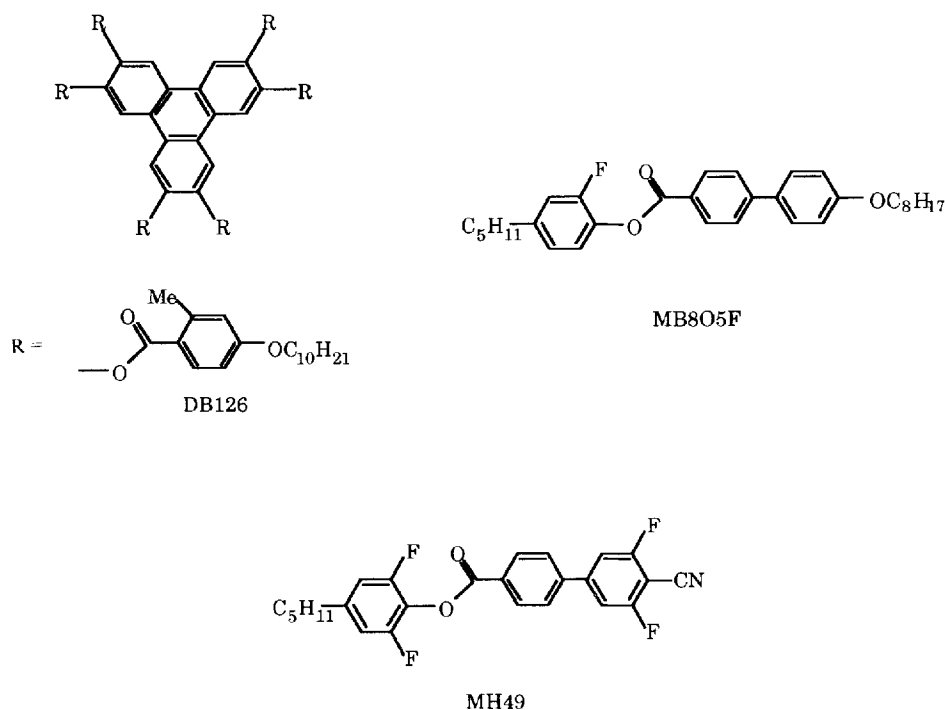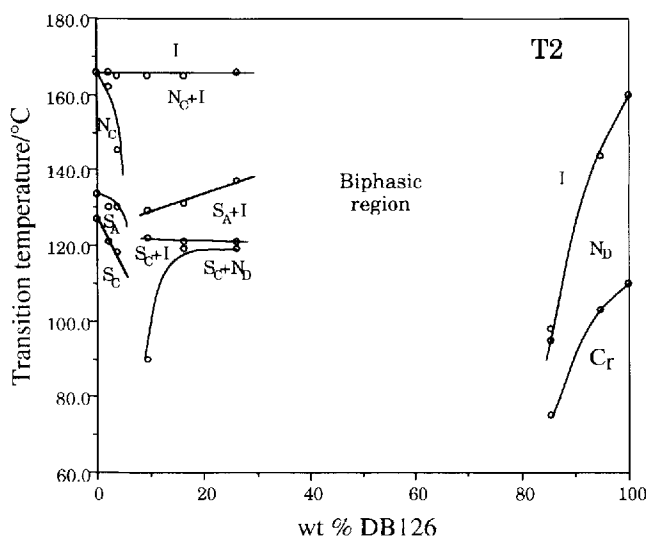
*Author for correspondence.

MB8O5F

DB126

MH49

Figure 1. Molecular structures.

Figure 2. Phase diagram of mixture **T2** (the notation N_C here refers to a calamitic nematic phase, and N_D to a discotic nematic phase).

MH49, with phase transitions:

Cr [35 N 70] 76 I (°C)

The nematic phase of this mixture aligned homeotropically in a cell with polymer aligning layers, although its high viscosity made this process rather slow. The material is indeed found to have a negative permittivity
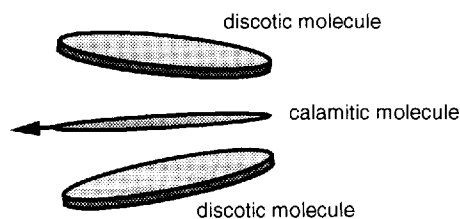

Figure 3. Relative orientation of discotic and calamitic molecules (schematic).

anisotropy at low frequencies and temperatures far from the I→N transition. This is demonstrated by switching the homeotropic state with an alternating electric field into a bright, mixed-planar aligned state (occasionally, areas occur in the cell that do not switch, for reasons that are unclear, as they do not appear to be regions of immiscibility).

An interesting feature of this material is that the perpendicular permittivity exhibits a relaxation behaviour at measureable frequencies, such that at high frequencies the permittivity anisotropy is again positive, and the cell can be switched back to the homeotropic state. This behaviour means that both permittivities can be measured in the same cell, by using a large voltage (~70 V) to switch the director and a small voltage (~1 V) to measure the appropriate value. The results are shown in figure 4 for a temperature of 40°C, with the solid line a fit to the Debye equation, which gives a
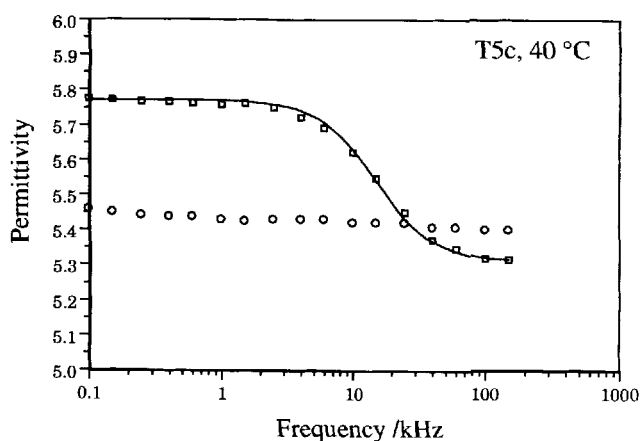
Figure 4. Permittivities of **T5c** as a function of frequency at 40°C. The solid line is a fit to the Debye equation with a relaxation frequency of 15 kHz.

relaxation frequency of 15 kHz. The activation energy could not be measured due to the very small range of nematic phase, and the difficulty in making the measurement. The relaxation is clearly due to a rotational motion of the calamitic molecule about a short axis, as the host material has no measurable relaxation behaviour at these frequencies [7]. The pure dopant, MH49, has a narrow nematic temperature range, allowing its relaxation behaviour to be measured. It is found to have a relaxation frequency of >600 kHz at 100°C, typical of the behaviour of three-ring compounds, and showing that its motion in the discotic host is, to first order, similar to that in the pure compound, since a typical activation energy of ~1 eV makes these results consistent.

3. The effect of a discotic dopant upon the physical properties of a calamitic

It was mentioned above that discotic materials are found to be soluble in calamitic materials to a small degree, especially at high temperatures. This observation at first suggested that a discotic dopant could be used to increase the biaxiality of the permittivity tensor in the S_C phase. The reason for this is that, when a discotic dopant is dissolved in a calamitic phase, it is likely to lie with the plane of the molecules along the long axes of the rod-like molecules (figure 3). It may then hinder the rotation of the calamitic molecules about their long axes, reducing the symmetry between the transverse dipole contributions to the permittivities. Unfortunately, it has been impossible to test this hypothesis, because a mixture that retains its solubility down to the smectic C phase has not been achieved. The mixture used here, **T6a**, is typical of the behaviour found. It consists of a difluoroterphenyl host, **F1** [13, 14], which was doped

with 2 wt % of T1a. In this material, immiscibility was seen as the material was cooled into the S_A phase, at around 83°C. Future materials may well enable a smectic C phase to be doped with a discotic, allowing the hypothesis to be tested.

The phase transitions of the two materials are

$$\text{F1} \quad S_C \ 74 \ S_A \ 90 \ N \ 114 \ I \ (°C)$$

$$\text{T6a} \quad S_A \ 83 \ N \ 111 \ I \ (°C)$$

As the mixture was found to be miscible over the whole nematic range, an experiment was carried out to determine the effect of the discotic dopant on the elastic constants of **F1**.

4. Elastic constant measurements

The elastic constant k_{33} was measured using a homeotropically aligned cell, and inducing a Fréedericksz transition using an applied electric field (the permittivity anisotropy of the material is negative). A typical set of raw data is shown in figure 5 for **F1**, where the threshold voltage is determined as the voltage where the permittivity starts to rise above its zero volt value. In practice this is achieved by fitting straight lines to the linear regions above and below the discontinuity in the gradient, and taking the voltage at which they meet as V_C. The elastic constant is then found from [15]

$$k_{33}(T) = \frac{\varepsilon_0 |\Delta\varepsilon(T)| V_C^2(T)}{\pi^2} \tag{1}$$

The dielectric anisotropy can either be measured separately using a planar aligned cell (as here) or using the high voltage extrapolation method of Clark *et al.* [16] on the permittivity versus voltage data. The resultant values for k_{33} are shown in figure 6, for the undoped and doped mixtures, versus reduced temperature, T/T_{NI}.
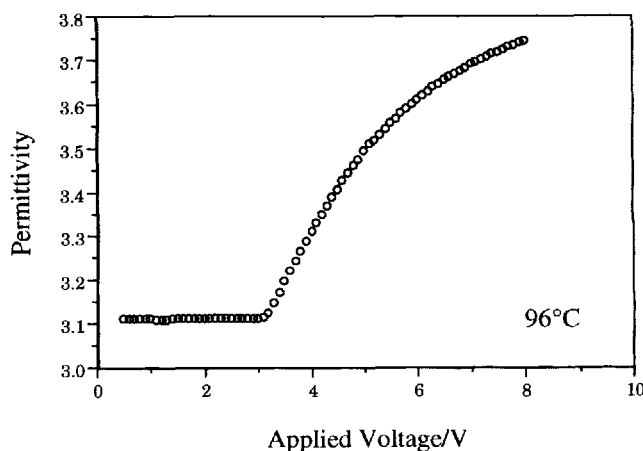

Figure 5. Measured permittivity versus applied voltage for **F1**, 9 μm cell with Cr complex alignment, 96°C.
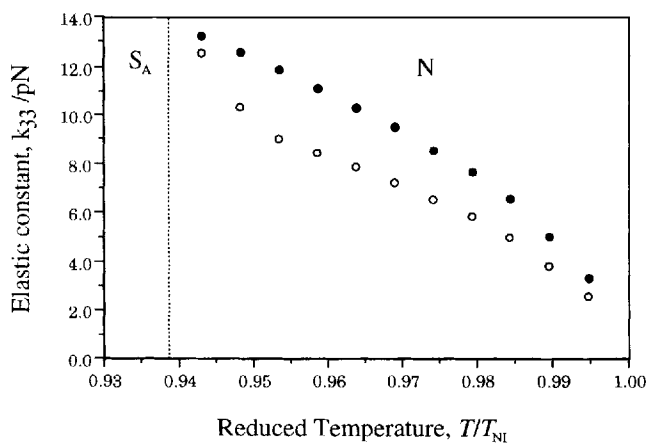
Figure 6. Elastic constants of undoped **F1** (open circles) and doped **T6a** (filled circles) DiFTP mixture as a function of reduced temperature. Error bars are too small to be shown.

In the undoped data, the typical variation of elastic constants with temperature near T_{NI} can be seen [17]. In addition, there is evidence of an enhancement in the elastic constant due to pretransitional effects near the $N \rightarrow S_A$ phase transition [17], which occurs at $T/T_{NI} = 0.938$. The doped material, **T6a**, shows a considerable increase in the elastic constant, of about 25%. This is a useful change, considering the small amount of dopant added, and indeed is of the order of the pretransitional increase shown in the undoped data, providing a possible alternative means of increasing the elastic constants of calamitics, which may well be used to alter the magnitude of specific constants while leaving others relatively unchanged.

5. Conclusions

In this paper the inter-mixing of calamitic and discotic materials has been discussed. The systems were found to be immiscible near the middle of the phase diagram, as predicted theoretically [4, 5]. However, a degree of miscibility was seen at each end of the phase diagram, allowing some interesting effects to be explored. A negative permittivity anisotropy was induced in a discotic material by dissolution of a polar calamitic dopant. The relaxation behaviour of the dopant in the material was studied and found to be similar to that in

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