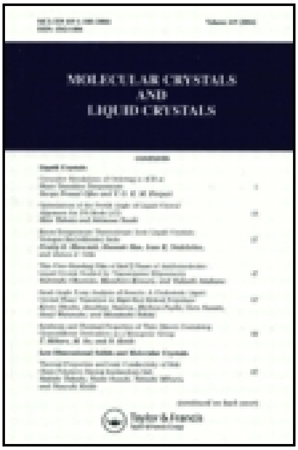

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Continuous Evolution from Ferroelectric to Antiferroelectric State in Chiral Smectics

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Continuous Evolution from Ferroelectric to Antiferroelectric State in Chiral Smectics

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Continuous evolution of polar properties from ferro- to antiferro- has been observed in binary mixtures. Pure components exhibit antiferroelectric or ferroelectric smectic phases. The static dielectric constant in antiferroelectric-like smectic phase increases continuously upon increasing the ferroelectric component concentration. This behavior could be attributed to changes of the strength of azimuthal tilt angle correlations leading to a frustrated state. In materials with frustrated phase ferroelectricity can be enforced by strong boundary conditions in thin cell. The switching behavior found in thin cells was similar to that observed in thresholdless antiferroelectrics.

Keywords: ferroelectric and antiferroelectric phases; frustrated phases; thresholdless switching

INTRODUCTION

Competing ferroelectric *(FE)* and antiferroelectric *(AF)* interactions in some mixed solid solution crystals lead to appearance of a frustrated state (glass or relaxor) devoid of long range dipolar order[1]. In such a state the dipole distribution is not yet random, the polar symmetry is broken on nanometric scale and the concentration of the *FE* and *AF* regions depends on the mixture composition. It results in continues evolution of polar properties of frustrated phase from *AF* to *FE* under a concentration change. *A* related behavior can be expected for liquid crystal mixtures of *FE* and *AF* compounds of similar chemical structure. These conditions can be fulfilled in mixtures of compounds of the same homologue series.

EXPERIMENTAL

For our studies two successive homologues (C12 and C13) of 4-(4'-alkoxy-biphenyl-4-yloxymethyl)-benzoic acid 2-octanol esters were chosen[2]. Compound C13 exhibits exclusively the *FE* phases (SmC* and hexatic SmI*) whilst C12 has dominant *AF* properties, broad temperature range of SmC_A* and $HexI_A$* phases is preceded by the narrow ferroelectric SmC* phase range (~1K). Mixtures of C12 and C13 were prepared and their dielectric and electrooptic properties were studied. The frequency dispersion of dielectric permittivity, ε, was measured in the 20Hz–300KHz frequency range (using Wayne Kerr impedance analyzer), in heating runs with planar glass cells covered with ITO electrodes and polyimid layers. The results yielded relaxation frequencies and dielectric strength of the relaxator. Besides a low frequency permittivity (at 120Hz) was measured in the vicinity of the SmC*-SmC_A* phase transition. Electrooptic response was detected during the sample switching under a triangular applied electric field. Samples of different thickness were studied to understand the role of surface interactions.

RESULTS

In pure C13 material in the SmC* phase the Goldstone mode was detected with relaxation frequency in the range of kHz. In the SmI* phase the relaxation frequency decreases to about few Hz. This results in decrease of dielectric constant measured at 120 Hz (Fig.1), although it is observed that the dielectric mode strength slightly increases in hexatic phase[3]. In pure C12 homologue below *FE-AF* phase transition temperature T_0 the Goldstone mode is suppressed, and no dielectric mode was found within the studied frequency range. In consequence, low frequency dielectric permittivity exhibits jump at the *AF-FE* phase transition temperature.

In mixtures of C12 and C13 compounds below short ferroelectric SmC* phase, the $\mathrm{SmC_A}$*-like and $\mathrm{SmI_A}$*-like phases are observed. Properties of these low temperature phases change continuously from *AF* to *FE* with increasing concentration of *FE*-component C13. This is signified by appearance of the Goldstone-like mode below T_0, which becomes gradually stronger as the concentration of C13 increases. The relaxation frequency of the Goldstone mode in $\mathrm{SmC_A}$*-like phase is nearly the same as in SmC* phase and the temperature dependence of the mode strength and its relaxation frequency around *AF*-like hexatic-liquid smectic phase transition is similar to that observed in pure *FE* - C13 compound[3].

The Goldstone mode strength jumps up at the *AF–FE* phase transition, the jump becomes lower for higher concentration of C13 component, as a result of the Goldstone mode strengthening in the $\mathrm{SmC_A}$*-like phase. For mixtures with mole fraction of C13 above ~0.9 the *AF-FE* phase transition is lost, the discontinuity of dielectric constant disappears and a smooth evolution of ε with temperature is detected.

Temperature dependence the Goldstone mode strength at *AF-FE* phase transition is apparently the same as that of the low frequency permittivity (Fig.1).

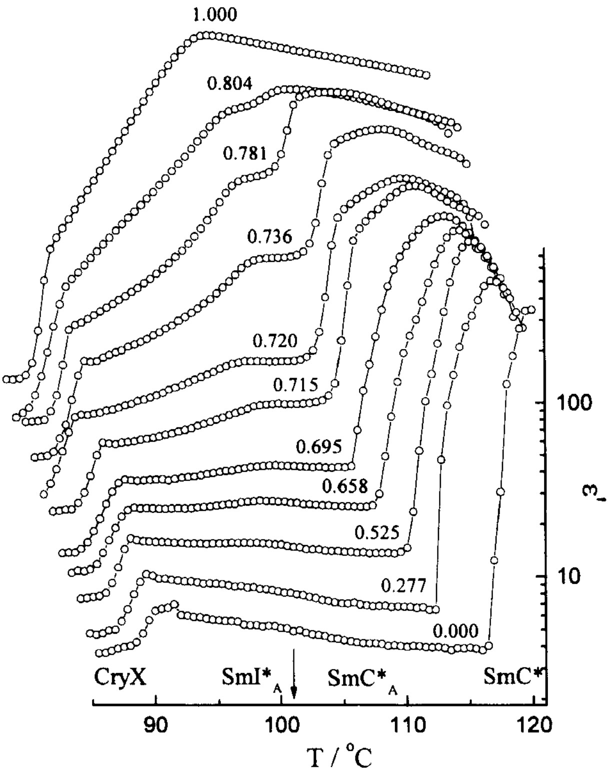
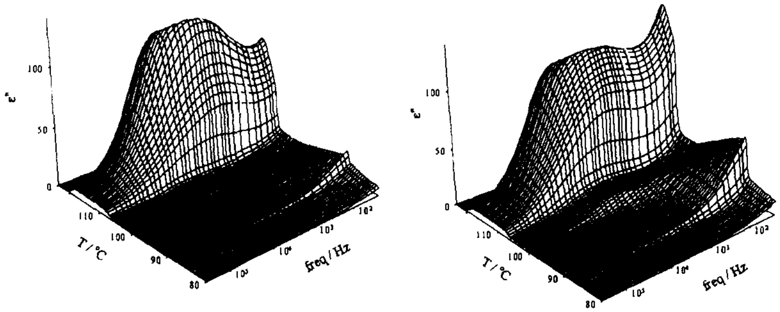


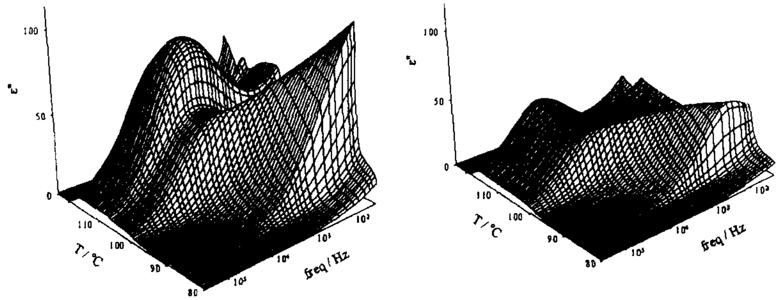
FIGURE1. Temperature dependence of dielectric constant (logarithmic scale) measured at 120Hz in 23 μm thick cells for mixtures of homologues C12 and C13. The curve parameters show the concentration of C13. Arrow indicates the SmI*-SmC* phase transition.

It has been also observed that the polar properties of the phases below T_o are strongly affected by interactions with sample boundaries. It was found that surfaces favor *FE* alignment. With decreasing sample thickness the strength of Goldstone mode in *AF*-like phase increases (Fig.2), the effect being more pronounced for less *AF*-like mixtures.



(a) 23 μm

(b) 16 μm



(c) 9 μm

(d) 5.3 μm

FIGURE 2. Imaginary part of the dielectric constant in mixture with 0.72 mole fraction of C13measured in cells of various thickness.

It is worth noticing that the behavior of the mode in phases below temperature T_0 is reversed to that detected in regular *FE*–SmC* phase above T_0, where the mode is suppressed by decreasing cell thickness[4]. Below certain sample thickness the *AF-FE* transition is lost and smooth temperature evolution of the Goldstone mode strength is observed (Fig. 2d). This critical thickness depends strongly on the mixture composition e.g it is about 5 μm and 80 μm for mixtures of 0.72 and 0.83 mole fraction of C13, respectively.

Also electrooptic response studies confirm the effect of surface interactions on polar properties of low temperature phases (Fig. 3).

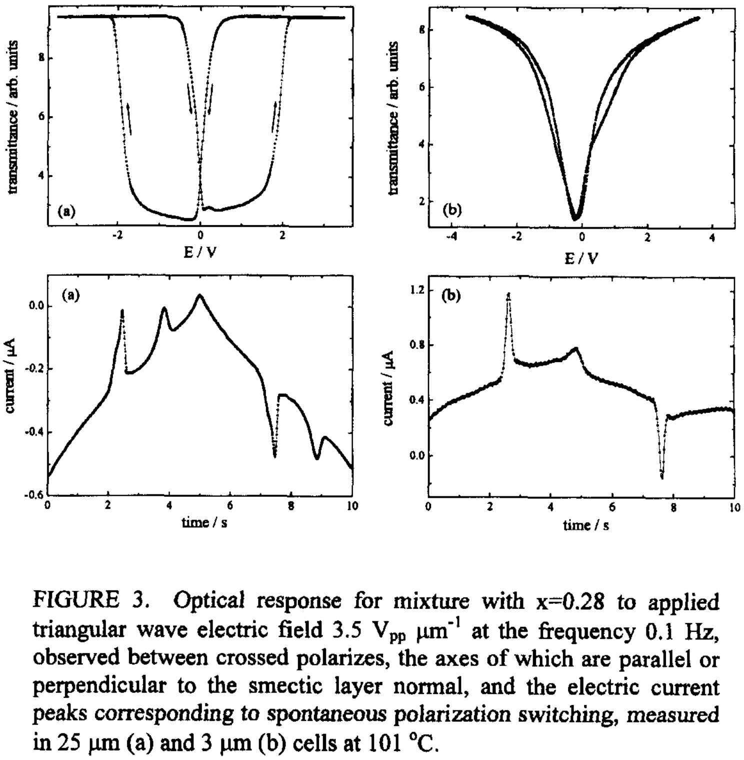


FIGURE 3. Optical response for mixture with x=0.28 to applied triangular wave electric field 3.5 V_{pp} μm^{-1} at the frequency 0.1 Hz, observed between crossed polarizes, the axes of which are parallel or perpendicular to the smectic layer normal, and the electric current peaks corresponding to spontaneous polarization switching, measured in 25 μm (a) and 3 μm (b) cells at 101 °C.

In thick samples tristable switching with considerable hysteresis was observed in the whole temperature range below T_0, in thin cells the switching became V-shaped[5]. In the thick cells a double electric current peak was resolved at spontaneous polarization reversal (at a frequency below 0.5Hz) while in thin cell a single peak was recorded.

It is worth noticing that in both thin and thick samples the excitation direction is along the layer normal and the formation of uniform tilt state goes through the stripe domains under applying electric field, even if in thin samples dielectric measurements suggests ferroelectric behavior.

DISCUSSION

In mixtures of C12 and C13 homologues, the observed gradual evolution of the low temperature phase properties from *AF* - like to *FE* - like under increasing concentration of the ferroelectric component is probably caused by decreasing antiparallel azimuthal tilt angle correlations of molecules from neighboring layers. In such a system the frustration between *AF* or *FE* arrangements and formation of clusters of both phases could be expected. Phase separation occurs on micron scale and *FE* regions are sufficiently big to bear the Goldstone mode. The relative concentration of *AF* and *FE* domains is controlled by mixture composition. In mixtures with the strength of the azimuthal correlations sufficiently reduced, the concentration of clusters may be also strongly influenced by interactions with surfaces which favor ferroelectric state.

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