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

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Sebastian Gauza, Krzysztof Czupryński, Roman Dabrowski, Wojciech Kuczyński & Damian Pociecha (2001): Bicomponent System with Induced Antiferroelectric SmC_A^* Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 189-198

To link to this article: http://dx.doi.org/10.1080/10587250108025295

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 189-198
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Bicomponent System with Induced Antiferroelectric SmC_A^* Phase

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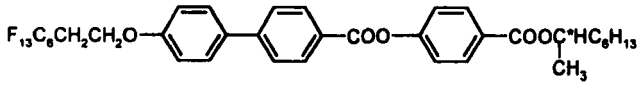
In mixture of two ferroelectric compounds: 4-(1-methyloctyloxy-carbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate and 4-(1-methyl-heptyloxycarbonyl)phenyl 4-(perfluorohexyl-2-etoxy) biphenyl-4-carboxylate an antiferroelectric SmC_A^* phase was induced. Dielectric and electrooptic properties were investigated and discussed. V-shaped switching was observed in this mixture.

Keywords: phase diagram; chiral smectic C_β^*; induced antiferroelectric phase; X-ray scattering; dielectric permittivity; V-shaped switching

INTRODUCTION

Recently we observed that an antiferroelectric smectic phase (SmC_A^*) was induced in a mixture of two chiral esters[1]. The first ester had a partially fluorinated terminal chain and phase sequence SmC_β^*-SmA-Iso and the second ester had only a hydrogenous terminal chain and phase sequence SmA-Iso. The maximum stability of the induced

SmC_A^* phase was observed for mole ratio 1:1 and equilibrium between induced SmC_A^* and SmC_β^* phases existed in the broad temperature range on the side of excess of the fluorinated compound. This material showed V-shaped switching in this labile region. We decided to look for other, similar systems, especially for that which could have the phase transition sequence SmC_β^*-SmA on both sides of the induced SmC_A^* phase. We found that such properties show the bicomponent system composed of compound 1 (the same as previously investigated) and compound 2 having the following formulas and phase transitions:



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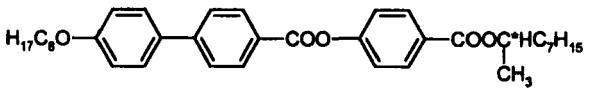
Cr_1 80,7 Cr 98,1 SmC_β^* 148,1 SmA 183,6 Iso



2

Cr_1 60,8 Cr 79,7 (SmI_A^* 65.8) SmC_β^* 118,4 SmC_α^* 118,7 SmA 144,1 Iso

Both components of the mixture possess the ferroelectric SmC_β^* phase. None of them exhibits (enantiotropic or monotropic) the antiferroelectric SmC_A^* phase which was confirmed by miscibility studies of compounds of similar structure having a SmC_A^* phase.

In this work we present thermomicroscopic, X-ray, dielectric and electrooptic studies of mixture 1-2. We believed that better knowledge of systems with induced SmC_A^* phase would input to discussion about sense of frustration in V-shaped switching phenomena [2] as well as it would introduce a new method of the formulation of antiferroelectric materials with strictly adjusted properties.

EXPERIMENTAL PART AND RESULTS

Thermomicroscopic studies

The phase diagram of bicomponent mixture 1-2 is presented in Figure 1. It was obtained by weighting separate samples of each concentration. The temperatures of phase transitions were determined by using a Linkam THMS 600 hot stage and Biolar PZO polarizing microscope. A liquid crystal was placed between thin microscope plates without spacer. The induced antiferroelectric SmC_A^* phase started to create after introducing a fluorinated compound 1, only in amount of 0,05 mole fraction of 1, to non-fluorinated compound 2 and it existed for

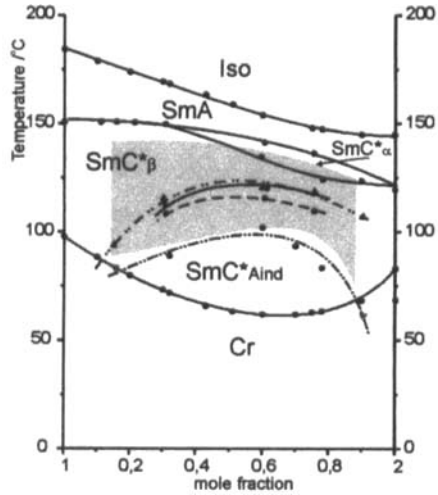


FIGURE 1 Phase diagram of mixture 1-2 from polarizing microscopic observations during ——heating, - - - cooling. The curves —··· relate to hysteresis of SmC_A^* to SmC_β^* transition from dielectric measurements. The gray colour shows the area, wherein V-shaped switching is observed.

wide concentration range of 2 between 0,25-0,95 mole fraction of it. The temperature 110°C was the maximum value for the thermal stability of the induced antiferroelectric SmC_A^* phase. We observed wide temperature hysteresis for transitions between induced antiferroelectric SmC_A^* and ferroelectric SmC_β^* phases during heating and cooling cycles. The hysteresis is smaller in the central part of induced SmC_A^* phase and wider on its sides, where it begins to form.

X-ray studies. Temperature and concentration dependence of smectic layer spacings

The smectic layer spacings were measured by difractometer DRON-UH2 and by Guinier camera during cooling cycles also a semifree liquid crystal film supported on thin glass plate was used. The change of the smectic layer spacings (d) and relative layer spacings (ratio d/d_A) for the mixture 1-2 upon temperature and for different concentration of 2 is presented in Figure 2a and 2b. The values of d in the SmA phase of both single compounds change. They are 3,46 nm and 3,77 nm, respectively, for compounds 1 and 2 at 10 °C above the transition to the tilted phase.

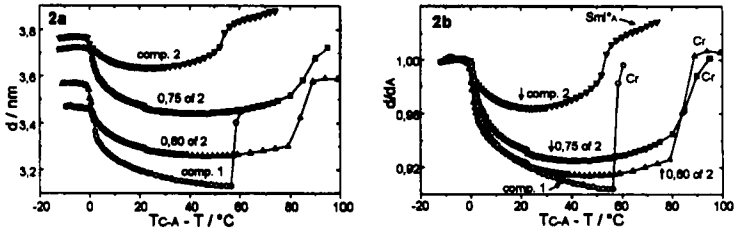


FIGURE 2 Temperature dependence of the smectic layer spacings **d** –a and relative layer spacings ($\mathbf{d/d_A}$) –b of compounds 1 and 2 and their mixtures. d_A – maximum spacing of SmA phase.

The smectic layer spacings of their mixtures for SmC_β^* and SmC_A^* phases are decreased quicker than the fall of the concentration of non-fluorinated compound (see Figure 2b). The transition between SmC_β^* and SmC_A^* phase is well seen as the small drop of value d what confirms that the internal layer structure is actually being rebuilt and that the phase of separation is not observed. The layers are tilted at $T_{C\text{-}A}$-T = 50°, respectively for compound 1 - 0,78 and 2 - 0,93 (calculated from d/l), 1 - 0,91 and 2 - 0,98 (calculated from d/d_A). At low temperature the observed increase of d is related to the presence of SmI_A^* phase for single compounds 2 and to crystallization for other samples.

Dielectric permittivity and switching measurements

Dielectric and electrooptic investigations were performed using 2 μm thick cells purchased from EHC (Japan) and 5 μm thick cells purchased from Linkam (UK). The investigated materials were introduced in their isotropic phase into the measuring cells by capillary action. The samples were heated up to the isotropic phase prior to the measurement and then slowly cooled to the SmA phase. In most cases this procedure was sufficient for obtaining good homogeneous planar alignment of samples. The electric permittivity was measured with the impedance analyzer HP 4192A using the voltage of 0.5V. Switching observations were carried out on the sample in extinction position between crossed polarizers on the microscope stage using a modified Mettler stage connected with Unipan (Warsaw) type 650 temperature controller which secured the temperature stability of about ±0.01 K. Triangle-shaped voltage of 10 to 40V amplitude and 0.03 to 300 Hz frequencies was applied to the electrodes. The intensity of light passing through the

sample, polarizer and analyzer was registered using a photodiode connected to a preamplifier and storage oscilloscope HP 54602A. More details are given in work [3].

Dielectric measurement gives further confirmation of the existence of induced SmC_A^* phase in 1-2 mixture, see Figure 3. During cooling, the dielectric permittivity increases from the value 5 in the paraelectric SmA phase to about 75 in the ferroelectric state. During further cooling, the high value of permittivity persists up to 98 °C for 0.6 mole fraction of 2 for example, and then quickly starts to decrease (Figure 3Ac). The microscope field observations simultaneously reveal that a change of texture starts to perform at this temperature, Figure 3Bb. At 50 °C, for the same composition, the dielectric permittivity settles slightly below 10 and the texture in the whole sample is characteristic of SmC_A^* phase. During heating, this texture and low value of permittivity ε persist up to 119 °C, in this temperature a sudden transition to the ferroelectric state takes place, what is demonstrated by the change of both texture and the value of ε. The observed hysteresis strongly depends on composition, Figure 3A. The transition temperatures measured during cooling and during heating differ, respectively, for mole fractions of compound 2: 0.15 – 9, 0.3 – 40, 0.6 – 22, 0.75 – 22, 0.9 – 49 degrees. The largest temperature hysteresis of the transition between ferroelectric and antiferroelectric phases was observed while SmC_A^* was arising. It is a very striking feature of the induced antiferroelectric phase, Figure 3. Similar features are shown for the electrooptic responses (Figure 3B). Thresholdless, V-shaped switching can be observed in all investigated mixtures with induced SmC_A^* phase, but for different electric field conditions, see Figure 4 and Figure 5. As Figure 4 demonstrates, at low

frequencies of the applied triangle-shaped voltage, the typical V-shaped switching is observed (the small hysteresis in the low-frequency region is probably caused by ionic current effects). This type of switching appears at high temperatures, wherein the ferroelectric SmC_β^* phase is stable in bulk samples but it also exists at lower temperatures, wherein the SmC_β^* and SmC_A^* phases are in equilibrium (Figure 5). The texture observation revealed that in a large part of the induced SmC_A^* phase a strong electric field caused the transition to the SmC_β^* phase. Hence, the SmC_β^* phase exists in whole temperature range where the thresholdless change of light transmission occurs. They cover almost the same temperature range as the hysteresis region (see Figure 5).

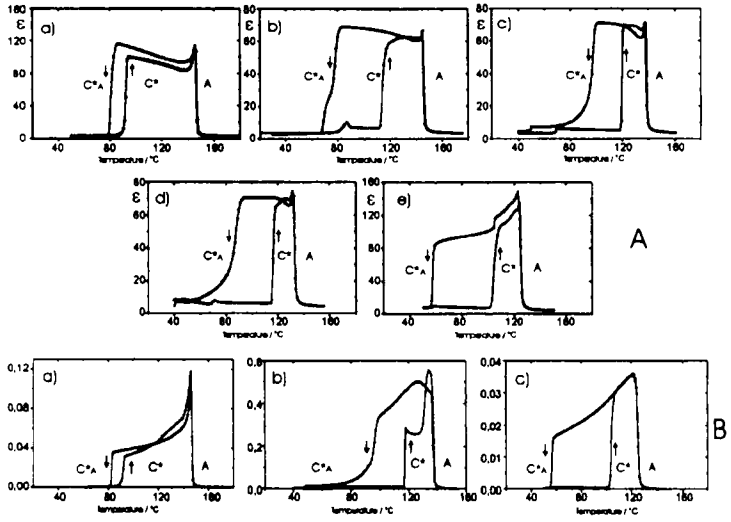


FIGURE 3 Temperature hysteresis of electric permittivity – A and light transmittion – B measured at frequency 440 Hz in the 1-2 mixture for a-0.15, b-0.3, c-0.6, d-0.75, e-0.9 mole fraction of compound 2.

This observation agrees with the current hypothesis, that the thresholdless switching appears in SmC_β^* phase under certain conditions [4].

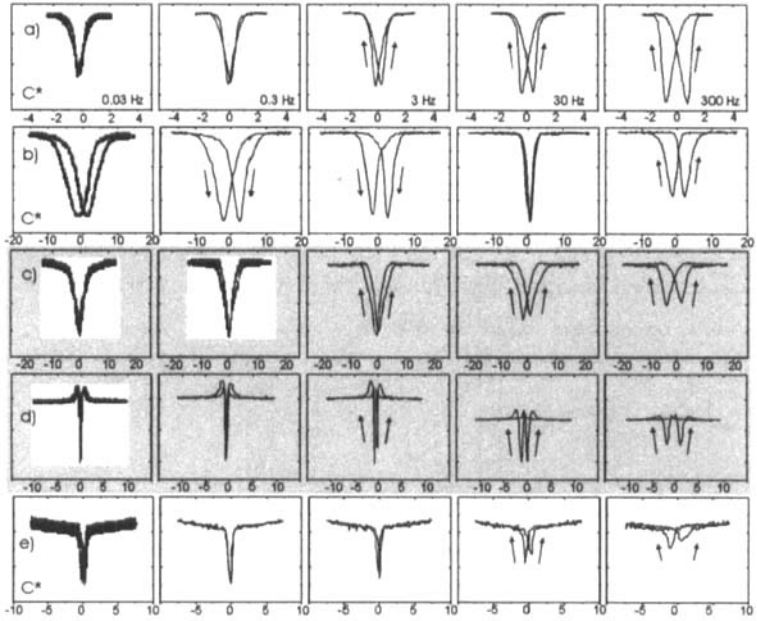


FIGURE 4 V-shaped switching in the mixture 1-2 for a-0.15, b-0.3, c-0.60, d-0.75, e-0.9 mole fraction of compound 2 upon frequency at temperature 115 °C. $SmC_A^* \rightleftarrows SmC_\beta^*$ equilibrium region from the dielectric observations is marked by gray color.

DISCUSSION AND CONCLUSIONS

Performed experiments demonstrated that the antiferroelectric SmC_A^* phase may be induced by mixing ferroelectric components. The observed enhancement of SmC_A^* phase is probably the result of

molecular layering in such way, that the chain of fluorinated molecules alternate each other with the chain of hydrogenous molecules. It reduces repulsive forces and increases attraction force due to greater dipole-induced dipole interaction. Such dimmer like ordering of molecules was

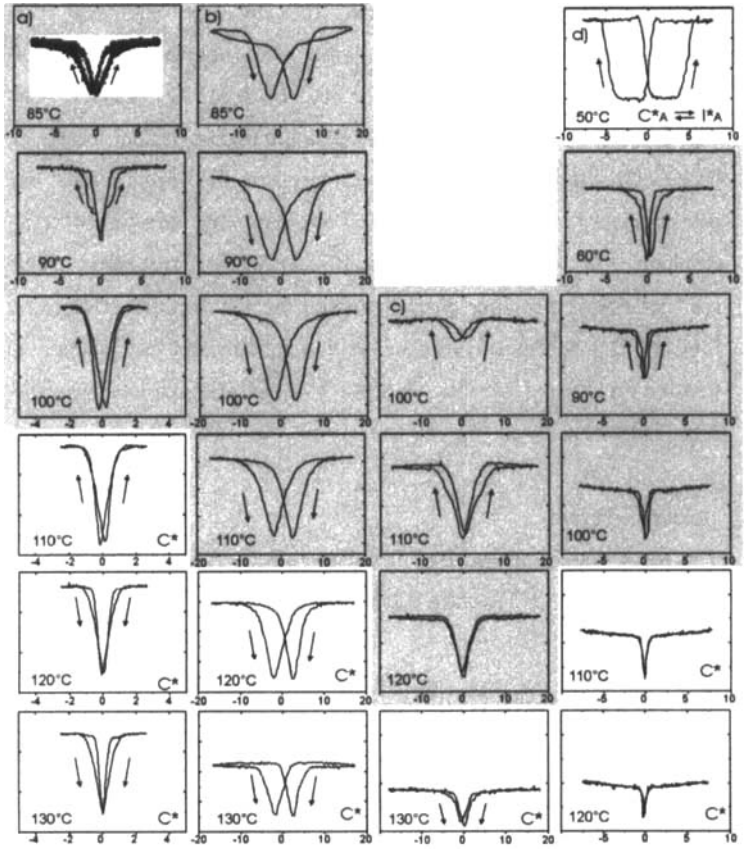


FIGURE 5. Electrooptic switching in mixture 1-2 for: a-0.15, b-0.3, c-0.6, d-0.9 mole fraction of compound 2 at frequency 0,3 Hz and various temperatures. $SmC_A^* \rightleftarrows SmC_\beta^*$ equilibrium region from the dielectric observations is marked by gray color.

proposed for chain fluorinated smectic C esters by Janulis et al.[5]. In such mixtures, the molecular interactions leading to either synclinic (ferroelectric) or anticlinic (antiferroelectric) order can be of very similar strength in some concentrations and temperature regions, especially where SmC_A^* phase starts to induce, see Figure 1. The SmC_A^* order is strengthened at lower temperatures especially for concentration 1:1. The switching for antiferroelectric-ferroelectric field which induced transition at lower temperature region was not measured because the threshold was too high for used field voltage and the measurement results will be presented in other work soon. Frustrations resulting from the competition between ferroelectric and antiferroelectric ordering gives hysteresis in high temperature for the $SmC_A^* \rightleftarrows SmC^*$ transition as well as V-shaped switching. We suppose, that the presence of hysteresis is a token of the threshold-less switching (see Figure 1).

Acknowledgments

This work was supported by Polish Research Committee (KBN) under grant No. 3TO9A07315 and 2PO3B-097-15.

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