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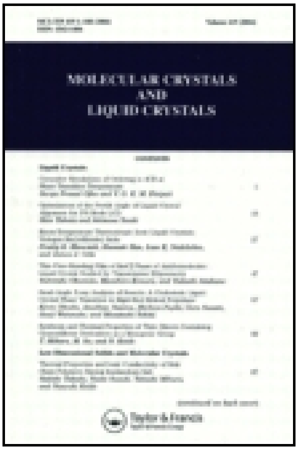

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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INVESTIGATIONS ON THE DYNAMIC BEHAVIOUR AND THRESHOLD VOLTAGES OF BINARY ANTIFERROELECTRIC LIQUID-CRYSTALLINE MIXTURES

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Version of record first published: 24 Sep 2006

To cite this article: T. Fütterer, D. D. Parghi, K. D'Havé & G. Heppke (2001): INVESTIGATIONS ON THE DYNAMIC BEHAVIOUR AND THRESHOLD VOLTAGES OF BINARY ANTIFERROELECTRIC LIQUID-CRYSTALLINE MIXTURES, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 683-692

To link to this article: http://dx.doi.org/10.1080/10587250108024009

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Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 683-692
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Investigations on the Dynamic Behaviour and Threshold Voltages of Binary Antiferroelectric Liquid-Crystalline Mixtures

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We present the results from our investigations on the dynamic behaviour and threshold voltages of two novel binary antiferroelectric liquid-crystalline mixtures comprising of different quantities of two components. The first component, (*S*)-TFMHPBC-11, is classed as a *hard* antiferroelectric material and exhibits a direct SmA* to SmC_A* (paraelectric to antiferroelectric) phase transition. The second component, (*S*)-DAF-9, is a *soft* antiferroelectric material in which both ferroelectric (SmC*) and antiferroelectric (SmC_A*) phases, separated by several subphases, are observed. By varying the concentration of the two components the observed apparent tilt angle vs. applied field curves of the resulting mixture, in the SmC_A* phase, can be 'tuned' from the characteristic tristate curve to a low-hysteresis structure more characteristic for a SmC* phase, whilst maintaining low threshold voltages.

Keywords: AFLC; subphase; hysteresis; threshold; cell thickness

INTRODUCTION

Antiferroelectric liquid crystals are recognised as useful materials for the next generation of high-performance display devices. The advantages of devices utilising the SmC_A* phase over those that utilise the nematic phase (prinicipally the TN and STN devices) are well known and have been described previously [1].

An important consideration for LC devices utilizing antiferroelectric materials, in addition to low thresholds for switching to the ferroelectric state, is the shape of the transmission vs. applied voltage hysteresis curves of the materials used in the devices. This characteristic governs how the device may be driven and consequently its operation in an application. Within recent years a novel electrooptic effect has been observed in an apparently antiferroelectric liquid-crystalline mixture (the 'Tokyo Mixture') which exhibits the phenomenon now referred to as 'V-shaped switching'. Although the physical nature of this effect is as yet unresolved two principal models exist which attempt to rationalise the effect [2, 3]. Although both models differ quite significantly they do, however, share a number of common factors that are believed to contribute to the appearance of the characteristic 'V-shaped' hysteresis-free electrooptic response. These include:

i. the significance of the mixing ratios of the components;
ii. the importance of the alignment layers and cell thickness on the electrooptic response, and
iii. the frequency of the applied electric field.

In order to investigate the role of some of these factors on controlling the appearance and 'shape' of the transmission vs. applied voltage hysteresis curves in AFLCs, we have measured the mesomorphic and electrooptic properties of two binary mixtures composed of different quantities of the same antiferroelectric materials.

This work was also intended to investigate the concept of mixing together *hard* and *soft* antiferroelectric materials in order to realise mixtures with useful properties for application in devices; in particular low switching thresholds and the 'tuning' of the hysteresis curves.

RESULTS AND DISCUSSION

1. Mesomorphic Properties

The materials investigated are (*S*)-TFMHPBC-11 and (*S*)-DAF-9 [4] (figure 1).

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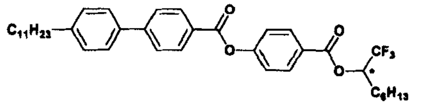
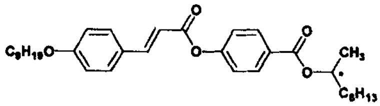


(*S*)-TFMHPBC-11
(*hard* AFLC)

Cr. 33 SmC_A* 64.6 SmA* 65.2 I (°C)

(*S*)-DAF-9
(*soft* AFLC)



Cr. 26 (SmC_A* 10.2 SmCγ* 12.5 "AF" 26.1) SmC* 49.4 SmA* 55.9 I (°C)

FIGURE 1 Structures and phase sequences of (*S*)-TFMHPBC-11 and (*S*)-DAF-9.

The first component, (*S*)-TFMHPBC-11, is classed as a *hard* antiferroelectric material since it exhibits a direct SmA* to SmC_A* phase transition and a very high threshold for switching to the ferroelectric state in the antiferroelectric phase. This, together with the narrow phase width of the SmA* phase observed in this material defines its strongly anticlinic character.

The second component, (*S*)-DAF-9, is classed as a *soft* antiferroelectric material since it exhibits both SmC* and SmC_A* phases separated by several subphases. The threshold for switching to the ferroelectric state in the antiferroelectric phase is much lower than that of (*S*)-TFMHPBC-11 at comparable reduced temperatures. Furthermore this material was selected from an homologous series of two-ring antiferroelectric materials prepared recently [5] which exhibits a very wide "AF" ("$SmC_{1/4}$*") phase (figure 2).

Figure 3 shows the static apparent tilt-angle vs. applied field curves obtained for the "AF" ($SmC_{1/4}$*) phase of (*S*)-DAF-9 (measured using positive and negative DC fields). The electrooptic response is rather complex and may be accounted for by the different meta-stable structures which arise between the two ferroelectric states.

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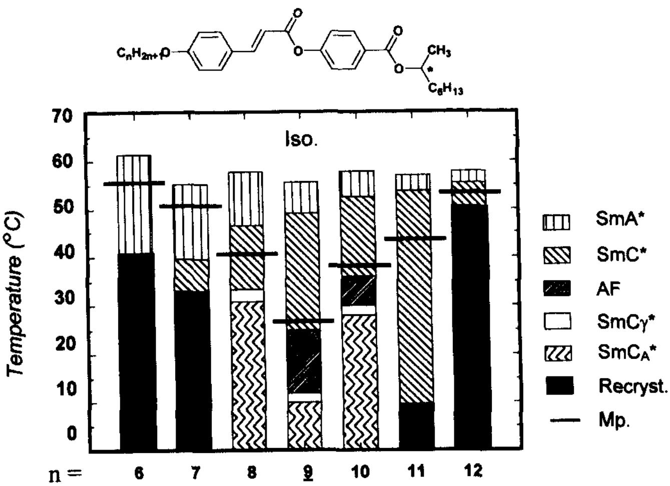

FIGURE 2 Transition temperatures for the homologous series of (*S*)-DAF-n (n = 6 to 12).

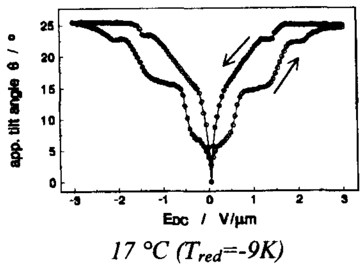

FIGURE 3 Static apparent tilt-angle vs. applied field curve obtained for (*S*)-DAF-9 in the "AF" ($SmC_{1/4}$*) phase (10 μm parallel-rubbed EHC cell, DC fields).

Recent investigations have shown that the occurrence of subphases between the *synclinic* SmC* and *anticlinic* SmC_A* phases is strongly dependent on the alignment layers present in the cell. By decreasing the thickness of the cell, in which the liquid crystal is being investigated, the alignment layers are believed to effect a greater influence on the ordering of the smectic layers of the liquid crystal.

As a preliminary investigation the influence of cell thickness on the

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SmC* to "AF" transition temperature was measured for pure (*S*)-DAF-9 (figure 4).

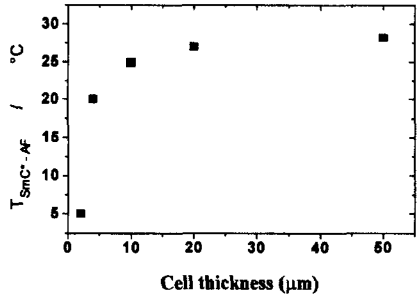

FIGURE 4 Dependence of the SmC* to "AF" transition temperature on the cell thickness for pure (*S*)-DAF-9 (measured by dielectric spectroscopy on cooling at 0.3 $Kmin^{-1}$) *[10 μm parallel-rubbed EHC cells]*.

The transition temperature of the "AF" phase decreases with decreasing cell thickness. This confirms that thin cells have the effect of de-stabilising this subphase.

2. Mixture Studies

Figure 5 shows the phase diagram between the two components (mol. %). A SmC* phase appears below the SmA* phase at approximately 50 mol.% of (*S*)-DAF-9. The SmCγ* and "AF" ($SmC_{1/4}$*) phases are observed in the binary mixtures above a concentration of 80 mol.% (*S*)-DAF-9 (the *soft* component). The dashed-vertical lines represent the concentrations selected for further investigations (see section 3: Electrooptic Investigations below).

In order to investigate the influence of mixture concentration on the switching behaviour of this series of mixtures, the threshold required for switching to the ferroelectric state (in the antiferroelectric phase) was measured for several concentrations of the binary mixture between pure (*S*)-TFMHPBC-11 and pure (*S*)-DAF-9. The results are shown in figure 6; the measurements were taken 13 °C below the transition to the anticlinic (SmC_A* or "AF") phase from the SmC* or SmA* phase (indicated with open crosses in figure 5).

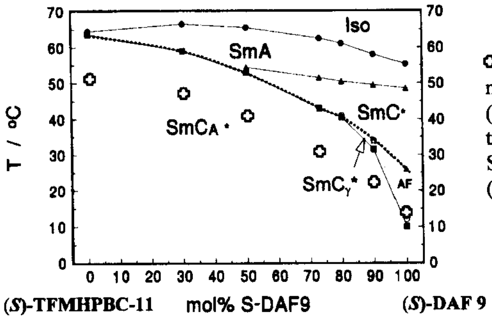

FIGURE 5 Phase diagram between the (*S*)-TFMHPBC-11 and (*S*)-DAF-9 (mol.%).

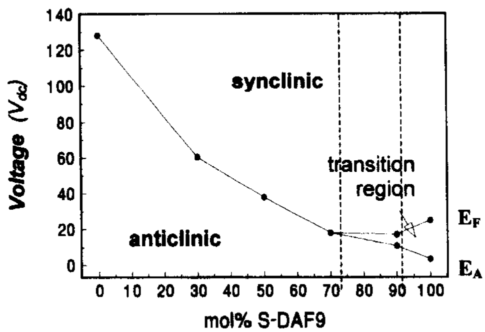

FIGURE 6 Threshold voltages for switching the antiferroelectric phase to the ferroelectric state for several different concentrations of the binary mixture. The dotted lines represent the concentrations of the components in the mixtures selected for further studies (see below).

An increase in the quantity of the *soft* ((*S*)-DAF-9) component relative to the *hard* ((*S*)-TFMHBC-11) component had the effect of lowering the measured threshold.

Two thresholds are observed for concentrations above 70 mol.% (*S*)-DAF-9 and are defined below (figure 7). The area between these two boundaries can be regarded as the region in which switching

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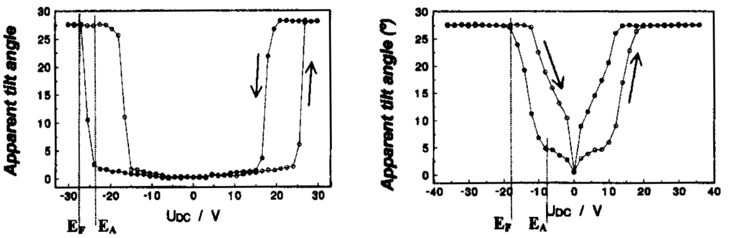
"occurs".



(a) *15.2 °C (SmC$_A$*) [70 % (S)-DAF-9]* (b) *20.2 °C (SmC$_A$*) [90 % (S)-DAF-9]*

FIGURE 7 Apparent tilt angle vs. applied field (DC voltage) curves obtained for mixtures composed of 70 mol.% and 90 mol.% (*S*)-DAF-9 in (*S*)-TFMHPBC-11 ((a) and (b) respectively). *[10 µm parallel-rubbed EHC cells]*

The composition (in mol.% of each component) and transition temperatures of two of the mixtures selected for these investigations from the phase diagram (marked with dashed-lines in figure 6) are shown in table 1 (in comparison with the pure materials).

TABLE 1 Transition temperatures of the two binary mixtures in comparison with the pure components.

Mixture	Cr.		SmC$_A$*		SmCγ*		"AF"		SmC*		SmA*		I
100% (S)-TFMHPBC-11	•	33	•	64.6	-	-	-	-	-	-	•	65.2	•
73.3% (S)-DAF-9 in (S)-TFMHPBC-11	•	<25	•	42.5	-	-	-	-	•	50.5	•	62.0	•
91.4% (S)-DAF-9 in (S)-TFMHPBC-11	•	<25	•	29.6	-	31.2	-	-	•	50	•	57.3	•
100% (S)-DAF-9	•	26	•	10.2	•	12.5	•	26.1	•	49.4	•	55.9	•

3. Electrooptic Investigations

Transmission vs. applied field curves were plotted for both the pure materials and binary mixtures in self-made test-cells of different

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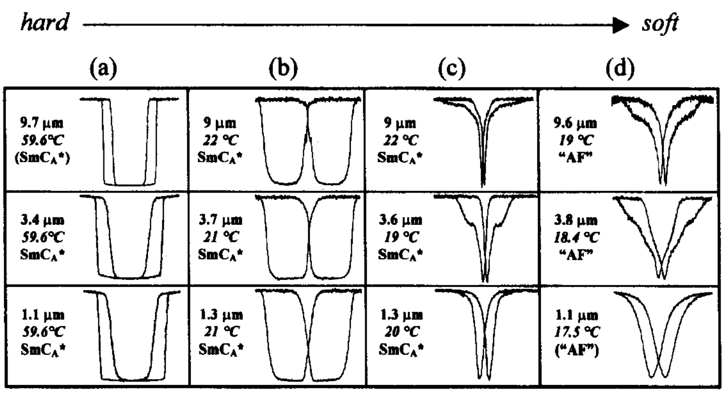
thickness (figure 8). The alignment layer in the cells was antiparallel-rubbed pyralin. A triangular wave AC field was generated by a Keithley 3930A Multifunction Synthesizer and applied across the cells via a Krohn-Hite 7500 power amplifier at a frequency of 0.1 Hz. The curves were recorded on a Gould 1624 oscilloscope from am SMT photomultiplier attached to a WILD M420 microscope.

The materials were aligned in the cell on cooling from the isotropic phase under application of a suitable AC square-wave electric field at 100 Hz frequency. The curves for the binary mixtures and pure (*S*)-DAF-9 were plotted after an averaging period of 1024 cycles.

By adjusting the composition of the components present in the binary mixtures the shape of the transmission vs. applied field curves could be altered quite significantly. Furthermore, cell thickness appeared to play a significant role in determining the observed switching properties.

FIGURE 8 Transmission vs. applied field curves (at 0.1 Hz) obtained for:-
(a) pure (*S*)-TFMHPBC-11 (*hard* component);
(b) the 73.3 mol.% (*S*)-DAF-9 in (*S*)-TFMHPBC-11 mixture;
(c) the 91.4 mol.% (*S*)-DAF-9 in (*S*)-TFMHPBC-11 mixture, and;
(d) pure (*S*)-DAF-9 (*soft* component).



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hard

(a) The *hard* AFLC ((*S*)-TFMHPBC-11) showed clear tristate switching in all thicknesses of cells.

(b) The first mixture (73.3 mol.% (*S*)-DAF-9 in (*S*)-TFMHPBC-11) is also quite a *hard* AFLC and showed clear tristate switching in all thicknesses of cells in the SmC_A* phase in comparison with the bistate switching of the overlying SmC* phase. The thresholds for switching to the ferroelectric state in all the cells were, however, found to be considerably lower than those of pure (*S*)-TFMHPBC-11 in cells of comparable thickness.

(c) The shape of the curve of the 91.4 mol.% (*S*)-DAF-9 mixture in the 3.6 μm-thick cell, in the temperature range of the SmC_A* phase, implies that both tristate and bistate switching occured simultaneously in this sample. In the "thin" (1.3 μm) cell the switching (in the same temperature range) was completely bistate at the measured frequency of 0.1 Hz (ie. SmC* behaviour appears to be favoured over SmC_A* in a thin cell). In the thicker (10 μm) cell the nature of the switching is unclear although we speculate that helical winding and unwinding dominated at this frequency.

(d) The *soft* AFLC showed an electrooptic response in both the "thick" and "medium" (3.8 μm) cells that are typical for the "AF" ($SmC_{1/4}$*) phase. In contrast, the response in the "thin" (1.1 μm) cell, in this temperature range, was typical for that of a SmC* phase.

soft

CONCLUSIONS

A series of binary mixtures were prepared and their physical properties were investigated. By combining *hard* and *soft* AFLC materials it was possible to 'fine-tune' the shape of the observed transmission vs. applied voltage curves whilst maintaining low thresholds for switching to the ferroelectric state. As has also been observed in related antiferroelectric systems the dynamic behaviour of one of the mixtures investigated was found to be strongly dependent on cell thickness. Although one would not use (*S*)-DAF-9 in a commercial antiferroelectric mixture (due to the potentially facile transformation, under UV light, of the *trans*-isomer to the non-mesogenic *cis*-form of the molecule) it is hoped that the work presented here has served to introduce a novel method for achieving AFLC mixtures with potentially useful properties for exploitation in devices.

Further investigations on these and related materials are underway and will be presented in the near future.

Acknowledgements
The authors thank the EU-TMR program 'ORCHIS' for funding this work.

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