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Properties of System with Induced SmC_A^* Phase

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Physical macroscopic properties such as the spontaneous polarization Ps, the tilt angle θ, dielectric permittivity $\varepsilon_\perp$ as a function of temperature were measured for system with induced SmC_A^* composed simultaneously of three ring chiral esters with partially fluorinated terminal chain and nonfluorinated. Dielectric and spontaneous polarization measurements on heating and cooling runs show a thermal hysteresis for the phase transition between SmC* and SmC_A^* phases.

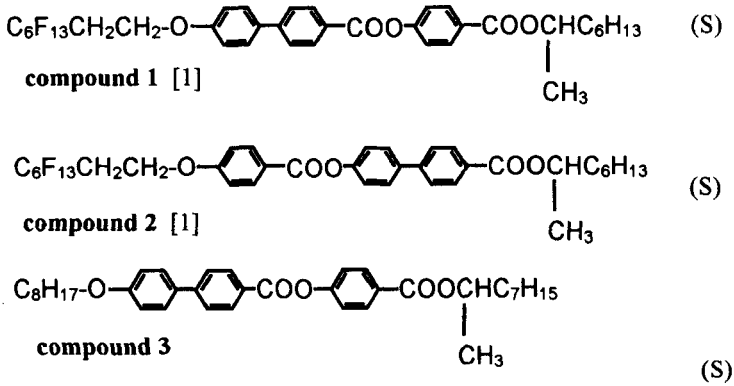
Keywords: induced antiferroelectric phase; spontaneous polarization; tilt angle; dielectric permittivity; thermal hysteresis; phase transition

INTRODUCTION

Recently appearance of induced antiferroelectric phase in mixtures was observed [1,2,3,4]. In these systems the equilibrium between the induced antiferroelectric and ferroelectric phases strongly depends on the concentration of all components although they do not posses the antiferroelectric phase at all. To better know physical properties of such

systems in this paper we reported measurements of spontaneous polarization P_s, the tilt angle θ and dielectric permittivity $\varepsilon_\perp$ as a function of temperature and concentration.

The following three ring chiral esters with partially fluorinated terminal chain (compound 1 and compound 2) and hydrogenous analogue (compound 3) have been chosen as the studied compound:



The phase transition temperatures of compounds 1 and 2, their bicomponent equimolar mixture (mixture 1:2) and three component mixtures 1:2-3 composed of mixture 1:2 with 0.30, 0.50, 0.50 of molar fraction of compound 3 are following:

compound 1	Cr 98.9 SmC* 150.4 SmA 184.4 Iso
compound 2	Cr 94.3 SmC* 155.0 SmA 184.0 Iso
mixture 1:2	Cr 90.2 SmC* 149.5 SmA 182.0 Iso
compound 3	Cr_1 60.8 Cr 79.7 (SmI_A*) SmC*118.4 SmC_α* 118.7 SmA 144.1 Iso
mixture 1:2-3(0.30)	Cr 70 SmC_A* 77 SmC* 143 SmA 172 Iso
mixture 1:2-3(0.50)	Cr 52 SmC_A* 102-121 SmC* 138 SmA 153 Iso
mixture 1:2-3(0.70)	Cr 61 SmC_A* 100-108 SmC* 128 SmA 154 Iso

In mixtures 1:2-3 above temperatures was obtained by observation of texture under polarizng microscope and by single concentration method. Temperature intervals between SmC_A^* and SmC* phase mean temperatures obtained on cooling and heating cycle by microscopic observation.

In the investigated system the induced SmC_A^* phase was observed in the concentration range above 0.30 to 0.90 mole ratio of compound 3 and the temperature 105°C was the maximum value for thermal stability of the induced SmC_A^* phase [2].

EXPERIMENTAL AND RESULTS

The tilt angle θ of molecules in the smectic layers was derived from optical switching angle of the cell during observation under polarizing microscope. The spontaneous polarization P_s obtained from Diamant method was measured by applying sinusoidal wave voltage of 15 V amplitude and 100 Hz frequency. Measurements of tilt angle were done during cooling from SmA phase to SmC* phase and spontaneous polarization was measured during cooling and heating cycles. Temperature dependence of tilt angle and spontaneous polarization for compound 3, equimolar mixture1:2 and mixtures 1:2-3 with different molar fraction of compound 3 are presented in Figures 1A and 1B, respectively.

The SmC* phase of mixture 1:2 which was a binary system of chiral esters with fluorinated terminal chain is strongly tilted with tilt angle about 40°. The spontaneous polarization of this mixture reaches a value of saturation at 140 $nCcm^{-2}$. These values are similar to values obtained of other three ring compounds with fluorinated chain studied

in [5,6]. Values of θ and P_s of not fluorinated compound 3 are lower, especially the tilt angle. They are about 22.5° and 110 $nCcm^{-2}$, respectively.

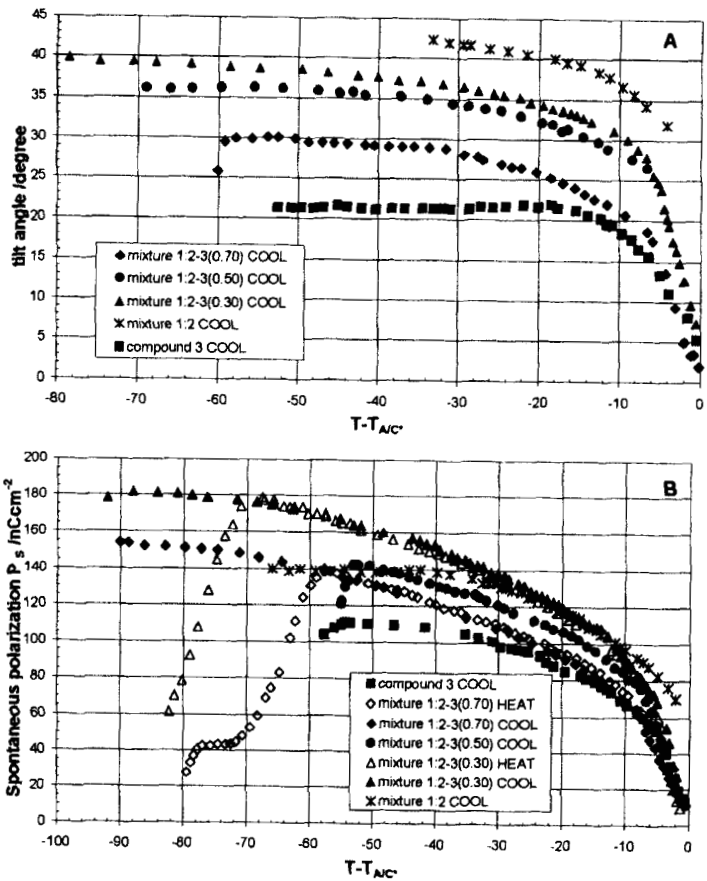


FIGURE 1 Tilt angle - A and spontaneous polarization - B as a function of temperature for all investigated compounds. $T_{A/C*}$ is the temperature of SmA-SmC* phase transition.

According to expectations, increasing of molar fraction of compound 3 in studied mixtures 1:2-3 leads to decreasing of the tilt angle and the spontaneous polarization, slower for low contents of it than for high contents. The mixture 1:2-3(0.30) has greater polarization than mixture 1:2. The increase of dipole-dipole induced interaction in the mixture probably hinders the rotation of the molecules, so value of the spontaneous polarization increases, additionally.

The phase transition in ferroelectric liquid crystals could be well observed from the temperature dependences of the dielectric permittivity. The real ε' and imaginary ε'' parts of the complex dielectric permittivity were studied by us in the frequency range from 50 Hz to 1 MHz. It is perpendicular component $\varepsilon_\perp$, because measuring voltage 0.1 V was applied perpendicular to the helical axis i.e. parallel to the smectic layer.

Figure 2 shows the results of dielectric measurements of compound 3 for four frequencies. The phase transition to SmC* phase is characterized by strong maximum for low frequencies and minimum for high frequencies dielectric responses [7,8]. Thus, in 118°C one can see phase transition to SmC* phase. In Figure 3 the relaxation frequency f_R and the inverse of dielectric strength $\Delta\varepsilon_\perp$ obtained from fitting experimental values ε' and ε'' to Debye equation are shown as a function of temperature. These results can be explained by presence of the SmC_α^* phase in temperature range from 118 to 121°C, what found confirmation in DSC measurements, where it was observed between 118,4°C and 118,7°C. The temperature range of existence of SmC_α^* phase found by us differs much from typical range of the order 1 K. But because of the strong electroclinic effect and fluctuations of the tilt

angle in the SmA phase near the phase transition to SmC_α^*, the range of phase transition is difficult to establish exactly by dielectric measurements.

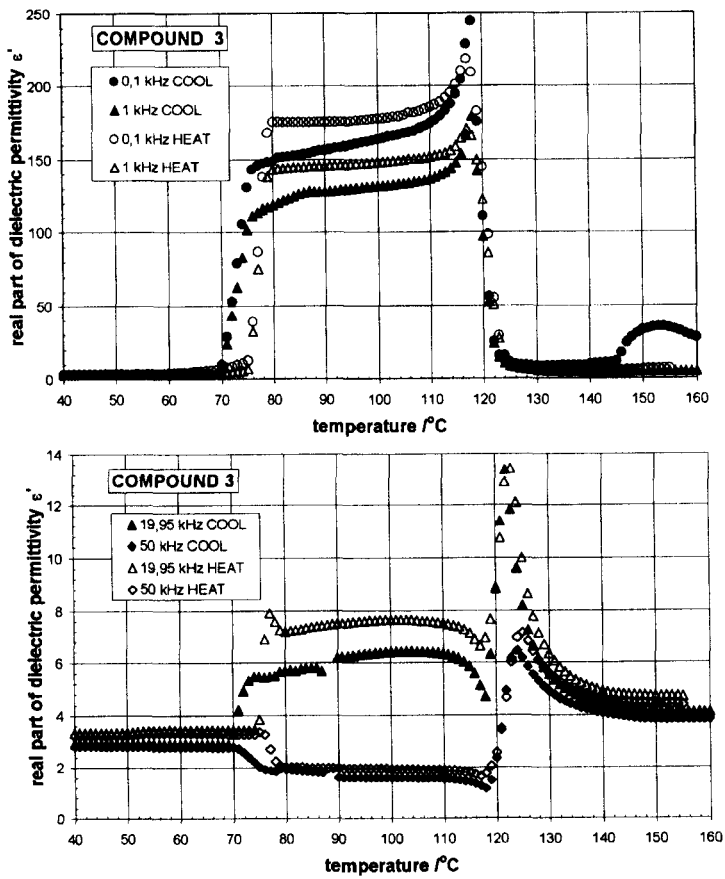


FIGURE 2 The temperature dependence of the dielectric permittivity obtained on cooling and heating cycle at the rate 0.1°C/min for compound 3 (thickness of sample - 6.1 μm, planar alignment).

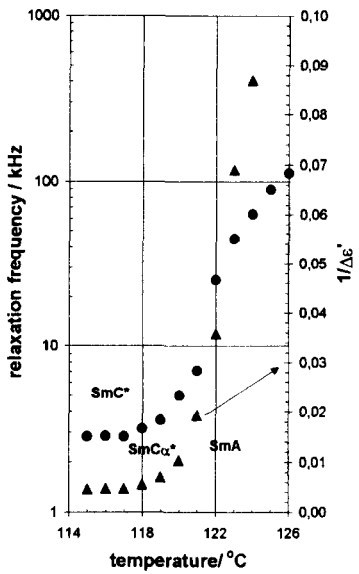


FIGURE 3 The relaxation frequency (circle) and inverse of dielectric strength (triangle) for compound 3.

The temperature dependences of dielectric permittivity for mixture 1:2-3(0.30), mixture 1:2-3(0.50) and mixture 1:2-3(0.70) are presented in figures 4,5,6 respectively. All of these mixtures exhibit antiferroelectric phase in some range of temperature, although their components do not possess this phase. It is interesting that dielectric measurements on heating and cooling runs show a thermal hysteresis for the SmC^*-SmC_A^* transition. It is seemed that in studied mixtures for molar fraction of compound 3 bigger than 0.5 the difference of phase transition temperature SmC^*-SmC_A^* is almost constant. It is about 35 K.

Similar thermal hysteresis is observed from measurements of spontaneous polarization (Fig.1). On cooling cycle from SmA phase the spontaneous polarization increases when the temperature decreases in the whole temperature region of existence of SmC^* phase obtained from dielectric measurements on cooling. But values of spontaneous

polarization obtained during heating from crystal phase agree with values obtained during cooling not in the whole this region.

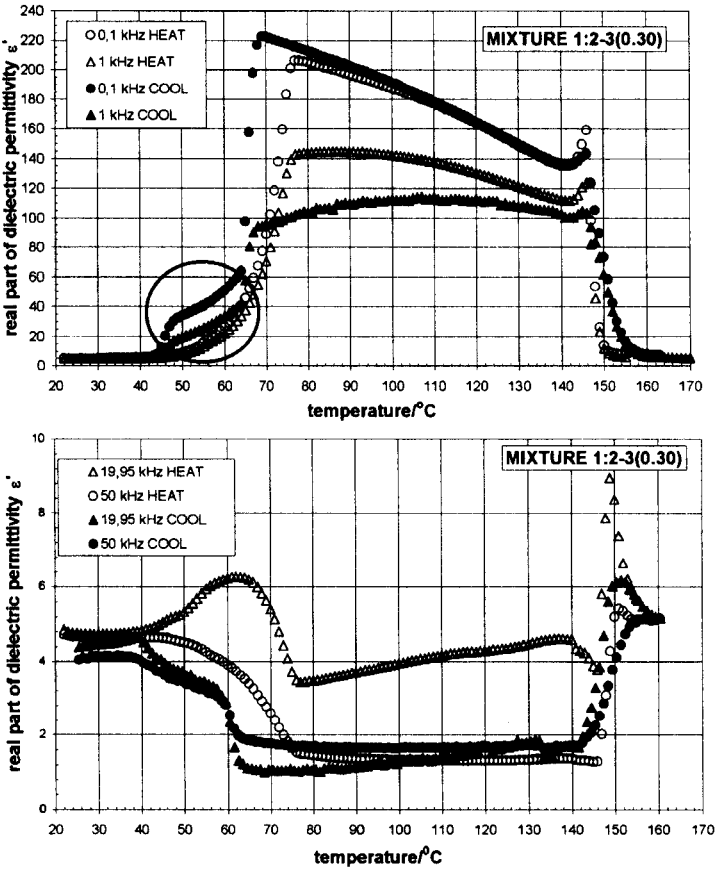


FIGURE 4 The temperature dependence of the dielectric permittivity obtained on cooling and heating cycle at the rate 0.1°C/min for mixture 1:2-3(0.30) (thickness of sample – 6.23 μm, planar alignment).

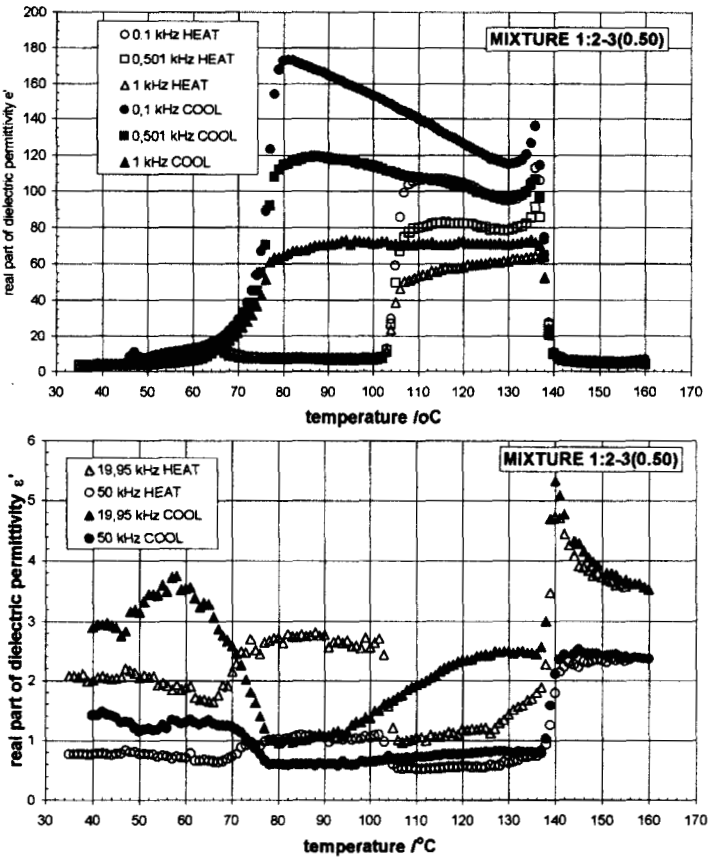


FIGURE 5 The temperature dependence of the dielectric permittivity obtained on cooling and heating cycle at the rate 0.1°C/min for mixture 1:2-3(0.50) (thickness of sample – 6.17 μm, planar alignment).

On heating cycle for the temperature interval corresponding to appearance of thermal hysteresis of phase transition SmC_A*-SmC* spontaneous polarization starts to increase slowly when the temperature

increases. It shows that SmC_A^* phase requires higher field to accomplish transition to the ferroelectric phase than that applied by our measurement. This threshold field decreases while the temperature increases

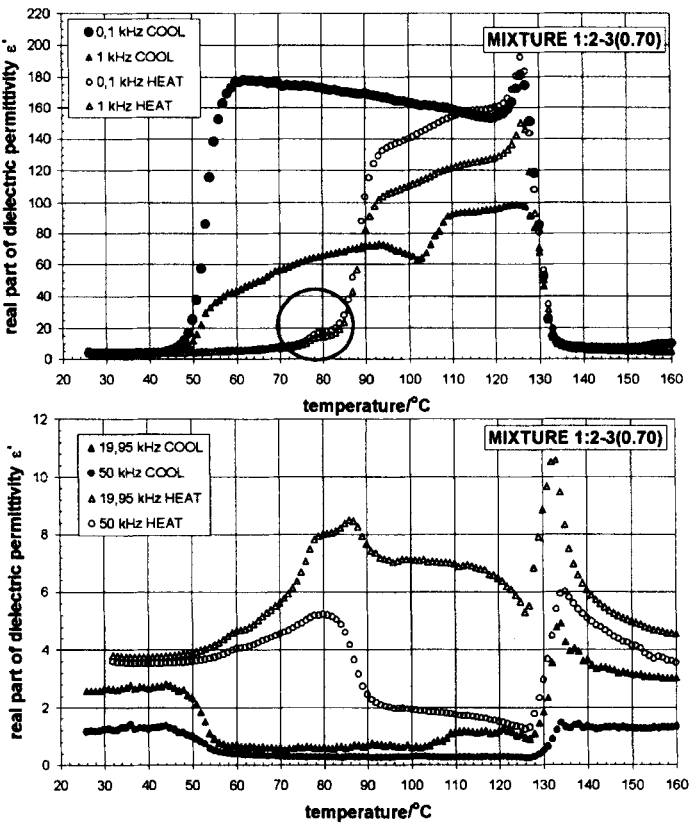


FIGURE 6 The temperature dependence of the dielectric permittivity obtained on cooling and heating cycle at the rate 0.1°C/min for mixture 1:2-3(0.70) (thickness of sample – 6.35 μm, planar alignment).

The analysis of temperature dependences of dielectric permitivittity for low and high frequencies (Figs.4, 5, 6) and relaxation frequencies (Fig.7A) permits to suppose that for all studied mixtures between SmA and SmC* phases SmC_α^* phase appears. It is agreed with the DSC measurements for single compound 3, which show that transitions between SmA-SmC_α^* and SmC_α^*-SmC_β^* phase are weak first order transitions.

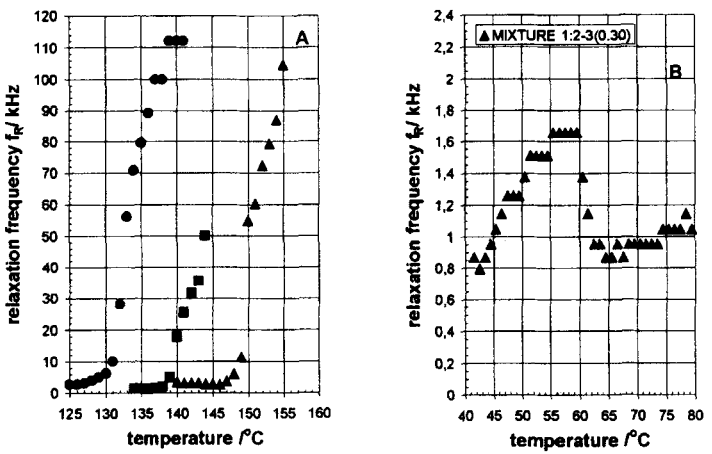


FIGURE 7 A-Temperature dependences of relaxation frequency nearly phase transition SmA-SmC* obtained on heating for mixture 1:2-3(0.30) (triangle), mixture 1:2-3(0.50) (square), mixture 1:2-3(0.70) (circle)m, B - temperature dependence of relaxation frequency on cooling for mixture 1:2-3(0.70) near an anomaly below SmC* phase.

An anomaly can be seen between the antiferroelectric SmC_A^* phase and SmC* phase for mixture 1:2-3(0.30) in temperature dependences of the real part of the dielectric permittivity (marked by circle in Fig.4) and the relaxation frequency (Fig.7B) measured on

cooling. In the dielectric measurements obtained on heating for the mixture 1:2-3(0.70) the small step below the SmC* phase occurs as well (marked by circle in Fig.6). In these temperature intervals one can consider a coexistence ferroelectric and antiferroelectric phases, but they may overwhelm narrow ferielectric phases. To explanation of these doubts the dielectric and DSC investigation will be continued.

CONCLUSSION

Dielectric and spontaneous polarization measurements show that in the systems with induced antiferroelectric phase (SmC_A*) large hysteresis of temperatures between antiferroelectric to ferroelectric transitions occurs during heating and cooling cycles, that inform us the system is labile (frustrated). Dielectric investigations at low field frequency are useful method to discover the such frustrated phases. Results of dielectric measurements confirm the existence SmC_α*phase in compound 3, that was parallel seen during DSC measurement.

Acknowledgments

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